Pyrotechnic Reference Series No. 4

Pyrotechnic Chemistry

by

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CAUTION

The experimentation with, and the use of, pyrotechnic materials can be dangerous; it is important for the reader to be duly cautioned. Anyone without the required training and experience should never experiment with nor use pyrotechnic materials. Also, the amount of information presented in this text is not a substitute for the necessary training and experience.

A major effort has been undertaken to review this text for correctness. However, it is possible that errors remain. Further, it must be acknowledged that there are many areas of pyrotechnics, fireworks in particular, for which there is much "common knowledge", but for which there has been little or no documented research. For the sake of completeness, this text certainly contains some of this unproven common knowledge. It is the responsibility of the reader to verify any information herein before applying that information in situations where death, injury, or property damage could result.

Preface

This text is written at an introductory to intermediate level. As such it is intended for readers with limited prior knowledge of chemistry or limited knowledge regarding specific areas of applied pyrotechnics. One goal of this text was to provide an extensive list of references, thus directing readers to sources of additional information. With a total of approximately 400 references that goal has been met; however, for the most part, citations to material that is readily found in numerous reference texts have not been included. Only when the information is attributable to a limited number of authors are specific references generally cited.

The chapters are a collection of 19 papers written by 13 authors, covering most of the important areas of pyrotechnic chemistry. While this format causes the text to be written in styles that differ somewhat from chapter to chapter, it also provides an opportunity to have each of the chapters written by persons with expertise and current knowledge in each of the various subject areas. (Brief biographical information about the authors is included at the end of this preface.) Also, having each subject written as a stand alone chapter, means that a reader wishing information on a specific subject will generally not have to refer to other chapters for the background and ancillary information needed to fully comprehend the subject.

Almost all of the chapters have been published previously; however, they were originally written with the intention of being chapters in this text and have been updated since their original publication. The authors of each chapter are identified at the start of each chapter, and the citation for where the material was originally published appears at the end of each chapter. Because most of the chapters have been published previously, and to simplify the task publishing this compilation, in most cases the authors were individually responsible for editing their chapters. Nonetheless, the Journal of Pyrotechnic, Inc. would appreciate learning of any errors appearing in this text such that they might be corrected in future printings.

The Table of Contents is quite extensive, running to 9 pages with approximately 600 entries. For this reason there is also a basic list of chapter titles to help orient the reader. Because of the extensive table of contents, this text has not been provided with an index. It is suggested that readers wishing to research a specific topic first consult the list of chapters to find the one most relevant to the topic, and then consult the detailed table of contents to locate the page number(s) of the section addressing that topic.

The publisher acknowledges that there are a number of subjects that this first edition does not adequately cover. It is anticipated that subsequent editions will be produced periodically that will fill in subject areas such as flash powder chemistry, smoke chemistry, and the kinetics of pyrotechnic reactions. Subsequent editions will also seek to update and expand some of the current chapters. Volunteer authors for these and other potential chapters are encouraged to contact the Journal of Pyrotechnics, Inc.

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Mr. Chapman graduated from Bath University in 1972 with a degree in Chemistry. He obtained an M. Phil. degree in Pharmaceutical Chemistry in 1975 from Sunderland Polytechnic. This was followed by 10 years teaching pre-University students in general chemical areas. For the past 20 or so years he has been involved in the area of explosives, propellants and pyrotechnics, more recently specializing in accidents investigation and related research. He is a Fellow of the (UK) Institute of Explosives Engineers and has over 10 publications dealing with pyrotechnics and pyrotechnic related areas. He is currently Head of the Explosives Section at the Health and Safety Laboratory at Buxton, UK.

David R. Dillehay, Ph.D.

Dr. Dillehay graduated from Rice University in 1958 with a degree in chemistry. He obtained a Doctorate in chemistry in 1983 from Clayton University. For more than 38 years he worked for Thiokol Corporation in the fields of propellants, explosives and pyrotechnics. In 1996, he became president of Technical Consultants, Inc. He has published over 52 papers in the field of pyrotechnics and energetic materials’ processing and holds 11 patents in the field, including processes and formulations. In 1980, he became a co-founder of the International Pyrotechnics Society and served 4 years as Secretary, 2 years as Vice-President and 2 years as President. He is currently a Life Member of the IPS. He served as President of the local Ark-La-Tex Chapter of the American Defense Preparedness Association and was President of the Longhorn Chapter of the National Management Association. He is currently serving as Treasurer of the Steering Committee of the International Pyrotechnic Seminars and Treasurer of International Pyrotechnics Seminars USA, Inc. He was a guest speaker at Pyrochem International ’75 in the UK, the Pyroteknikdagen in Sweden and was a guest of the USSR Academy of Science at the 2nd International Symposium on Flame Structure in Alma-ata, Khazakstan. He also served on the Navy investigating team for the USS Iowa Battleship Incident.

Ron Hancox, B.S.

Mr. Hancox is a graduate in Applied Chemistry from the Royal Melbourne Institute of Technology. For the last 20 years he worked at the Defence Science Technology Organization (DSTO). He has been involved in most aspects of pyrotechnics technology from the chemical development of compositions, system failure investigations through to project management of air countermeasure programs for the RAAF. He has also been involved in a number of international cooperative studies on specialized pyrotechnic topics. Ron left DSTO in 1998 and joined Pains Wessex Australia and was initially tasked with setting up a Technical Services capability within the organization and more recently, with improved formulations for a wide range of pyrotechnic signals for use in the marine environment.

Clive Jennings-White, Ph. D.

Dr. Jennings-White was born and grew up in England. First attempts at making fireworks were at age six, and the decision to pursue chemistry was at age seven. As one might expect, Kentish and Lancaster were very influential on the development of his approach to fireworks. After obtaining a Doctorate in chemistry at the University of Cambridge, he moved to the United States. His professional positions have included vice president of manufacturing and product development for a perfumery company, as well as vice president of chemical research for a pharmaceutical company. His fireworks interests have been focused on chemistry and formulation development, resulting in many publications. The most notable inventions are probably bismuth-based crackling microstars and blue strobe formulations. In addition, he competes regularly at Pyrotechnics Guild International competitions, where his principal areas of expertise are wheels, small gerbs, and ground display items.

Bonnie J. Kosanke, M.S.

Ms. Kosanke graduated from Michigan State University with a Masters of Science degree in biology. She has more than 25 years of experience working with and researching pyrotechnics and has authored and coauthored more that 200 articles and papers on pyrotechnics. She is a past lecturer on general chemistry at Mesa State College, has taught graduate level courses on pyrotechnic chemistry at Miami University, and is a frequent lecturer on various subjects in pyrotechnics. She is the founder and publisher of the *Journal of Pyrotechnics*, a technical journal devoted to civilian pyrotechnics.

Ken L. Kosanke, Ph.D.

Dr. Kosanke received a Doctorate in chemistry from Michigan State University, as well as Post Doctoral studies in nuclear physics at what is now the National Superconducting Cyclotron Laboratory. He has more than 25 years working with and researching pyrotechnics, and has authored and coauthored nearly 300 articles and papers on pyrotechnics. He is a past lecturer on general chemistry at Mesa State College, has taught graduate level courses on pyrotechnic chemistry at Miami University, and is a frequent lecturer on various subjects in pyrotechnics. He is president of PyroLabs, Inc., a small research laboratory devoted to the study of pyrotechnics and is also managing editor of the *Journal of Pyrotechnics*.

Naminosuke Kubota, Ph.D.

Dr. Kubota received a Doctorate from Princeton University in 1973, majoring in “Solid Propellant Combustion” and “Rocket Propulsion”. His current position is as an Advisory Professor at Nanjing University of Science and Technology. Previously he was Director, Third Research Center, TRDI, Japan Defense Agency, which is responsible for the research relating to aircraft and missiles. He is the author of *Propellants and Explosives*.

Michael Podlesak, Ph. D.

Dr. Podlesak received a Doctorate in Physics in 1986 at La Trobe University, Victoria, Australia. After two years of postdoctoral work in acoustics and fibreoptic sensor technology at La Trobe and Victoria University of Technology, he joined the Australian Defence Science and Technology Organization (DSTO). The first five years there involved research in shock wave physics and contribution to the development of slapper detonator fuses for conventional munitions. Since 1993, he has worked on active approaches to noise and vibration control on naval vessels, and in 1998-99, he was posted to Naval Research Laboratory, Washington DC, to investigate special applications of laser detection of underwater sound. In 1999 he commenced research in electro-optics and image processing with emphasis on automatic target acquisition for guided weapons.

Takeo Shimizu, Ph.D.

In 1933, Dr. Shimizu graduated from the military Academy at Ichigaya Hill, which started him on a distinguished military career. In 1940 he graduated from the School of Explosives at Tokyo University. In 1945, when the war was over, he decided no longer to make explosives. In 1951, he obtained a position at Hosoyo Fireworks Co. In 1958 he received a Doctorate in engineering with his thesis *The Design Criteria of Chrysanthemum Shells*. In 1963 he accepted a position at the Perfect Liberty (PL) Fireworks company, where he worked until 1967 when he accepted a position at the KOA Fireworks factory. In 2002 at the age of 90, he retired from the KOA Fireworks factory. He has written several books on fireworks and pyrotechnics. Two of the books have been translated into English: *Fireworks, The Art, Science and Technique* and *Fireworks from a Physical Standpoint*. He has also written numerous articles on various aspects of pyrotechnics and explosives.

Tom Smith, Ph.D.

Dr. Smith graduated from Oxford University in 1983 with a degree in Chemistry. He remained there to receive his doctorate in 1986. He then worked for the Dow Chemical Company on fungicide research and for OCTS lecturing and developing software. In 1989 he joined Kimbolton Fireworks as their display manager, having worked part-time with the company all through his university career. Indeed his long term fascination with fireworks stems from his Grandfather, who was at school with Roy Brock and worked with Brocks in the early 1920s. In 1988 he left Kimbolton and setup a specialist explosive consultancy ranging from work with Disney, the Commonwealth Games and the 2004 Athens Olympics to advising smaller UK fireworks and explosive companies on aspects of legal compliance. He is chairman of the Confederation of British Industry Pyrotechnics group and secretary of the British Pyrotechnists Association and represents these bodies on many government committees including the Advisory Committee on Dangerous Substances, the British Standards Committee and the EU and UN working groups on pyrotechnics and classification.

Barry Sturman, M.S.

Mr. Sturman has a Master of Applied Science degree in chemistry. For the past 24 years he has been a research and development scientist and manager in the scientific instrument industry, specializing in analytical atomic spectrometry. His interest in fireworks began when he was about four years old and has persisted for over half a century. This interest has led him to assemble an extensive collection of books, periodicals and paper ephemera related to the history and technology of fireworks. He contributes a regular column to the British periodical *Fireworks* and is an editor and policy board member for the *Journal of Pyrotechnics*. He has worked as a laborer on many firework displays and has designed and fired displays for local festivals and school fetes. More recently he has given up display work and restricts his pyrotechnic activities to writing and research.

Ian von Maltiz, B.S.

Mr. von Maltitz is South African born and bred and he immigrated to the United States in 1995. He has a Diploma of Electrical Engineering from Witwatarsrand College for Advanced Technical Education. He has had a fascination with pyrotechnics since the tender age of six. His interest in fireworks was encouraged and mentored by his father, who was a keen amateur pyrotechnics enthusiast. He has written numerous amateur pyrotechnic magazine articles and is the author of *Black Powder Manufacturing Methods and Techniques* and *Black Powder Manufacturing, Testing & Optimizing*.

Mike Wilson, B.S.

Mr. Wilson has a Certificate of Applied Chemistry (Propellants and Pyrotechnics) and has worked for Defence Science and Technology Organization (DSTO) as a Technical Officer in pyrotechnics research and development for over 30 years. He has had wide practical experience in the development of pyrotechnic compositions, equipment and processes relating to the energetic materials requirements of the Australian Defence Force. Mike left DSTO in 1998 and joined the Technical Support Section of Pains Wessex Australia where he is responsible for device development. He was project officer for the team that designed the underwater Olympic torch, which was successfully used on the Great Barrier Reef for the 2000 Sydney Olympic Games.

Pyrotechnic Literature Series No. 4

Pyrotechnic Chemistry

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Introduction to Pyrotechnics

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Pyrotechnics is, literally, the *art of fire* from the Greek pyr (fire) and *tekhne* (art). Originally, the word covered many technological applications of fire, particularly metallurgy.[1] Later, "Pyrotechnics" came to mean the art of making or using fireworks. Originally fireworks were devices containing mixtures of various combustible solids with saltpeter (potassium nitrate).[2] The saltpeter provided oxygen, allowing the combustion to proceed vigorously until all the mixture was consumed, producing flame, sparks, smoke, noise, and sometimes setting the firework in motion. Fireworks were used for entertainment and in warfare. The earliest documentation of fireworks is found in the ancient Chinese literature.[3–7] Later, firework mixtures were used to propel stones and other missiles from tubes, leading to the development of guns. One such mixture, which came to be known as "Gunpowder" or "Black Powder", became universally used as the propellant in firearms and as a military explosive. It was also used in mining and quarrying and still remains an important component of many fireworks and other pyrotechnic devices.

With the development of modern chemistry more and more materials were found to be useful in pyrotechnics. A practical definition of a pyrotechnic mixture in the early nineteenth century might have been "a mixture, capable of self-sustaining combustion, consisting of one or more powdered solid fuels mixed with one or more powdered solids capable of yielding oxygen for the combustion of the fuels". While this definition might have sufficed for all commercial and military pyrotechnic compositions of the time, there are mixtures and even pure substances that behave like pyrotechnic compositions but do not fit the definition. For example, mixtures of powdered metals (such as zinc, aluminum and magnesium) with powdered sulfur burn like fireworks but contain no oxygen. Ammonium dichromate burns like a firework, but is not a mixture. Mercury fulminate and silver fulminate explode when heated or struck, and there are many other pure substances that exhibit "pyrotechnic" qualities. Some of them, such as nitrocellulose and nitroglycerine, became important components of military and commercial explosives. Are such compounds, and devices using them, within the scope of pyrotechnics? Modern usage suggests that they are, with the proviso that 'bombs, warheads, land mines, and other munitions, which are commonly associated with the military term "ordnance" are "specifically not included"'.[8] The definition of "pyrotechnics" is further clouded by the tradition of writers of books on pyrotechnics to discuss such interesting but peripherally relevant matters as spontaneously flammable chemicals[9,10] and high-temperature gas flames.[11] Even if such things are excluded, the old definitions that specified mixtures of solid fuels and oxygen donors are clearly inadequate. Practical pyrotechnic mixtures have been based on combinations of powdered polytetrafluoroethylene and magnesium,[12] of powdered carbon and titanium,[13] and of palladium and aluminum.[12]

The word "pyrotechnics" is used to refer not only to the technology, but also to its products. A definition of "pyrotechnics" that is broadly consistent with current usage should include both senses of the word. Such a definition might be:

1. *The area of technology that deals with the application of self-contained and self-sustained exothermic chemical reactions of solids to produce heat, light, sound, smoke, motion, combinations of these, and/or useful reaction products*

2. *Materials or devices for producing or exploiting such reactions.*

A definition of "fireworks" could then be:

"Pyrotechnics intended for amusement, public entertainment or artistic purposes".

Americans use the terms pyrotechnics, propellants and explosives to distinguish between various types of energetic materials. However, this does not mean that violent explosions are not possible with pyrotechnics. On the contrary, very powerful explosions have resulted from mishandling of pyrotechnic compositions. The defining difference between pyrotechnic explosions and detonations is in the presence of a shockwave in the explosive and the propagation velocity. In a detonation, high temperature and pressure gradients are generated in the wave front, so that the chemical reaction is initiated instantaneously. By definition, detonations produce violently destructive shockwaves and are characterized by a propagation velocity greater than approximately 1,500 m/s (5,000 ft/s). [Most materials that detonate are not classified as "pyrotechnics" and will not be addressed in this text.]

Black Powder is classified as a low explosive; its velocity of propagation is only about 460 m/s (1,500 ft/s). It undergoes what can be described as a deflagration, which does not propagate via a shockwave and is characterized by the release of hot gases to do useful work. Black Powder is one of the oldest known compositions and enjoys a unique place in the annals of pyrotechnics, yet it still plays an important role today.

Other pyrotechnic chemical reactions are known, some with considerably more energy released per unit weight compared with Black Powder, and some with considerably less energy. The amount of work that can be done by a composition is known as the impetus. The units are usually given in joules per gram (J/g) or foot-pounds$_{\text{(force)}}$ per pound$_{\text{(weight)}}$ (ft·lbf/lb). This derivation comes from the well-known ideal gas equation,

$$PV = nRT$$

where P = pressure,
V = volume,
n = moles of gas,
R = universal gas constant, and
T = temperature of the gas.

The impetus is most easily measured in a *closed vessel* by burning a known weight in a known volume and measuring the maximum pressure produced. If the vessel is insulated to achieve near adiabatic conditions (no heat loss), then the impetus can be calculated from the following equation:

$$F = \frac{KP_{\max}V}{W}$$

where F = impetus (J/g),
P_{max} = peak pressure (atm)
V = volume (L)
W = mass (g), and
K = 0.00987 (a conversion factor to convert from liter-atmospheres to joules).

The performance characteristics of pyrotechnics can be tailored to fulfill a number of applications by controlling the burning rate and limiting the venting of the pressure. Delays and fuses can be made to burn very slowly (many seconds per centimeter) or very rapidly (milliseconds per centimeter). This wide performance range provides the pyrotechnist with considerable latitude for controlling the sequence of events. Some delay formulations are shown in Table 1.

Table 1. Delay Formulations.

Formulation	Wt. (%)	Burning Rate (s/cm)
Boron, amorphous Barium chromate	10 90	0.2
Boron, amorphous Barium chromate	5 95	0.6
Manganese Barium chromate Lead chromate	33 31 36	5.1

Pyrotechnics have a number of other functions. They can be used in incendiary devices to generate heat for cutting, welding, warming, vaporizing or igniting other materials. They can produce smoke, either directly or indirectly. Pyrotechnics, in the form of fireworks displays, are a major source of entertainment on holidays and special occasions all over the world. The production of light for illumination or signaling has been a major application of pyrotechnics, particularly in the military. Battlefield illumination was of primary importance in many past wars, using visible light to strip the cloak of darkness from the enemy. Today, the same principle exists but the wavelengths have shifted from the visible to the infrared region of the spectrum. This provides an advantage to those with the technology to use infrared vision sensors to allow the "covert" illumination of the battlefield, limiting the good vision to the well-equipped troops. Many times, the enemy will not even realize that they are being illuminated and observed. The advent of heat-seeking missiles tipped the advantage to the hunter-killer until the use of infrared decoys was perfected to attract and distract the missiles while the target made a get-away. All of these applications involve burning a fuel and oxidizer to generate heat, smoke, light (of various wavelengths) and/or pressure.

In the earliest years, pyrotechnics was basically a "black art". Like the early chemists and alchemists, pyrotechnists used secret formulations to create effects that produced wonderment in the general population. The methods and formulae were closely guarded secrets that were handed down from master to apprentice. For years, the actual science was unknown, even to the master practitioners. Their expertise was based on trial-and-error and many an accident can be attributed to mistakes in formulations or handling. Even now, many techniques are still based on very limited knowledge of the mechanisms producing the effects. A number of research projects were started; however, they frequently failed because of a lack of knowledge of the science behind the pyrotechnic effects. Few definitive reference books have been available to guide practitioners in pyrotechnics. Most of the early works were of necessity little more than recipe books, with none of the science explained. The authors were wise to avoid attempts at scientific explanations, because in most cases the relevant science had not yet been developed. Colored flames were known from the early nineteenth century, but a detailed scientific explanation was not possible for another hundred years or more.

More recently the situation has improved greatly. In 1943 Shidlovskiy[14] published a book on Russian pyrotechnics that provided a compilation of test data with some consideration toward the science behind the observations. This book was translated into English by the military and became widely available in 1964. In 1961 Ellern[12] published one of the most erudite books on pyrotechnics, with the comment in the introduction that no definitive works on pyrotechnics existed at that time. He followed it with a second work[12] in 1968. In 1980, McLain[15] published his work on pyrotechnics and solid state chemistry. This book covered a wide range of subjects and provided some guidance on the science of pyrotechnics, including a summary of the Spice and Staveley[16,17] contribution to pyrotechnics on the "pre-ignition reaction". Shimizu, in 1976 published a very significant work in German,[18] later translated to English,[19] that offers much insight into the science of pyrotechnics applied to fireworks. Another important work by Shimizu was published in 1981[20]. Other more recent publications include work by Conkling,[21] Urbanski,[22] and Hardt[10] [published posthumously]. Ronald Lancaster's book, *Fireworks Principles and Practice*, was first published in 1972[23]; its 3rd edition appeared in 1998.[24] All of these books are valuable assets to anyone seeking to learn more than the "cookbook" approach to pyrotechnics.

Over the last fifty years, considerable progress has been made in understanding the chemistry and physics behind pyrotechnic effects. This has led to solid science being used in the prediction of performance and in maximizing the desired effects of pyrotechnic formulations, while enhancing the safety of operations. A considerable amount of research was carried out with military funding and can be found in the proceedings of seminars sponsored by the International Pyrotechnics Society,[25] the National Defense Industrial Association (NDIA) (formerly called the American Defense Preparedness Association),[26]and the Fraunhofer Institute.[27] Numerous papers are available from the National Technical Information Service (NTIS) and Defense Technical Information Center (DTIC); many of the documents from DTIC are not, however, available to the general public.) Additional refereed technical journals include *Propellants, Explosives and Pyrotechnics*, published by Wiley-VCH Verlag GmbH, Weinhein, Germany and the *Journal of Pyrotechnics*, published by the Journal of Pyrotechnics, Whitewater, CO, USA.

Even with these recent advances, pyrotechnic compositions can still react with deadly results when the science is ignored or misunderstood. The science of pyrotechnic physics and chemistry is now coming into reality, but there are still vast areas needing additional research. It is also necessary to take full advantage of this growing understanding.

Processes for dealing with the manufacture of pyrotechnics (mixing, pressing, extrusion, drying and packaging) have run a large gamut. The oldest mixing method used was probably the mortar and pestle technique used by early alchemists to reduce particle sizes and blend materials. This was effective though labor intensive and must have led to accidents as the compositions became more sensitive with more intimate contact between the fuel and oxidizer. This technique was mechanized by the early mixers for Black Powder that utilized large wheel mills (sometimes called edge-runners). Some of these mills used 10-ton wheels to combine charcoal, sulfur and potassium nitrate into an intimate mixture (with the help of some processing water) to form Black Powder (gunpowder).

Many pyrotechnic compositions were processed in large wooden bowls with water as a processing aid. The mixtures were blended and cast or pressed into molds then cut into pellets. The pellets were dried in the sun. Fuses were made by braiding paper with Black Powder, and lift charges of Black Powder were used to propel stars from Roman candles and aerial shells from mortars.

As processing became more sophisticated, binders became more prominent. Almost any sticky material found application as a binder to hold fuel and oxidizer together and keep the compositions from crumbling or cracking under ignition and/or flight. Some of the early binders included dextrin, linseed oil, tung oil, gum Arabic (acacia), and red gum (accroides or acaroid resin). These natural products were used for many years until the development of synthetic binders, such as polyester resins (used in fiberglass), polysulfide-epoxy binders and vinyl-alcohol acetate resin (VAAR). These provided improved composition strength and sometimes improved performance. Generally, only a small amount of binder is used since they do not add much to the energy released by the burning mixture. Compositions are also sensitive to the amount of binder because it affects the burning rate of a formulation. Along with the new compositions came more modern mixing techniques such as the use of sigma-blade mixers, Muller-type mixers, Hobart blenders, twin-shell blenders and Cowles Dissolvers. Techniques becoming popular now include twin-screw extruders and shock-precipitation (coacervation). These techniques are considered state-of-the-art today. The resultant compositions may be pressed, cast or extruded into shapes for a variety of applications.

Empirical formulations were the norm for many years. Fireworks makers jealously guarded their recipes, with the intensity and purity of their blue formulations considered as the gauge of their expertise. The metal compounds that produced specific colors were identified by the early chemists and were used by pyrotechnists to make the variety of flame colors. The chemistry behind the colors came much later. It was found that certain chlorine compounds would increase the intensity and purity of colors in pyrotechnic flames, and their use was adopted as the norm. As spectroscopy flourished, the reasons for the effects were eventually revealed. With the formation of simple gaseous metal monochloride molecules in the flame, the colors become brighter and of higher purity.

The availability of metal powders for addition to compositions led to new and dramatic effects. Although historically coarse charcoal had been used to create beautiful glowing sparks in some compositions, the addition of iron particles and later aluminum and titanium created new and exotic effects, such as glitter and brighter sparklers. New oxidizers also became available and were immediately put to good use. The use of sodium nitrate in place of potassium nitrate made a dramatic improvement in the light output of illuminants. Pyro-aluminum was developed in Germany and became the standard for flash charges to make brilliant flash-bang effects in the sky. All of these new compositions paved the way for science to overtake the trial-and-error methods that had held sway over pyrotechnics for so many years.

Applications

Pyrotechnics are still the most viable and cost effective method of accomplishing many tasks. Examples of some current pyrotechnic devices that include both military and civilian items are shown in Table 2. Typical formulations for compositions used in these applications are readily available in texts listed in the references.

Table 2. Current Pyrotechnic Devices.

Item	Military or Civilian	Service	Description
Line rocket	Military	Coast Guard	Propulsion device to carry a line between vessels.
Signal flare	Military	All	Small, hand-held or weapon-launched device to propel colored stars or smokes to altitude for signaling.
Signal flare	Civilian	Individual or commercial marine usage	1. Small, hand-held device to propel colored stars or smokes to an altitude for signaling, 2. Hand-held device to generate a very bright colored flame for signaling.
Illuminating flare	Military	All	Small hand-held or weapon-launched device (up to 155 mm artillery shells) that deploy parachute-supported candles to provide ground or sea illumination.
Highway distress flare	Military or Civilian	All	Distress flares to mark highway accidents or dangerous situations.
Display fireworks	Civilian	Commercial	Aerial shells, mines, rockets, roman candles, fountains, lance work, etc.
Consumer fireworks	Civilian	Individual	Small fountains, mines, rockets, roman candles, firecrackers, sparklers.
Toy noisemakers	Civilian	Individual	Caps for toy pistols, party poppers, blaster balls; based on potassium chlorate.
Matches	Civilian	Individual	Safety matches, 'strike anywhere' matches, windproof/waterproof matches, Bengal matches (produce colored flames), and smoke-generating matches for testing smoke detectors and exhaust hoods.
Model rocket motor	Civilian	Individual	Uses Black Powder or composite pyrotechnic compositions to propel model rockets.
Igniter	Military	All	Pyrotechnic compositions used to transfer primer output to propulsive charges for mortars, artillery and similar military projectiles.
Igniter (electric match)	Civilian	Commercial	Used to ignite fireworks in electrically fired fireworks displays and airbag initiators.
Fuse (as opposed to mechanical or electronic fuze)	Military	All	Pyrotechnic fuse trains are used to provide delays and/or transfer of ignition action in a variety of devices, such as training items or projectiles.
Thermite	Military	All	Destructive devices for classified documents, weapons, electronics, etc.
Thermite	Civilian	Commercial	Welding and cutting devices.
Gas generators	Civilian or Military	Commercial	Emergency oxygen supplies for aircraft, oxygen for welding, airbag inflators for vehicles, engine starters.
Smoke	Military	All	Smoke generation for screening and signaling.
Smoke	Civilian	Commercial	Tracing of leaks in plumbing, dispersion of pesticides, ground or aerial signals.

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Notes

Chemical Components of Fireworks Compositions

T. Shimizu

The firework industry is quite small in scale, and generally it is necessary to use materials that are produced for other purposes or in some cases by-products, which change according to the needs of other industries. This chapter describes the important materials, including materials that are not always easy to obtain, but which cannot be ignored. From the standpoint of function, the chemical components that are used in fireworks may be classified (and are presented in this chapter) as follows:

- Oxidizing Agents
  - Ammonium perchlorate, NH_4ClO_4
  - Potassium chlorate, $KClO_3$
  - Potassium nitrate, KNO_3
  - Potassium perchlorate, $KClO_4$
- Combined Oxidizing and Color Agents
  - Barium chlorate, $Ba(ClO_3)_2 \cdot H_2O$
  - Barium nitrate, $Ba(NO_3)_2$
  - Sodium nitrate, $NaNO_3$
  - Strontium nitrate, $Sr(NO_3)_2$
- Red Color Producing Agents
  - Strontium carbonate, $SrCO_3$
  - Strontium oxalate, $SrC_2O_4 \cdot H_2O$
- Orange Color Producing Agent
  - Calcium carbonate, $CaCO_3$
- Yellow Color Producing Agents
  - Sodium bicarbonate, $NaHCO_3$
  - Sodium carbonate, Na_2CO_3
  - Sodium chloride, NaCl
  - Sodium oxalate, $Na_2C_2O_4$
- Green Color producing Agent
  - Barium carbonate, $BaCO_3$
- Blue Color Producing Agents
  - Basic copper carbonate (two types)
    $CuCO_3 \cdot Cu(OH)_2$ and
    $2CuCO_3 \cdot Cu(OH)_2$
  - Copper acetoarsenite,
    $Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$
  - Copper arsenite, $CuHAsO_3$
  - Copper powder, Cu
  - Copper sulfate, $CuSO_4 \cdot 5H_2O$
- Combustion Agents (Fuels)
  - Accroides resin (red gum)
  - Aluminum, Al
  - Amber powder (Kunroku)
  - Antimony trisulfide, Sb_2S_3
  - Arsenic sulfide (realgar), As_2S_2
  - Charcoal
    Hemp coal
    Paulownia charcoal
    Pine charcoal
  - Dextrin, $(C_6H_{10}O_5)_n \cdot xH_2O$
  - Ferro-silicon, FeSi
  - Iron filings, Fe
  - Lactose (milk sugar), $C_{12}H_{22}O_{11} \cdot H_2O$
  - Lampblack (pine black)
    Carbon black
  - Magnalium, MgAl
  - Magnesium, Mg
  - Pine root pitch
  - Red phosphorus, P
  - Rosin
    Combustion Agent BL
    Wood rosin FF
  - Shellac
  - Silicon, Si
  - Starch, $(C_6H_{10}O_5)_n$
  - Sucrose (cane sugar), $C_{12}H_{22}O_{11}$
  - Sulfur, S
  - Titanium, Ti
  - Wood meal
  - Zinc dust, Zn

- Smoke Dyes
  - Auramine
  - Indigo pure
  - Oil orange
  - Oil red
  - Oil yellow
  - Para red (p-nitroaniline red)
  - Phthalocyanine blue
  - Rhodamine B
- Other Chemicals
  - Anthracene, $C_{14}H_{10}$
  - Benzene hexachloride (BHC), $C_6H_6Cl_6$
  - Boric acid, H_3BO_3
  - Boron, B
  - Chlorinated isoprene rubber (Parlon in the USA or ADEKA in Japan)
  - Gallic acid
  - Guanidine nitrate, $NH{:}C(NH_2)_2{\cdot}HNO_3$
  - Hexachloroethane (HCE), C_2Cl_6
  - Iron oxide, red, Fe_2O_3
  - Lead oxide, red (minium), Pb_3O_4
  - Naphthalene, $C_{10}H_8$
  - Picric acid, trinitrophenol, $C_6H_2(NO_2)_3OH$
  - Polyvinyl chloride (PVC), $CH_2{:}CH{\cdot}Cl$
  - Potassium dichromate, $K_2Cr_2O_7$
  - Ultramarine, $Na_2S_2{\cdot}3NaAlSiO_4$
  - Zinc oxide, ZnO
- Binding Agents
  - Casein
  - Gelatin
  - Nitrocellulose
  - Polyester (unsaturated polyester)
  - Soluble glutinous rice starch (Mizinko)
  - Wheat flour
  - Wheat starch

Oxidizing Agents

Ammonium Perchlorate, NH_4ClO_4

Molecular weight: 117.49; colorless with a rhombic crystal structure, specific gravity: l.95. It is the least used of all the oxidizers in the fireworks industry. It has a transition point to the tetragonal system at about 240 °C. It is said that pure ammonium perchlorate sublimes without melting when it is slowly heated in the air, but when the commercial material is heated in a porcelain crucible with an electric heater, it decomposes violently between 260 and 360 °C. A sample that was recrystallized four times decomposed at 386 °C. From this fact, it is known that ammonium perchlorate decomposes easily as a result of some impurities, Cr, etc.

Ammonium perchlorate has been extensively studied because it is used for solid rocket fuel.[1,2] It is thought that there are two kinds of decomposition; the first occurs below 300 °C, and the other above 300 °C. The reactions seem to be different. They are very complicated and the products detected are N_2O, N_2, NO, NO_2, NH_3, $HClO_4$ HNO_3, HCl, HNO_2, and O_2.

Ammonium perchlorate is very soluble in water even at room temperature (29.4 g at 0 °C, 33.2 g at 10 °C, 37.2 g at 20 °C, 65.6 g at 80 °C, 77.3 g at l00 °C per 100 g of water).

Commercial ammonium perchlorate is a white powder. Its solution in water is almost neutral; the pH value was 6.8 at 24 °C in a 10% solution. It absorbs more moisture than potassium nitrate and potassium chlorate; 0.19% water was detected after a 50 day test at an average temperature of 10 °C and about 80% relative humidity. It is slightly soluble in alcohol (2 g per 100 g of ethanol); soluble in acetone and insoluble in ether.

Ammonium perchlorate powder tends to eventually cake but not as quickly as potassium nitrate or potassium chlorate.

Ammonium perchlorate is a strong oxidizer at high temperatures. It burns with shellac, rosin, etc. in a ratio of about 10:2 producing a high temperature flame. The combustion products are mostly gaseous substances that do not produce smoke in dry air, but they do smell of hydrogen chloride gas. In moist air, however, a dense white smoke appears due to the reaction of hydrogen chloride gas with water vapor in the air. The available oxygen per 1 g of ammonium perchlorate is 0.342 g, which is 0.74 times as much as that of potassium perchlorate, based on the reaction:

$$2\ NH_4ClO_4 \rightarrow N_2 + 3\ H_2O + 2\ HCl + 2.5\ O_2$$

Ammonium perchlorate alone explodes with a strong impact, but it showed no tendency to explode when initiated by a No. 6 detonator.

As described above, compositions that contain ammonium perchlorate as the oxidizer produce a high temperature flame that is high enough to excite color producing molecules or atoms to generate a good flame color. Also, the flame contains hydrogen chloride gas, which reduces the molecules to SrCl, BaCl, CuCl, etc. to deepen the color, or it reduces the solid metal oxide particles in the flame to the chloride [e.g., MgO (solid) to MgCl (gas)] to increase the transparency of the flame and to give a bright color.

Ammonium perchlorate reacts with magnesium in the presence of moisture or water to produce ammonia gas and magnesium perchlorate:

$$2\ NH_4ClO_4 + Mg \rightarrow 2\ NH_3 + Mg(ClO_4)_2 + H_2$$

The reaction can be detected by the smell of ammonia. The reaction results in a large amount of heat being generated, often enough to cause a fire due to the accumulation of heat. Under perfectly dry conditions this reaction does not occur. This reaction can be suppressed by potassium dichromate ($K_2Cr_2O_7$) even in the presence of moisture or water. Ammonium perchlorate also reacts with copper.

$$2\ NH_4ClO_4 + Cu \rightarrow 2\ NH_3 + Cu(ClO_4)_2 + H_2$$

When ammonium perchlorate is mixed with red phosphorus, it becomes very sensitive to impact, but not as sensitive to friction. It also becomes sensitive with arsenic sulfide, sulfur, antimony trisulfide, etc. The degree of impact sensitivity of ammonium perchlorate in such mixtures is almost the same as that of potassium chlorate, but higher than that of potassium perchlorate. However, the low friction sensitivity of ammonium perchlorate in such mixtures is one of its attractive features when compared to potassium chlorate and potassium perchlorate.[3]

Nitric acid and hydrochloric acid do not react with ammonium perchlorate, but when concentrated sulfuric acid is added, it generates a white smoke that smells slightly of ClO_2.

Ammonium perchlorate causes double decomposition with potassium nitrate, but no double decomposition with sodium nitrate.

$$NH_4ClO_4 + KNO_3 \rightarrow KClO_4 + NH_4NO_3$$

The ammonium nitrate that is produced by the above reaction is quite hygroscopic. Therefore if a composition containing ammonium perchlorate comes in contact with another composition that contains potassium nitrate, such as Black Powder, a wet layer of ammonium nitrate occurs between the two compositions and may result in a misfire. This double decomposition does not occur with barium nitrate, and mixtures of barium nitrate and ammonium perchlorate are permissible in the preparation of firework compositions.

Ammonium perchlorate and potassium chlorate result in a double decomposition to produce ammonium chlorate and potassium perchlorate when they are mixed in a wet state:

$$NH_4ClO_4 + KClO_3 \rightarrow NH_4ClO_3 + KClO_4$$

Ammonium chlorate decomposes gradually at room temperature. Needless to say compositions that contain ammonium perchlorate and potassium chlorate must be avoided. An experiment to produce ammonium chlorate by above reaction can be carried out as follows: Add 35 g of potassium chlorate, $KClO_3$, to 100 ml of water and dissolve it while heating. Add 36 g of ammonium perchlorate, NH_4ClO_4, to the solution and stir well until a large quantity of white crystals will appear; this is almost all potassium perchlorate. Let it cool to room temperature. Remove the crystals by filtration. The remaining liquid is mainly ammonium chlorate. Evaporate the mother liquor to about 30 ml over a water bath. Cool it to room temperature, and the ammonium chlorate will crystallize out as a crude product. Remove the crystals from the mother liquor. Dry the crystals at room temperature. The amount of ammonium chlorate thus obtained is about 19 g. The yield is about 55–63% of the theoretical value.

Ammonium chlorate, NH_4ClO_3, decomposes gradually, generating a yellow-brown gas that smells strongly of chlorine. The degree of decomposition is about 50% of the original amount at an average temperature of about 26 °C over 35 days. A quantity of ammonium chlorate thus prepared was stored in a glass bottle that had a loose fitting rubber stopper and left at room temperature during the summer; in 48 hours it decomposed explosively, breaking the bottle.

Ammonium chlorate, NH_4ClO_3, alone explodes on strong impact, but it is not as sensitive to impact and friction in the absence of other combustible substances. A mixture of ammonium chlorate and shellac in a ratio 10:2 burns at a rate of 1.2–1.3 mm/s, producing a slightly yellowish flame. This burning rate resembles that of a potassium chlorate composition.

Ammonium perchlorate is decomposed by ultraviolet radiation, but not as much as potassium chlorate; to be precise l/10 as much. According to Dr. Osada,[4] ammonium perchlorate that is exposed to ultraviolet radiation decreases its decomposition temperature to 210 °C after 1000 hours of exposure. As in the case of potassium perchlorate, $FeCl_3$, $CuCl_2$, Cr_2O_3, and $K_2Cr_2O_7$ promote the decomposition of ammonium perchlorate and decrease the decomposition temperature to 300 °C, where it decomposes entirely.

Potassium Chlorate, $KClO_3$

Molecular weight: 122.55; colorless with a monoclinic crystal structure; specific gravity: 2.33; melting point: 368 °C; dissociates at 400 °C and above, generating oxygen. This reaction proceeds as follows:

$$2\,KClO_3 \rightarrow 2\,KCl + 3\,O_2 + (+21.3\text{ kcal})$$

The reaction proceeds violently above 500 °C.[5]

Potassium chlorate is not as soluble in water as potassium nitrate (3.3 g at 0 °C, 7.3 g at 20 °C, 37.6 g at 80 °C and 56.3 g at 100 °C in 100 g of water). The solution in water is almost neutral; a pH of 6.8 (24 °C) was obtained from a commercial sample. It absorbs more moisture than potassium nitrate; 0.07% moisture was measured after leaving it in 80% relative humidity at an average temperature of 10 °C for 50 days. The solubility of potassium chlorate in alcohol is 0.83 g in 100 g. It is also soluble in alkali.

Potassium chlorate powder that is made by crushing the crystals, tends to cake more than potassium nitrate. Most commercial potassium chlorate has an anticaking ingredient added that prevents the powder grains from caking. However, in match and other industries that use potassium chlorate in a solution, potassium chlorate without the anticake is preferred.

Potassium chlorate is a strong oxidizer at high temperatures. It burns with fuels like shellac, rosin, etc. to produce a high temperature flame and white smoke that consists of KCl particles. The fuel to oxidizer ratio is generally 2:10 to give the highest flame temperature. The odor of chlorine or hydrogen chloride gas is not detectable. One gram of potassium chlorate produces 0.392 g of oxygen. This amount is similar to that of potassium nitrate.

Potassium chlorate alone explodes with strong impact but not when initiated by a No. 6 detonator.

Potassium chlorate in a composition produces a flame temperature that is high enough to excite molecules to emit colored light. It also contains chlorine atoms that are effective in deepening the color of the flame; (i.e., it can generate the color producing molecules, SrCl, CuCl, BaCl, etc. in the flame).

Potassium chlorate becomes quite sensitive in contact with red phosphorus and ignites very easily by friction. These properties are used in the manufacture of the striker portion of commercial matches. When potassium chlorate is mixed with sulfur or sulfur containing compounds like arsenic sulfide (realgar), antimony trisulfide, etc., the sensitivity to impact or friction is greatly increased. According to the late Professor S. Yamamoto[6a] of Tokyo University, when a mixture of potassium chlorate and arsenic sulfide was shaped into a small tablet, using a hand press, and the tablet was left sitting on a table, a little while later the tablet spontaneous ignited and burned. The same tests were tried several times and the results were the same. Dr. Yamamoto concluded that it was caused by internal friction that occurs upon the relaxation of the crystals from of the stress produced by the press.

Potassium chlorate reacts with sulfuric acid to produce chlorine dioxide, ClO_2, which is a heavy, yellow gas (about 2.3 times as dense as air); melting point: 10 °C; it decomposes explosively into chlorine and oxygen when exposed to sunlight, and it ignites any combustible material in contact with it. Accordingly, when a drop of 60% or more concentrated sulfuric acid is added to a mixture of potassium chlorate and sugar, it ignites spontaneously.

According to Langhous[7] potassium chlorate reacts with hydrochloric acid to produce chlorine dioxide, ClO_2, and chlorine, Cl_2, where the latter reduces the explosive tendency of the former. In this way it is as dangerous as it is with sulfuric acid. Potassium chlorate does not react with nitric acid; however, if potassium chloride is present in the potassium chlorate, it causes a violent reaction with the generation of chlorine dioxide. Accordingly, the amount of potassium chloride that might be present as an impurity is significant. Potassium chlorate reacts less violently with phosphoric acid than with hydrochloric acid, but it also generates chlorine dioxide. In view of this, the red phosphorus, which is used to manufacture toy pistol caps, etc., must be thoroughly purified from phosphoric acid.

In a commercial sample of potassium chlorate Dr. Osada[4] found 0.0002% of potassium chlorite and 0.016% potassium chloride, which increased gradually with exposure to sun light; in the sun during December the chlorite increased to 0.002% and under ultraviolet light after 500 hours the chloride increased to 0.16%. Potassium chlorite, $KClO_2$, when potassium chloride, KCl, is present, ignites or explodes on contact with sulfur or a sulfide. Therefore the chlorite probably promotes the decomposition of $KClO_3$ when it is heated. Of course, the amount of potassium chlorite or chloride may be too small to cause a spontaneous explosion, but exposure to ultraviolet light does degrade the quality of potassium chlorate.

Potassium chlorate reacts with ammonium perchlorate and other ammonium salts in a wet state or in solution to produce ammonium chlorate, which forms colorless crystals and gradually decomposes even below 100 °C [see ammonium perchlorate]. The late professor S. Yamamoto[6a] pointed out that some forms of the asphaltum contain ammonia, and the use of these types of asphaltum should be avoided in fireworks. In view of this asphaltum or pitch is not recommended for use in combination with potassium chlorate.[8a]

Potassium chlorate begins to decompose to produce oxygen at about 70 °C by catalytic action in the presence of metal oxides such as manganese dioxide, copper oxide, etc. The reaction progresses quickly above 100 °C. In addition, $FeCl_3$, $CuCl_2$, Cr_2O_3 and $K_2Cr_2O_7$ act as decomposition catalysts.

It would be preferred to eliminate potassium chlorate from fireworks, but it is quite difficult because no other oxidizer can surpass potassium chlorate in burning speed, in ease of ignition or in sound production when using the smallest amount of composition. Match head composition cannot be made without it. Also it is absolutely necessary for some colored smokes, small crackers and various kinds of toy caps. Unfortunately, these articles tend to become a source of explosions, and potassium chlorate compositions must be treated with respect and caution.

Potassium Nitrate, KNO_3

Molecular weight: 101.11; colorless with a rhombic crystal structure; specific gravity: 2.109 (16 °C); makes a transition to the trigonal system at 129 °C; melting point: 339 °C; generates oxygen at temperatures above 560 °C; at about 600 °C it generates a large amount of oxygen to become potassium nitrite:

$$2\,KNO_3 \rightarrow 2\,KNO_2 + O_2 + (-58.5\text{ kcal})$$

Potassium nitrate is not particularly soluble in cold water, but its solubility increases as the temperature increases (13.3 g at 0 °C, 31.6 g at 20 °C, 169 g at 80 °C and 246 g at 100 °C, in 100 g of water). The aqueous solution is almost neutral; a commercially available product showed a pH of 6.2 (14 °C) in a 10% aqueous solution. It is not very hygroscopic; fine grained commercial potassium nitrate absorbed only 0.03% moisture at 10 °C and 80% relative humidity over 50 days. It is insoluble in alcohol. Potassium nitrate powder tends to cake gradually. Most commercial potassium nitrate has an anticaking ingredient added that prevents the powder grains from caking. This form is handy to use in most cases, but when it is used in a solution or when it is consolidated in a composition using only pressure, without a binding agent (e.g., Black Powder in rocket propellants), it is better to use potassium nitrate without the anticaking agent.

Potassium nitrate alone does not explode even with a strong impact. However, potassium nitrate mixed with red phosphorus is very sensitive to impact. This is explained thus: the impact of iron upon iron often causes it to ignite, but with iron and aluminum or iron and brass, it is difficult to ignite. The mixture burns with a flame, but it does not explode when ignited. Potassium nitrate is a strong oxidizer at high temperature. However, in mixtures with an ordinary organic fuel (e.g., shellac or rosin) it burns irregularly—if at all, producing potassium nitrite in a liquid state. Used in this manner, 1 g of potassium nitrate produces about 0.158 g of effective oxygen. But when potassium nitrate is mixed with charcoal and sulfur or with magnesium, it decomposes, and the amount of effective oxygen increases to the maximum value of 0.396 g.

When potassium nitrate is used as the oxidizer in a composition, it does not produce a temperature high enough to generate a colored flame, except when combined with magnesium. However, it is useful for making good sparks.

A small amount of potassium nitrate mixed into the powder of some combustible substance, like carbon powder, can burn for hours.

The presence of potassium nitrate in dust makes it quite flammable and dangerous. The dust must be burned in small quantities. Potassium nitrate is not poisonous.

Potassium Perchlorate, $KClO_4$

Molecular weight: 138.55; colorless with a rhombic crystal structure; specific gravity: 2.524 and this high value is worth noting. It makes a transition to the tetragonal system at about 300 °C. The commercial material melts at about 570 °C. At this temperature it decomposes generating oxygen:

$$KClO_4 \rightarrow KCl + 2\,O_2 + (+0.68\text{ kcal})$$

(In some books it is written as an endothermic reaction, but this is due to the difference in the heats of formation for $KClO_4$ and KCl used in the calculation; $KClO_4$ and KCl have almost the same heat of formation.)

Potassium perchlorate is not very soluble in water, and the solubility does not change much with temperature (1.01 g at 0 °C, 1.06 g at 10 °C, 1.68 g at 20 °C, 13.4 g at 80 °C, 22.3 g at 100 °C per 100 g of water). This presents some problems with the recrystallization of this material. A solution of the commercial material is almost neutral (e.g., a 1% solution in water showed a pH value of 7.3 at 23 °C).

Potassium perchlorate is almost non-hygroscopic; but an experiment showed that it absorbed 6% moisture in an atmosphere with 100% relative humidity at room temperature over a period of 10 days. At room temperature 0.008 g of potassium perchlorate is soluble in 100 g of ethanol and 0.105 g in 100 g of methanol.

Crushed potassium perchlorate powder cakes gradually during storage, but it does not become as hard as potassium nitrate or chlorate.

Potassium perchlorate alone explodes with a strong impact, but in the detonator test no explosion occurs.

Potassium perchlorate is a strong oxidizer at high temperatures. It is similar to potassium chlorate in that it burns with a fuel such as rosin in a mixture of about 10:2 ratio, producing a high temperature flame and a white smoke of KCl particles. It burns less easily with shellac. It is used for colored flame compositions, but the burn rate is not as great as with potassium chlorate compositions. On burning it does not smell of chlorine gas. The available oxygen per 1 g of potassium perchlorate is 0.462 g, which is 1.18 times more than potassium chlorate.

A spectral analysis showed that the color producing mechanism of flames due to potassium perchlorate is exactly the same as that of potassium chlorate. Therefore replacing potassium chlorate with potassium perchlorate in a composition causes no color change in the flame.

Potassium perchlorate becomes sensitive in contact with red phosphorus; the mixture detonates with a loud noise when impacted between pieces of aluminum or bronze. When the mixture is ignited, it detonates instantaneously. However, match compositions or toy pistol caps cannot be made from compositions that contain potassium perchlorate in place of potassium chlorate, because the ignition is uncertain. When potassium perchlorate is mixed with arsenic sulfide, antimony trisulfide, sulfur, etc. it also becomes sensitive; arsenic sulfide greatly increases the sensitivity to friction. But the degree of sensitivity is not as great as it is with potassium chlorate.

When potassium perchlorate is added to hydrochloric acid or nitric acid, it causes no reaction. With concentrated sulfuric acid it smells only slightly of ClO_2, which is caused by some impurity such as KCl. A mixture of potassium perchlorate and a sulfide does not immediately ignite upon the addition of concentrated sulfuric acid; this is a principal difference from the potassium chlorate mixture.[6b]

According to Dr. Osada[9] KCl, $FeCl_3$, $CuCl_2$, Cr_2O_3, $K_2Cr_2O_7$, LiCl, etc. promote the decomposition of potassium perchlorate, similar to that of potassium chlorate. In particular Cr_2O_3 is very effective at 410 °C, and LiCl at 430 °C, but these temperatures are a little higher than they would be with potassium chlorate.

Potassium perchlorate is far less likely to decompose under ultraviolet light than potassium chlorate (i.e., l/10 the amount observed with potassium chlorate).

Color Agents that also Serve as Oxidizing Agents

These materials are the nitrates or chlorates of barium, sodium, strontium, etc.

Barium Chlorate, $Ba(ClO_3)_2 \cdot H_2O$

Molecular weight: 322.26; colorless, with a monoclinic crystal structure; specific gravity: 3.18, becomes anhydrous at 120 °C; melting point: 414 °C. When it is heated above the melting point, it decomposes, generating oxygen as follows:

$$Ba(ClO_3)_2 \rightarrow BaCl_2 + 3\ O_2$$

Barium chlorate is soluble in water (20.3 g at 0 °C, 33.8 g at 20 °C, 84.8 g at 80 °C, 105 g at 100 °C per 100 g of water); its solubility in water is greater than that of potassium chlorate. It dissolves very little in either ethanol or acetone and is not hygroscopic. The powder cakes in much the same way as potassium chlorate.

Barium chlorate alone explodes upon strong impact, but no reaction could be initiated with a No. 6 detonator.

Barium chlorate burns well in combination with shellac in a weight ratio 10:2, producing a beautiful green colored flame. The spectrum consists of three clear bands of BaCl molecules, thus it has the ability to produce green color even in low temperature flames (without magnesium as fuel), and consequently it is regarded as the most superior green color producing agent. However more care must be taken when handling the material than with potassium chlorate. It is said that compositions that contain barium chlorate are more sensitive than compositions that contain potassium chlorate and sometimes result in spontaneous combustion in the direct sunlight. The oxygen obtained on burning amounts to 0.298 g per 1 g of barium chlorate.

Acids, sulfur, arsenic sulfide, red phosphorus and ammonium salts must not be mixed with barium chlorate.

Barium Nitrate, $Ba(NO_3)_2$

Molecular weight: 261.35; colorless, with tesseral crystal structure; specific gravity: 3.24, which is 1.1 times greater than strontium nitrate, 1.5 times greater than potassium nitrate and 1.3 times greater than potassium perchlorate. The melting point is said to be 592 °C, but a commercial sample melted at 552 °C. When it is heated above its melting point, it decomposes as

$$Ba(NO_3)_2 \rightarrow Ba(NO_2)_2 + O_2$$

and

$$Ba(NO_2)_2 \rightarrow BaO + NO + NO_2$$

Barium nitrate is soluble in water (5.0 g at 0 °C, 6.7 g at 10 °C, 9.0 g at 20 °C, 27.2 g at 80 °C, 34.4 g at 100 °C in 100 g of water). A 5% solution of this material in water showed a pH value of 5.8. It is not very hygroscopic and is similar to potassium chlorate; it absorbs 0.02% moisture in an average humidity of 84% and an average temperature of 25 °C over 10 days. It is insoluble in ethanol, but slightly soluble in methanol (0.07 g at 0 °C, 0.05 g at 30 °C in 100 g of methanol).

Powdered barium nitrate cakes to form a very hard mass almost like a stone and thus is difficult to use.

Barium nitrate alone cannot be ignited or caused to explode even with a strong impact. A mixture of barium nitrate and shellac in the weight ratio of 10:2 burns well producing a slight green colored flame. The color may be due to the barium monohydroxide (BaOH) molecule in the spectrum; this green light is too weak to be used for fireworks. When the mixture is loaded into a paper tube and burned, the flame is interfered with by ash that consists mainly of barium nitrite. However a mixture of barium nitrate and magnesium in the weight ratio 6:4 burns with whitish blue flame producing almost no ash because of the complete decomposition of the barium nitrate due to the high temperature of the flame.

$$2\ Ba(NO_3)_2 \rightarrow 2\ BaO + N_2 + 5\ O_2$$

The oxygen produced with shellac is 0.061 g and that produced with magnesium is 0.184 g per 1 g of barium nitrate.

Barium nitrate is an important color producing agent for green and white flames. For example, we obtain an intense white light from a mixture of 65% barium nitrate and 35% magnesium that contains no chlorine. On the other hand, when 20% (additional) PVC is added to the mixture, it gives a brilliant green light due to the action of the chlorine.

Barium nitrate becomes a little sensitive when it is added to red phosphorus; it explodes on impact between iron and iron, it ignites with iron and brass, but does not easily ignite with brass and aluminum. Nevertheless, there are some occasions when it explodes; this means that when barium nitrate decomposes, it is sometimes more reactive than potassium nitrate or sodium nitrate. R. Lancaster[8b] lists a salute composition that uses barium nitrate as the oxidizer; 68% barium nitrate, 23% pyro aluminum and 9% sulfur. This kind of composition utilizes the reactive nature of barium nitrate.

Sodium Nitrate, $NaNO_3$

Molecular weight: 84.99; colorless with trigonal crystal structure; specific gravity: 2.257; melting point: 308 °C; decomposes above 380 °C generating oxygen and sodium nitrite:

$$2\ NaNO_3 \rightarrow 2\ NaNO_2 + O_2$$

Sodium nitrate is soluble in water (73 g at 0 °C, 80.8 g at 10 °C, 87.6 g at 20 °C, 148 g at 80 °C, 180 g at 100 °C in 100 g of water). The solubility is 1.8 times greater than strontium nitrate. A commercial sample showed a pH value of 8.6 at 18 °C. Its hygroscopic nature is not as great as some would suggest. A test showed that it absorbed 0.92% of moisture at 84% relative humidity over 10 days, which is less than strontium nitrate. It is slightly soluble in alcohol, very slightly soluble in acetone.

Sodium nitrate powder is produced by crushing the crystals, so it also cakes gradually but does not become as hard as potassium nitrate or potassium chlorate.

Sodium nitrate alone does not explode from a strong impact. It burns well in combination with shellac in the weight ratio 10:2, producing transparent liquid drops at the burning surface, which consist of mainly sodium nitrite. It burns in combination with magnesium in the weight ratio 6:4, then completely decomposes producing neither liquid drops nor a cinder column. The oxygen available from its decomposition to sodium nitrite amounts to 0.188 g. When it completely decomposes, it produces 0.424 g per 1 g of sodium nitrate. The reaction of the latter may be

$$2\ NaNO_3 \rightarrow N_2 + 2\ NaO + 2\ O_2$$

Sodium nitrate gives an intense yellow light and has been used for illumination. In combination with magnesium it burns well without producing either cinder or sparks in a wide range of fuel to oxidizer ratios (i.e., the ratio can vary from 3:7 to 8:2). This is a superior characteristic, which is not present in any other composition.

A mixture of sodium nitrate and red phosphorus is more sensitive to mechanical action than that of potassium nitrate and red phosphorus. The sodium nitrate and red phosphorus mixture ignites or explodes from an impact of iron and iron. In the case of iron and brass it does not explode, but only burns; with brass and aluminum it is difficult to ignite.

A mixture of sodium nitrate and dust is very flammable, and precautions must be taken to avoid fire.

Strontium Nitrate, $Sr(NO_3)_2$

Molecular weight: 211.63; colorless with tesseral crystal structure; specific gravity: 2.986, which is 1.4 times greater than potassium nitrate, and 1.2 times greater than potassium perchlorate. The high density is one of the characteristics of strontium nitrate; melting point: 570 °C; decomposes on heating as follows:

$$Sr(NO_3)_2 \rightarrow Sr(NO_2)_2 + O_2$$

and then

$$Sr(NO_2)_2 \rightarrow SrO + NO + NO_2$$

Strontium nitrate is soluble in water (40.1 g at 0 °C, 89.4 g at 35 °C, 93.4 g at 60 °C, 96.9 g at 80 °C, 104.9 g at 105 °C in 100 g of water). A substantial amount of strontium nitrate dissolves in water even at room temperature, however, the solubility does not increase much with and increase in temperature and at about 100 °C it is less than that of potassium nitrate. It is almost insoluble in ethanol or acetone.

Strontium nitrate also exists as a tetrahydrate, $Sr(NO_3)_2 \cdot 4H_2O$; it can be obtained by recrystallization from a solution in water, however, it becomes anhydrous above 100 °C.

The solution of strontium nitrate in water is almost neutral; 10 g dissolved in 100 g water produced a pH value of 7.0 at 25 °C. The anhydrous salt is somewhat hygroscopic like ammonium perchlorate. A well dried sample passing 80 mesh absorbed 1.61% of moisture at 84% relative humidity. Powdered strontium nitrate gradually cakes, but not to the same extent as potassium nitrate or potassium chlorate. When caked strontium nitrate is heated to 200–300 °C, it becomes a dry powder again.

Strontium nitrate alone does not explode even with a strong impact. Strontium nitrate burns in combination with shellac in the ratio 10:2 producing a red flame, but it also produces a large amount of solid ash. When the composition is packed into a paper tube and burned, the ash remains as a solid chimney and interferes with the flame to the point of extinguishing it. In such cases burning does not cease, but progresses without a flame. The ash consists mainly of strontium nitrite, $Sr(NO_2)_2$.

When a mixture of strontium nitrate and magnesium in a weight ratio of 6:4 burns, strontium nitrate decomposes completely due to the high flame temperature and produces little ash. The decomposition may be as follows:

$$Sr(NO_3)_2 \rightarrow SrO + N_2 + 2.5\,O_2 + (-92.15\text{ kcal})$$

The oxygen produced by 1 g of strontium nitrate is 0.076 g for a low temperature flame, but 0.189 g in a high temperature flame. Accordingly, strontium nitrate is used only as a color agent for low temperature flame compositions and as both color agent and oxidizer for high temperature flame compositions.

Strontium nitrate is an important color producing agent for red flames. Some recommend lithium nitrate for red flames, but the light from the flame is too weak for practical use as a replacement for strontium nitrate.

Strontium nitrate mixed with red phosphorus ignites from an impact between iron and iron or iron and brass, but it does not easily detonate. It is difficult to ignite it by impact with brass and aluminum.

A mixture of strontium nitrate and aluminum often degenerates producing ammonia and NO_x gas. This tendency is common with other nitrates except ammonium nitrate (see aluminum). Dust that contains strontium nitrate is flammable, and the same precautions must be taken as with other oxidizers.

Color Producing Agents

Color producing agents give color to flames by producing light emitting atoms or molecules in the flame. These color generating atoms or molecules are produced as part of the chemical reaction in the flame; they are not produced by vaporizing materials in an original form in the composition. For example, a green flame is not obtained by adding barium chloride, $BaCl_2$, to the composition, but rather by the creation of barium monochloride (BaCl) molecules in the flame by chemical reactions in the presence of a barium salt and HCl molecules.

Metal salts are generally used for color agents; only rarely would a metal powder be used (e.g., copper powder for blue flames). The metal salts consist of a metallic ion (a cation) and non-metallic ion (an anion); however, the color donor is the cation (e.g., strontium gives red, sodium–yellow, barium–green, and copper–blue). The anion has almost no influence upon the color. For example, $Sr(NO_3)_2$, $SrCO_3$, SrC_2O_4, $SrCl_2$, etc. produce almost the same color effect. However, the anions do have an influence upon the flame temperature; generally the nitrate anion (NO_3^-) increases the flame temperature, and thus increases the brilliancy of the light. However, other anions decrease both the flame temperature and the brilliancy. The flame temperature affects the excitation of the color producing molecules. In general the higher the temperature, the greater the number of excited molecules, and the anions exercise an indirect influence on the color of the flame by influencing the temperature.

Therefore the amount of color producing agent that is added to a composition, except for nitrates, should be kept as small as possible without diminishing the color effect. The limit may be 10 to 20% of the weight of the composition.

Red Color Producing Agents

Strontium Carbonate, $SrCO_3$

Molecular weight: 147.63; colorless with rhombic crystal structure or fine powder; specific gravity: 3.70; makes a transition at 920–927 °C to the hexagonal system; melting point: 1497 °C at 60 atm.

Strontium carbonate is not very hygroscopic; it absorbed only 0.65% moisture in 10 days at an average temperature of 25 °C and an average humidity of 84%. When heated, strontium carbonate changes into strontium oxide and generates carbon dioxide gas. The oxide is a white amorphous powder that changes into strontium hydroxide in the presence of moisture:

$$SrCO_3 \rightarrow SrO + CO_2$$

$$SrO + H_2O \rightarrow Sr(OH)_2 + (+14.7\ \text{kcal})$$

When a red star composition is burned, the ash often slowly becomes wet due to the hygroscopic nature of strontium hydroxide, $Sr(OH)_2$.

Strontium carbonate can be mixed with potassium chlorate.

Strontium carbonate is almost insoluble in water (0.001 g per 100 g of water at 24 °C). The solution is alkaline and the pH was 8.9 at 35 °C. If a composition consists mainly of aluminum and nitrates, including strontium carbonate, such an alkaline mixture has a risk of spontaneous decomposition in a damp state. Strontium carbonate dissolves in water as the bicarbonate, if the water contains CO_2.

Strontium carbonate in a composition produces carbon dioxide gas when it burns rather than oxygen. Too much strontium carbonate in a composition can decrease the burning rate and brilliancy of the flame; a 10 to 15% content may be the best.

Strontium Oxalate, $SrC_2O_4 \cdot H_2O$

Molecular weight: 193.66; colorless crystalline powder; specific gravity: 2.08; almost insoluble in water (0.0046 g at 18 °C, 5 g at 100 °C per 100 g of water); almost insoluble in alcohol; slightly soluble in water that contains an ammonium salt. It contains one mole of water of crystallization per mole, but loses its water at 150 °C. Strontium oxalate decomposes on heating as follows:

$$SrC_2O_4 \rightarrow SrO + CO_2 + CO$$

In fact the product has a reducing action due to CO. As a result, it reduces solid particles of MgO to magnesium gas in the flame produced by a composition that contains magnesium:

$$MgO_{(s)} + CO \rightarrow Mg_{(g)} + CO_2$$

This decreases the continuous spectrum due to the solid particles and makes the flame more clear for the production of good color. When magnesium is used in the composition, strontium oxalate may be more useful than strontium carbonate, however, when magnesium is not used, it seems that strontium carbonate is superior.

Orange Color Producing Agent

Calcium Carbonate, $CaCO_3$

Molecular weight: 100.09; colorless, amorphous and heavy powder; hardly soluble in water (0.008 g at 0 °C and 0.005 g at 20 °C per 100 g of water). If the water contains carbon dioxide, it is more soluble producing the bicarbonate:

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$$

When calcium carbonate is heated, it produces carbon dioxide gas above 700 °C, and at 900 °C almost completely:

$$CaCO_3 \rightarrow CaO + CO_2$$

Calcium carbonate in contact with ammonium perchlorate causes a reaction quite slowly in the presence of moisture:

$$CaCO_3 + 2\,NH_4ClO_4 \rightarrow Ca(ClO_4)_2 + 2\,NH_3 + H_2O + CO_2$$

Calcium carbonate produces an orange flame and often is used for toy fireworks, etc. as a substitute for strontium salts.

Yellow Color Producing Agents

Sodium Bicarbonate, $NaHCO_3$

Molecular weight: 84.01; colorless with monoclinic crystal structure; specific gravity: 2.2; forms sodium carbonate on heating, generating carbon dioxide gas; soluble in water (6.5 g at 0 °C, 8.8 g at 20 °C, 13.8 g at 60 °C per 100 g of water). Over 65 °C in water it actively generates carbon dioxide gas to become sodium carbonate. Sodium bicarbonate solution in water is slightly alkaline; the pH value of a saturated solution at 24 °C was 8.l. Sodium bicarbonate has been used in Japan for compositions that contain potassium chlorate. It does not decrease the burning rate as much as the sodium carbonate. In a wet state it reacts actively with magnesium and less actively with aluminum, generating hydrogen gas. As a result, sodium bicarbonate cannot be used for compositions that contain magnesium or aluminum.

Sodium Carbonate, Na_2CO_3

Molecular weight: 105.99; colorless powder; specific gravity: 2.53; melting point: 851 °C; more soluble in water than sodium oxalate (7.1 g at 0 °C, 21.6 g at 20 °C, 45.5 g at 100 °C per 100 g of water).

A pH value for 10 g sodium carbonate dissolved in 100 g of water was 12.7 at 24 °C, which is quite strongly alkaline.

Sodium carbonate absorbs some moisture; a test showed that it absorbed 10.74% moisture at an average relative humidity of 84% at an average temperature of 25 °C over 10 days.

Sodium carbonate corrodes magnesium or aluminum in the presence of moisture; accordingly it is not recommended to use it as an ingredient in a composition that contains magnesium or aluminum. It decreases the burning rate of the composition remarkably. Coloration with this material is so effective that it can be used in small amounts. Sodium carbonate is quite strongly alkaline, so it cannot be used in compositions that do not work well under alkaline conditions.

Sodium Chloride, NaCl

Molecular weight: 58.44; colorless with tesseral crystal structure; specific gravity: 2.164; melting point: 800.4 °C; boiling point: 1413 °C; soluble in water (26.28 g at 0 °C, 26.37 g at 20 °C, 28.12 g at 100 °C per 100 g of water); the solubility does not vary much with temperature. It is insoluble in alcohol or ether. The material can be rather hygroscopic due to impurities. A solution in water is a little alkaline; a pH value of a 10% solution in water was 9.6 at 25 °C. So-called “Table Salt” is not hygroscopic, but the pH value of a 10% solution was 10.8 at 26 °C, and the solution contained some insoluble matter.

Sodium chloride loses its hygroscopic nature on heating and can be used for firework compositions. However it is not recommended for compositions that contain metal powder or those that are used or stored in a metal container.

Sodium Oxalate, $Na_2C_2O_4$

Molecular weight: 134.00; colorless crystalline powder; specific gravity: 2.34; soluble in water (3.4 g at 20 °C, 6.3 g at 100 °C per 100 g of water). The pH of a saturated solution in water was 6.1 at 24 °C. It is barely soluble in alcohol. It causes no reaction with aluminum and a small reaction with magnesium; this is an important feature that is quite different from that of sodium chloride or sodium bicarbonate. A test showed that it absorbed no moisture at an average relative humidity of 84% at an average temperature of 25 °C over 10 days.

Green Color Producing Agent

Barium Carbonate, $BaCO_3$

Molecular weight: 197.35; colorless with a hexagonal crystal structure; specific gravity: 4.43; makes a transition to a tesseral crystal structure at 982 °C. When it is heated to high temperature, it decomposes generating carbon dioxide gas, but the partial pressure of the gas reaches 1 atm at 1350 °C. The solubility in water is small, but somewhat greater than that of strontium carbonate (0.0022 g at 18 °C, 0.0065 g at 100 °C). A pH value of a saturated solution was 9.9 at 20 °C; thus it is more alkaline than strontium carbonate.

Barium carbonate produces a pretty green flame in a composition that contains ammonium perchlorate as the oxidizer, and the color is better than that produced using barium nitrate.

Blue Color Producing Agents

Basic Copper Carbonate,
Type I: $CuCO_3{\cdot}Cu(OH)_2$
Type II: $2CuCO_3{\cdot}Cu(OH)_2$

There are two types of basic copper carbonate, I and II. In fireworks type I is commonly used. It has a molecular weight of 221.11, is rather dark green, consisting of a monoclinic crystal structure; specific gravity: 4.0; decomposes: 200 °C; insoluble in water. The green coat (patina) on weathered copper consists of this substance. It occurs naturally as malachite. Type II occurs naturally as azurite; specific gravity: 3.77–3.83 and varies from light blue to a deeper blue. Because of its pretty color, it is used as pigment.

Basic copper carbonate cannot produce as good a good blue as copper acetoarsenite, but it is not easily airborne and is not so poisonous. It is well suited to ammonium perchlorate compositions or high temperature flame compositions, especially where HCl gas is produced in the flame.

Copper Acetoarsenite (Paris Green), $3CuO{\cdot}As_2O_3 + Cu(CH_3COO)_2$

Copper acetoarsenite is also called “emerald green”. It is a pretty green powder with very fine particles; insoluble in water; its wash water is slightly acidic; stable against sunshine and weathering; soluble in acid; ammonia solution, decomposes by alkali; not hygroscopic.

Copper acetoarsenite is used in Japan in almost all blue compositions at present because it produces a very pretty blue. Note that the extra fine powder easily becomes airborne, and the chemical is quite poisonous. Care must be taken not to inhale this substance.

Copper Arsenite, $CuHAsO_3$

Molecular weight: 187.51; light yellow green powder of extra fine particles. Insoluble in water, but soluble in acid or ammonia solution. It colors a flame blue almost as well as copper acetoarsenite. It is almost non-hygroscopic. It is also poisonous and care must be taken as in the case of the acetoarsenite. It can be used in combination with chlorates.

Copper Powder, Cu

Copper powder is a reddish powder with pretty metallic luster. Atomic weight: 63.55; specific gravity: 8.9; melting point: 1083 °C; boiling point: 2595 °C. Gradually it becomes coated with a film of basic copper carbonate in the wet state due to the action of moisture and carbon dioxide gas in the air. When it is added to a composition that contains ammonium perchlorate, a pretty blue flame is obtained; 5% copper powder is adequate. Unfortunately, ammonium perchlorate reacts with copper powder generating heat and ammonia gas in the presence of moisture, so the composition must be well protected from moisture.

Copper Sulfate, $CuSO_4 \cdot 5H_2O$

Molecular weight: 249.69; blue with a triclinic crystal structure; specific gravity: 2.286. When it is heated, it changes to a trihydrate at 30 °C, the monohydrate at 110 °C, and it becomes anhydrous at 150 °C. The molecular weight of the anhydrous salt is 159.61. It is soluble in water or alcohol. This material is a strongly acidic salt, and it must not be used in combination with chlorates. A mixture of copper sulfate and red phosphorus in a wet state gradually rises in temperature until it undergoes spontaneous ignition. It can be used in combination with nitrates or perchlorates.

Copper sulfate is less expensive than copper acetoarsenite and produces a pretty blue color in combination with ammonium perchlorate, which is almost as good as the color produced by copper acetoarsenite. Another advantage is that it is not easily scattered, due to its density. Anhydrous copper sulfate absorbs moisture strongly, so it is also used as a desiccating agent, however it does not become wet.

Combustion Agents (Fuels)

Accroides Resin (Red Gum)

The burning rate of accroides resin as compared to shellac is as follows (see Table 1).

Table 1. Comparison of Burning Rate between Shellac and Accroides Resin.

Oxidizer	Burning Rate (mm/s)		Density (g/cm^3)
	Shellac (20%)	Accroides Resin(20%)	
NH_4ClO_4 (80%)	1.6	2.0	1.23–1.26
$KClO_3$ (80%)	1.3	2.5	1.18–1.27
$KClO_4$ (80%)	Incombustible	1.5	1.43–1.44

The sample compositions were charged in a powdered state. The significant importance of accroides resin is that it burns quite well with potassium perchlorate in comparison with shellac. The burning rate of the accroides resin is generally faster than that of shellac as seen in Table 1. This is quite good for chrysanthemum stars.

Aluminum, Al

Atomic weight: 26.982; specific gravity: 2.699; melting point: 660 °C; boiling point: about 2270 °C. The heat of combustion in an excess of oxygen is 7130 kcal per kg. This value is 690 kcal lower than that of carbon, which generates 7820 kcal of heat per 1 kg. However, aluminum does not produce as much gas as carbon, and the heat is well concentrated in the composition, which results in a high reaction temperature.

Aluminum powder is used in Japan in two forms; flake aluminum, which is a brilliant silver and consists of small flat plates, and atomized aluminum, which looks whitish grey and consists of spherical or pebble-like grains. The spherical is less ignitable than the flakes; only flakes are popular in fireworks. The flakes reflect infrared and ultraviolet rays.

Aluminum is chemically stable in the air, because its surface is covered by a film of aluminum oxide, which protects the aluminum from corrosion. It is also stable in water or weak acid at room temperature, because the surface is covered by a film of its hydroxide $Al(OH)_3$. However, when wet aluminum powder is kept at a higher temperature, it can suddenly cause a violent reaction over a few hours (see Table 2), because the film of the hydroxide is broken as it dissolves into the water. In a strong acid, aluminum dissolves, except in the case of an oxidizing acid like nitric acid, which makes a film of oxide on the metal surface that protects it from corrosion. Aluminum is easily corroded by alkaline substances (e.g., by sodium carbonate), but there is little corrosion with sodium bicarbonate.

Table 2. Comparison of the Resistance of Aluminum, Magnalium and Magnesium against Various Salts in the Wet State at Room Temperature.

	Aluminum	Magnalium	Magnesium
Distilled water	O	S	X
NH_4ClO_4	O	X	XXX
KNO_3	S (XXXX)	X	XX
$Ba(NO_3)_2$	S (XXXX)	X	XX
NH_4NO_3	O (O)	O	XXX
$KClO_3$	O	X	XXX
$KClO_4$	O	S	XXXX
$Na_2C_2O_4$	XX	XXX	XXXX
NaCl	S	XXXX	XXXX
$CuSO_4$	S	XXXX	XXXX
$NaHCO_3$	S	O	XXXX
Na_2CO_3	XXXX	XX	XXX
NaOH	XXXX	XX	XXX
H_3BO_3	O	XX	XXXX
CH_3COOH	O	XXXX	XXXX
$K_2Cr_2O_7$	O	O	O

Note: (1) The symbols are as follows:

O	No reaction occurs.	XX	Attacked considerably.
S	Very slightly attacked but useful in practice.	XXX	Attacked actively.
X	Attacked slowly.	XXXX	Attacked violently.

(2) Samples were used in a powdered state.

(3) 50/50 magnalium was used.

(4) ( ) denotes the resistance when heated to about 60 °C.
It also often occurs spontaneously at room temperature in summer.

Aluminum reacts with nitrates, except with ammonium nitrate, in the presence of water to produce H_2, NH_3, and NO_x gas. The reaction proceeds slowly at ordinary temperatures, but when the temperature rises to about 80 °C it becomes tremendously violent. In this case a large amount of heat is generated, and it accelerates the reaction even more, and sometimes it causes spontaneous ignition. A mixture of aluminum powder (flake) and a nitrate in the weight ratio 50:50, to which 35% additional water is added, seems to be the most reactive. When a weak acid like boric acid is added to the mixture to keep its pH value at 4.7–5.1, the reaction is suppressed. (See Table 3)

The symbol ∞ in Table 3 indicates that the composition did not decompose when heated for a long time. It must be noted that wet aluminum powder will decompose without other chemicals when it is heated for a long time. Glutinous rice starch does not react with aluminum.

Potassium nitrate, strontium nitrate, barium nitrate or sodium nitrate cause the most violent reaction in combination with aluminum, but as it has been stated above, ammonium nitrate does not cause such a reaction. (See Table 2.)

Aluminum reacts with potassium chlorate or perchlorate in the presence of moisture to generate hydrogen gas. The reaction proceeds very slowly at room temperature, but is accelerated above 85 °C. This reaction is not as violent as that of aluminum and a nitrate. Aluminum does

Table 3. Comparison of the Suppressing Effect of Weak Acids on the Decomposition of Wet Aluminum Powder and Wet Compositions with 5 mL Water Added that Contain Aluminum (100 g Samples in a Warm State).

Composition	Acid Added (Additional %)	Temperature for Test (°C)	Start of Decomposition (h:m)
100% Al	No acid	70–79	3:05
90% Al, 10% GRS	No acid	65–80	3:00
	0.5 % AA	65–80	2:00
	1.0% BA	65–80	∞
26% Al, 64% $KClO_3$, 10% GRS	No acid	70–73	9:30
	1.0% AA	70–73	3:00
	1.0% BA	70–73	∞
23% Al, 68% $KClO_3$, 10% S, 9% GRS	1.0% BA	70–73	
29% Al, 62% KClO3, 9% GRS	6.0% GA	60–70	3:30
40% Al, 50% $KClO_4$, 10% GRS	No acid	70–84	2:65
	0.25 % AA	70–84	3:45
	1.0% BA	70–84	∞
40% Al, 50% KNO_3, 10% GRS	No acid	72–77	1:42
	0.25 % AA	68–79	6:05
	1.0% BA	72–77	∞
40% Al, 50% $Ba(NO_3)_2$, 10% GRS	No acid	72–77	1:48
	0.5 % AA	68–75	1:28
	1.0% BA	72–77	∞

Note: Al = fine flake aluminum; GRS = glutinous rice starch; AA = acetic acid; BA = boric acid; GA = gum Arabic.

not react with ammonium perchlorate or starch (e.g., glutinous rice starch) in the presence of moisture.

The flake aluminum on the market generally contains an oily impurity such as stearine. Insoluble matter after digestion in hydrochloric acid is hardly detectable. The mesh size of the aluminum is selected according to use. For “report” compositions very fine flake aluminum is used. For fire dust, coarse flakes are often used; the size of flakes has an influence upon the life of the fire dust. The flake aluminum on the market passes 170–270 mesh and the thickness of a flake is about 0.3 – 2.0 microns. For waterfalls flakes of about 5 mm in diameter are added to the ordinary flake aluminum.

Amber Powder (Kunroku)

“Kun” means smell and “Roku” came from the name of the district “Rikuchu” where this material is produced. It is used for incense sticks. It seems to be a fossil resin, but the quality is not as good as the Baltic amber. In English it is called “amber powder”, but the chemical composition is said to be rather different from the Baltic amber. This material is yellowish or dark brown

Antimony Trisulfide, Sb_2S_3

Molecular weight: 339.70. It is stable in a rhombic prismatic crystal structure, which have a black grey metallic luster; specific gravity: 4.64; melting point: 548 °C; dissolves in alkali sulfide, concentrated hydrochloric acid, and alkali. It has another unstable form, an orange red amorphous substance, which has a specific gravity of 4.64; melting point: 548 °C; dissolves in ammonium sulfide and potassium sulfide. When it is heated to 200 °C in carbon dioxide gas, it changes to the stable form.

The heat of combustion is about 1000 kcal per 1 kg of antimony trisulfide, when Sb_2S_3 is oxidized to SO_2 and Sb_2O_3; this is equal to about half of the heat of combustion for sulfur. The maximum purity of natural antimony trisulfide is about 88%, and the practical heat of combustion may be lower than that.

Antimony trisulfide burns in combination with ammonium perchlorate to produce a slightly green flame (when burned with sulfur it produces a slightly red flame) and can generate red brown smoke in combination with potassium nitrate and charcoal.

When antimony trisulfide is slowly dropped on the surface of potassium chlorate, the temperature rises gradually by self-heating, then it ignites as soon as the chlorate begins to melt at about 360 °C. (arsenic sulfide reacts similar to antimony trisulfide; whereas sulfur ignites less quickly, even at 500 °C.) Therefore it may be said that antimony trisulfide is more ignitable than sulfur.

A mixture of antimony trisulfide and an oxidizer is generally sensitive to impact and friction. Roughly speaking antimony trisulfide is less sensitive than sulfur or arsenic sulfide to impact, but it has a higher friction sensitivity than sulfur and a lower friction sensitivity than arsenic sulfide. Generally friction must be taken into consideration in the ordinary handling of firework articles, and from this point of view it may be thought that antimony trisulfide lies between sulfur and arsenic sulfide in sensitivity. With potassium chlorate it is sensitive to both impact and friction; with potassium perchlorate it is sensitive to friction, but quite insensitive to impact; with ammonium perchlorate, on the contrary, arsenic sulfide is insensitive to friction, but as sensitive to impact as it is with potassium chlorate; with potassium nitrate it is insensitive to both impact and friction.

Arsenic Sulfide (Realgar), As_2S_2

The powder of arsenic sulfide is orange; with a monoclinic crystal structure, the fracture of which has a fat-like luster; specific gravity: 3.4–3.9; melts in the range from 308 to 320 °C; boiling point: 565 °C. It makes a transition from α (red) to β (black) at 267 °C. The α form has a specific gravity of 3.506 and the β form is 3.254. The heat of formation is 40.3 kcal per mol. It is slowly oxidized by the air especially in the sun producing orpiment, As_2S_3, and arsenious acid, As_2O_3. Namely

$$3\ As_2S_2 + 3/2\ O_2 = 2\ As_2S_3 + As_2O_3$$

In this case the arsenic sulfide powder changes color from red to yellow.

Arsenic sulfide is insoluble in water, but when it is boiled in water, it changes to As_2S_3 generating hydrogen sulfide gas. When it is treated with dilute bromine water, it becomes arsenious acid. When it is treated with an iodine solution in carbon disulfide it becomes arsenic iodide, AsI_3. When it is boiled in nitric acid, it becomes arsenic acid and sulfuric acid. When it is treated with a dilute ammonia solution, no change occurs, but with a concentrated ammonia solution, the crystal surface is attacked. It is only slightly soluble in carbon disulfide or benzene.

When arsenic sulfide is mixed with an oxidizer, it becomes generally quite sensitive to impact and friction, which could lead to an explosion. But the degree of sensitivity differs very much depending upon the kind of mechanical action (i.e., impact or friction) and the kind of oxidizer. In combination with potassium chlorate it is quite sensitive to both impact and friction. When an amount of water is added to the mixture, it suddenly loses its sensitivity, but even up to 15% water content (a muddy state) it is not perfectly safe for handling. Alcohol does lower the sensitivity. In combination with potassium perchlorate it is sensitive to friction, but not very sensitive to impact; with ammonium perchlorate, to the contrary, it is sensitive to impact, but not very sensitive to friction; the difference between the two is quite clearly observed. With potassium nitrate it is generally not very sensitive to either kind of action, impact or friction, and the sensitivity to impact is almost the same as that of potassium perchlorate.

Arsenic sulfide is used for report compositions for relatively small items utilizing the high sensitivity in combination with chlorate. It is also used for yellow smoke compositions, because it boils at a relatively low temperature as stated above.

Charcoal

Charcoal is used for many purposes, for example to obtain an explosive force, as a fuel producing a large amount of heat and gas in combination with an oxidizer, to adjust the burning rate of compositions, to obtain sparks or fire dust, to modify the ignition characteristics of compositions, to increase the brightness of flames, or simply as a combustion agent that helps the burning of compositions.

Charcoal is not soluble in any chemical and it does not melt. Charcoal, including the hemp coal, belong to the so called amorphous carbon allotrope. This material has many atoms in a parallel row. The main fine structure of the carbon is a plate on which carbon atoms are placed like a hexagonal net (one hexagon is 20–30 Å in length), and these fine structures fold at random. The microstructure under the electron microscope consists of a mass that has many parallel small holes. Charcoal contains a small amount of hydrogen and oxygen. A highly carbonized charcoal is written as $C_{20}H_7O$, the weight ratio of the elements, C:H:O, amounts to 91:3:6.

Hemp Coal. This is a black fine powder that has a somewhat hygroscopic feeling; apparent specific gravity: $0.22 g/cm^3$. The dye adsorption power is the greatest of all the kinds of plant charcoal. A mixture of hemp coal, sulfur and potassium nitrate burns to produce a violet flame and less fire dust than pine charcoal. It is used to obtain a large force of explosion as a component of Black Powder or in combination with potassium chlorate or perchlorate for the bursting charge of chrysanthemum shells.

It is more hygroscopic than pine charcoal; this may be caused by a phosphorus compound that is commonly found in cultivated plants. One analysis showed 9.15% moisture and 8.64% ash, and the carbon content may be less than 82%. Such a low carbon content is a defect of this material, and the ash contains Si, Cu, K, Al and phosphorus compounds. The wash water (5 g of hemp coal in 30 mL of water) showed a pH value of 10.5, and it changes the color of phenolphthalein to red. The purification of hemp coal by washing it with water takes a lot of time, because the filtration is very slow due to its alkaline nature. The particle size of commercial hemp coal is less than 20 microns, but it is better to sieve it before use to remove foreign matter.

Paulownia Charcoal. This is a light powder; quite dusty; apparent specific gravity: $0.12 g/cm^3$. This value is the lowest for all the kinds of charcoal presently available. The dye adsorption power in water lies between pine charcoal and hemp coal, which has the greatest absorption power. One analysis showed that it contained 4.9% moisture and 2.5 ash. The pH value of the wash water (5 g of charcoal in 30 mL of water) was 7.5. A mixture of the paulownia charcoal, sulfur and potassium nitrate burns as well as the pine charcoal, but it produces less fire dust than the pine charcoal. Paulownia charcoal is one of the most superior kinds of carbon particle as a Black Powder component for producing power, but it is not cheap, and for some time it has been replaced by hemp coal. Recently paulownia charcoal has recovered its use again because of the decrease in the culture of hemp.

Pine Charcoal. This is a very fine black powder; apparent specific gravity: about $0.37 g/cm^3$. The adsorption power of dye in water is quite small, which may show that it is not very porous. One analysis showed that it contained 7.07% moisture, 1.05% ash. The pH value of the wash water (5 g of charcoal in 30 mL of water) was 7.7. Pine charcoal burns in combination with ammonium perchlorate at a fuel to oxidizer ratio of 2:10 producing a yellow flame, but no sparks or fire dust. A mixture of pine charcoal, sulfur and potassium nitrate in the weight ratio 30:10:60 burns producing pretty orange red fire dust. This characteristic is generally seen with other charcoals but pine charcoal produces the prettiest fire dust of all. On the other hand, the phenomenon shows that pine charcoal does not complete the reaction and produces less gas in Black Powder-type compositions. Therefore pine charcoal is used to produce fire dust and not to obtain force. Commercial pine charcoal generally passes 300 mesh.

Dextrin, $(C_6H_{10}O_5)_n{\cdot}xH_2O$

Dextrin is a white or yellowish powder or grains; soluble in water, but not soluble in alcohol or ether. A brownish material is sometimes also sold. Dextrin is not crystalline and always contains some insoluble starch, not as much in the yellowish dextrin, as in the white. Dextrin does not have much cohesive strength so it is not widely used as a binding agent in firework compositions in Japan, but it is used as the fuel for colored smoke compositions. When it comes in contact with heated potassium chlorate, it reacts with the chlorate at 342 °C, which is higher than that of lactose or sucrose. Dextrin burns more easily than starch.

Ferro-Silicon

Ferro-silicon powder has a black gray metallic luster. It is reactive with alkali solution and dissolves in it, generating hydrogen gas. It is stable against ordinary acids.

Ferro-silicon is used for red thermite as an ignition composition. The more silicon present, the more the heat of combustion increases.

Iron Filings, Fe

Iron filings are used for producing sparks. The branching of the sparks is different based on the carbon content of the iron. Carbon burns explosively in melted iron; this causes the branching of the iron particle into a spark. When the carbon content is less than 0.20%, sparks seldom occur. As the carbon content increases up to 0.7–0.8%, the iron particles are activated more and more to produce many large sparks. A greater carbon content is not as effective.[10,11] Iron that contains 0.7% carbon melts about 1300 °C.

When iron filings are used as a component of a spark composition, corrosion is a significant problem (i.e., the production of sparks decreases the longer the items are stored). This effect is worse in acidic conditions but is not as bad under alkaline conditions. However, the corrosion does not occur without air and moisture. Therefore the composition must be kept in a dry state as much as possible, and the filings must be coated with some material. Table 4, with information about coatings for magnesium, may be helpful for suggested coatings.

Lactose (Milk Sugar), $C_{12}H_{22}O_{11}\cdot H_2O$

Lactose is contained in milk; the solid matter in milk contains about 40% lactose (milk sugar). There are two forms of the molecular configuration; α and β. Ordinary milk contains α and β in the ratio 4:3. The molecular weight: 360.32; specific gravity: 1.525; melting point: 202 °C (α) and 252 °C (β); moisture content: about 5%, which increases to about 7% at high humidity. It is soluble in water, but not as much as other sugars; almost insoluble in alcohol. When it comes in contact with heated potassium chlorate, it reacts with the chlorate at 322 °C, which is lower than the melting point of the chlorate, 368 °C. This ignition temperature is somewhat higher than that of sucrose, but lower than that of wheat or potato starch. For this reason lactose is favored more than wheat or potato starch as a fuel for colored smoke compositions.

Lampblack (Pine Black)

The lampblack used in Japan is obtained by the incomplete burning of pine wood, and it consists of very fine particles. It contains a small amount of tar, and when water is added to the powder, it floats on the water and the two cannot be easily mixed together. A mixture of lampblack, sulfur and potassium nitrate in the ratio 25:15:60 burns producing a reddish violet flame, but with no sparks or fire dust. As a component of Black Powder it produces quite a large force of explosion. The particles are so fine that it distributes well into a mixture, even if the amount is small. This characteristic is a great advantage as an ignition agent. As a component of the Senko-Hanabi composition, it creates a big spark with many branches and has been used for this from olden times. Its high price is the major problem with its use.

Carbon Black Used for Industry. This is different from lampblack. It is made from natural gas, acetylene gas, anthracene or coal tar; specific gravity: 1.8 to 2.1 g/cm^3; contains carbon with a graphite structure; the crystalline nature can be observed by X-ray techniques. It is rather difficult to burn in the air, and it did not produce sparks in Senko-Hanabi when it was tested by the author.

Magnalium, MgAl

Magnalium is an alloy of aluminum and magnesium. It is a silver mass, which is easily crushed to powder with an iron mortar. The magnalium powder that is currently available commercially contains 50% aluminum and 50% magnesium. This is a solid solution of Al_3Mg_2 in Al_2Mg_3; specific gravity: about 2.0; melts at about 460 °C. It is called 50/50 magnalium.

Magnalium is also attacked by various salts in the wet state or in the presence of moisture, but the degree of attack lies in general between those of aluminum and magnesium. Table 2 shows the comparison.

The 50/50 magnalium powder produces pretty yellowish white sparks, which branch like pine-needles, when it is mixed in a Black Powder-type composition and ignited. It burns smoothly in combination with chlorate or perchlorate, producing a brilliant flame and a small amount of fire dust sparks. With nitrates, however, magnalium does not burn smoothly, but vibrationally especially with barium nitrate or strontium nitrate. Therefore, it is difficult to use this item as an illuminant, but it is admired as material for spark or stars with vibrational burning (strobe stars).

Magnesium, Mg

Atomic weight: 24.312; specific gravity: l.74, melting point: 650 °C; boiling point: 1107 °C. Magnesium has a lower specific gravity than aluminum; it has the same melting point but a lower boiling point. Magnesium burns well in combination with an oxidizer, even if the oxygen content is not enough for complete combustion, because magnesium is easily vaporized and burns with a large long flame reacting with oxygen in the air. The flame is easily colored by a color producing agent (i.e., the flame temperature is so high that the color producing atoms or molecules in the flame are highly excited to produce a clear and pretty color). It can produce colored flame even in combination with only a nitrate, which is peculiar to magnesium.

The heat of combustion per 1 g of magnesium is 6000 kcal, which is not as high as that of aluminum.

Magnesium powder is slowly oxidized at the surface, and it loses its metallic luster. Cold water reacts very slowly with magnesium, but it is quite active with hot water; when the water is cold, magnesium hydroxide is formed on the surface to protect the metal from corrosion, but in hot water, the hydroxide dissolves to allow the reaction:

$$Mg + 2\,H_2O \rightarrow Mg(OH)_2 + H_2$$

At room temperature, alcohol and acetone do not react with magnesium, but they react slowly with heat.

Magnesium is violently attacked by various kinds of acid and even by a weak acid (e.g., boric acid or acetic acid). This is a quite different property from aluminum. Strong alkali (e.g., sodium hydroxide) reacts with magnesium very slowly and even with heat there is little activity. It is thought that a film of magnesium hydroxide formed on the surface of the metal interferes with the reaction.

Magnesium is attacked by various salts as well as sulfur in the presence of moisture or water. Based on the order of reactivity, first is copper sulfate, which reacts violently with magnesium generating hydrogen gas. Both ammonium nitrate and ammonium perchlorate react violently with magnesium generating ammonia gas. In this case, quite hygroscopic magnesium nitrate or perchlorate is formed. If a composition contains magnesium and ammonium perchlorate or nitrate, it is rapidly destroyed in the presence of moisture. However, in a well dried state, the reaction scarcely occurs and the composition can be stored for a long time. Sodium bicarbonate is a weakly alkaline salt, but it reacts considerably with magnesium generating hydrogen gas. Sodium carbonate is more alkaline than the bicarbonate and less active than the bicarbonate with magnesium. Sodium oxalate is unexpectedly reactive with magnesium. Sulfur quite slowly attacks magnesium generating hydrogen sulfide, H_2S, gas. Both potassium chlorate and sodium chloride react rather actively with magnesium; potassium perchlorate reacts less actively than potassium chlorate or sodium chlorate; potassium nitrate reacts very slowly, and at room temperature it looks as if no reaction occurs at all; barium nitrate, strontium nitrate or potassium dichromate cause no reaction.

It has already been suggested that the above reactions do not occur in practice if the materials are well dried. Therefore, compositions that contain magnesium as a component must be kept very dry if they are to be stored for a long time.

Magnesium is also attacked by some organic materials, especially by organic acids that are dissolved in alcohol or acetone. Wood rosin FF is the most reactive; however, shellac, accroides resin (red gum) or combustion agent BL cause almost no reaction.

Coating of magnesium powder. When magnesium powder is used as a component of firework compositions, it must be protected from the actions of moisture and chemicals by coating the grains with a suitable material. The coating must be used in a proper ratio of the material to the magnesium powder to avoid coagulating the powder. Generally 2 to 5% additional weight of the material is used. The coated magnesium powder is sieved one or two times before the coating material becomes hard. Table 4 shows the degree of resistance obtained by different coating materials against various chemicals.

Coating with potassium dichromate is carried out as follows: 50 g of potassium dichromate is dissolved in 300 mL of hot water. 1000 g of magnesium powder is heated to about 100 °C in an air oven for one hour. It is placed in a large aluminum bowl and the hot solution of potassium dichromate is added to the magnesium. It is quickly mixed stirring by hand with gloves until the powder is colored uniformly brown. Then the powder is spread on a Kraft paper and dried well in the sun. When dried, it is passed through a 30 mesh sieve. The dust must not be inhaled because potassium dichromate is poisonous.

According to Table 4, each of the coatings is effective against moisture or water. Against chemicals, the resistance depends on the kind of coating material. Against ammonium perchlorate only the potassium dichromate coating is generally used. This coating is almost perfectly chemical proof. The linseed oil coating is quite effective for almost all chemicals except ammonium perchlorate. The paraffin coating is also unexpectedly useful. The polyester coating is not as effective as the paraffin coating; even when the amount of the polyester is increased to the additional ratio of 25 weight percent, the resistance remains almost unchanged.

Table 4. Chemical Resistance of Magnesium Coatings (Tested in Wet State at Room Temperature).

Solution	pH	No Coating	Linseed Oil (4%)	Paraffin (5%)	Cashew (5%)	Polyester (7%)	Potassium dichromate
Water	5.8	X	O	O	O	O	O
0.1 N HCl	—	XXXX	O	O	XXX	X	XXXX
1N NH_4ClO_4	4.8	XXXX	XXXX	XXXX	XXXX	XXXX	S
0.5 N $KClO_3$	5.5	XXX	O	XX	XX	S	S
.015 N $KClO_4$	5.6	XXXX	O	XX	XX	S	S
0.1 N $Ba(NO_3)_2$	5.5	XXX	O	S	S	O	S
1 N $Sr(NO_3)_2$	5.1	XXX	O	S	O	S	S
1 N KNO_3	5.6	XXX	O	S	S	S	S
1 N $NaNO_3$	6.4	XXX	O	O	S	XX	S
1 N Na_2CO_3	—	—	XX	O	XXX	XXXX	O

Note: The symbols are as follows:

O	No reaction occurs.	XX	Attacked considerably.
S	Very slightly attacked but useful in practice.	XXX	Attacked actively.
X	Attacked slowly.	XXXX	Attacked violently.

Pine Root Pitch

Pine root pitch is a black mass that softens at 40 to 60 °C and is glossy rather like coal pitch. It is insoluble in water, but partly soluble in alcohol. Owing to the low softening temperature, powdered pine root pitch cakes like wood rosin FF during storage.

One analysis showed that pine root pitch contained 75% C, 17% O, 7% H and 0.8% ash. The carbon content is somewhat less and the oxygen content is more than that of wood rosin FF. Pine root pitch therefore interferes with the flame color less than wood rosin FF or the combustion agent BL. It burns in combination with ammonium perchlorate at a fuel to oxidizer ration of 2:10 producing a brilliant white flame. When it is used in combination with potassium perchlorate, it produces a burning rate that is as fast as that of chlorate compositions. It is therefore very useful as a fuel for non-chlorate compositions for chrysanthemum stars.

Red Phosphorus, P

Red phosphorus is a red brown powder, which has no odor, but if it contains yellow phosphorus, it smells like ozone; specific gravity: 2.20; ignites: 260 °C; melting point: about 550 °C, when it is rapidly heated in the absence of air. It is insoluble in water or carbon disulfide. Dissolves in nitric acid to become phosphoric acid.

Red phosphorus is not poisonous. If commercial material absorbs moisture and slowly becomes wet, this indicates that the red phosphorus contains a trace of yellow phosphorus, which is poisonous. The yellow phosphorus is gradually oxidized by the oxygen in the air to phosphoric acid. Red phosphorus needs to be purified before it is used.

When a drop of 90% nitric acid is added to red phosphorus, it ignites instantaneously. Red phosphorus reacts with copper sulfide in the presence of moisture, generating heat, which causes spontaneous ignition. Red phosphorus does not react with dilute or concentrated sulfuric acid. Also it is not reactive with other sulfides; K_2SO_4, $KHSO_4$, etc.

Red phosphorus is said to be a mixture of violet phosphorus, imperfect violet phosphorus and amorphous phosphorus.[12]

Red phosphorus burns in the air producing a pretty yellow flame, at the top of which the white smoke of phosphorus pentoxide is generated. This property is used for a day and night signal. The flame spectrum probably results from PHO molecules; λ 6436–4879 Å.[13]

Red phosphorus alone is ignited by a strong impact in the air. Red phosphorus becomes quite sensitive especially to friction and ignites or explodes easily when it is mixed with an oxidizer. This property is more pronounced with red phosphorus than with arsenic sulfide, and it is used for matches. Table 5 shows a series of qualitative tests.

Care must be taken since $KClO_3$, $KClO_4$ and NH_4ClO_4 are quite sensitive to friction and impact with red phosphorus.

Red phosphorus that is scattered on the floor cannot be removed completely by washing with water because of the fineness of the particles and its insolubility in water. Accordingly one must have a workroom that is used exclusively for red phosphorus. The same care must be taken with tools, furniture, fixtures, clothing, etc.

A trace of yellow phosphorus tends to become phosphoric acid in the air, absorbing moisture during storage. This acid corrodes many kinds of metals, cotton and other materials. Stainless steel (18-8 chrome-nickel) can be used with red phosphorus without corrosion.

Table 5. A Series of Qualitative Tests for Mixtures of Red Phosphorus and an Oxidizer To Determine Sensitivity to Impact and Friction Using a Hammer and Anvil of Different Kinds of Metal.

	Hammer: →	Iron	Iron	Iron	Brass
Oxidizer	Anvil: →	Iron	Aluminum	Brass	Aluminum
KNO_3	Impact	O E	O E	O E	no
	Friction	no	no	no	no
$KClO_3$	Impact	O EEE	O EEE	O EEE	O EEE
	Friction	BBB	BBB	BBB	BBB
$KClO_4$	Impact	O EE	O EE	O EE	O EE
	Friction	BB	no	no	no
NH_4ClO_4	Impact	O EE	O EE	O EE	O EE
	Friction	B	no	no	no
$Ba(NO_3)_2$	Impact	O E	B	no	no
	Friction	no	no	no	no
$Sr(NO_3)_2$	Impact	E	E	no	E
	Friction	no	no	no	no
$NaNO_3$	Impact	Δ E	Δ E	E	Δ E
	Friction	no	no	no	no
R. T.	Impact	Δ B	Δ B	Δ B	Δ B
	Friction	no	no	no	no
MnO_2	Impact	BB	B	no	B
	Friction	no	no	no	no

Note (1) The iron hammer is a 255 g block that is 20 mm in diameter with a 300 mm long handle.
The brass hammer is a 140 g block that is 20 mm in diameter with a 300 mm long handle.
The impulsive force of impact corresponds more or less to that of a 1 kg drop hammer from a height of 18 cm.
The pressure of the friction test amounts to about 1 kg.

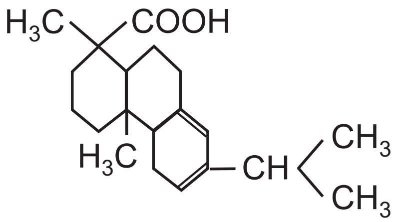
Note (2) The ratio of red phosphorus to oxidizer is about 1:5 by weight.

Note (3) Symbols:

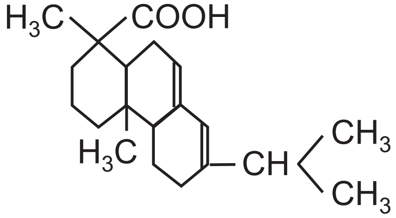
no	no explosion or burning	EE	frequently explodes
O	with a loud noise	EEE	always explodes very sensitively
Δ	with a low noise	B	sometimes burns
R.T.	red thermite (80% red lead + 20% iron silicide)	BB	frequently burns
E	sometimes explodes	BBB	always burns very sensitively

Rosin (Colophony, Common Rosin, Wood Resin-Pine, Resin-Colophony)

There are three kinds of rosin at present: “gum rosin”, “wood rosin”, and “tall oil rosin” Rosin contains –COOH and double bonds in its molecular structure. Rosin contains mainly cyclic compounds as follows.



Levoabietic acid



Dextroabietic acid

Rosin is slowly oxidized in the air, but it does not seem to be problematic for firework use. It can be used safely in combination with chlorates. There are many kinds of rosin products, each of which has a slightly different burning character from the others. The two most popular items are described here.

Combustion Agent BL. This was named by H. Murai, who first introduced this substance into firework use in Japan after World War II. It is sold as a dark brown powder. It melts at 82 °C, and this melting point is 10 °C higher than that of wood rosin FF. This material seems to correspond to a product sold by Hercules Inc. in the USA. Another chemical difference between this material and wood rosin FF may be in the acid value (the number of milligrams of potassium hydroxide required to neutralize the acid (–COOH) contained in 1 g of the material); the acid value of this material is about a half of that of wood rosin FF.

Powdered combustion material BL does not cake during storage. From the melting point (82 °C) to 200 °C it remains in a liquid state without any change; upon further heating, it is carbonized producing a combustible gas. These characteristics produce stable combustion in any composition, a superior characteristic that cannot be obtained from wood rosin FF. It is insoluble in water, but soluble in alcohol and especially in acetone. Wash water (100 g of water per 10 g of BL rosin) showed a pH value of 5.1 at 15 °C.

It burns in combination with ammonium perchlorate at a fuel to oxidizer ratio of 2:10 producing a brilliant white flame. This shows that it contains a large amount of carbon. When small grains of the combustion agent BL are dropped one by one on melted potassium nitrate, which is gradually heated to raise the temperature, the grains melt without ignition and are carbonized up to 480 °C and at higher temperatures it finally ignites. It can produce a greater burning rate in compositions than shellac. Because of the high carbon content, it should be used in a quantity that does not interfere with the color of the flame.

Wood Rosin FF. This is the so called “Yo-Chan”, which means a foreign resin in Japanese, is the most popularly used resin in Japan. It is a slightly yellowish mass. When it is powdered, it gradually cakes. It melts at 72 °C and remains in a clear liquid state up to about 200 °C without any color change. When it is heated further, it vaporizes without carbonization. Having such character, it melts and envelopes the surface of oxidizer particles to cause an interruption or irregularity or even delay in the combustion of compositions when it is used alone as the fuel.

One analysis showed that it contained 75.77% C, 15.35% O, 8.81% H and 0.07% ash. In comparison with shellac, it has more carbon and less oxygen. The excess carbon produces a very bright flame that interferes with the production of color. For example, it burns in combination with ammonium perchlorate at a fuel to oxidizer ratio of 2:10 producing a bright white flame. As a result, this is used only as a partial substitute for shellac.

When small grains of the wood rosin FF are dropped one by one on melted potassium nitrate, which is gradually heated to raise the temperature, the grains melt without ignition and are only vaporized up to 460 °C; at higher temperatures they ignite. Clearly there are difficulties in the combustion of this material; in fact it is not combustible in a solid or liquid state, but only in the vaporized state. This is where it differs from shellac. With potassium chlorate it ignites in excess of 404 °C.

Shellac

The principal component of shellac is trihydroxypalmitic acid,

$CH_3(CH_2)_{11}(CHOH)_3COOH$

This is a chain compound, but another kind of ring compound, $C_{15}H_{20}O_6$, is contained in shellac. One analysis showed that shellac contained 7.00% C, 23.87% O and 9.00% H, and a formula $C_{16}H_{26}O_4$ was applied to it.

The most remarkable characteristic of shellac is that the carbon content is smaller, and hydrogen content is larger than that of other fuels (e.g., rosin). Apart from the 4 molecules of water, H_2O, which should be formed at burning, it contains an additional 9 molecules of hydrogen, H_2; consequently when it is burned in combination with an oxidizer, a lack of oxygen in the flame does not cause the generation of carbon particles. In addition, a high flame temperature is obtained by the reaction of the hydrogen during combustion. This is the reason why shellac is regarded as a superior fuel for colored flame compositions. It burns in combination with ammonium perchlorate at a fuel to oxidizer ratio of 2:10, creating a slight reddish orange flame.

Treated shellac is sold as yellowish orange flakes. The melting point is not clearly defined, but it softens at 50 to 90 °C to a liquid state, and is blackened at 180 °C, losing its adhesive power. When heated, it decomposes and is carbonized with the generation of flammable gas.

When a small grain of shellac is dropped on the surface of melted potassium nitrate, the nitrate directly reacts on the shellac at the contact surface. In this case the surface of the potassium nitrate begins to move radially from the grain (see Figure 1).

Shellac is insoluble in water; soluble in alcohol, acetone and turpentine; and it slowly absorbs paraffin and swells up. The solution in alcohol is popular as shellac varnish. Shellac can be used in combination with chlorates. Shellac powder does not cake as much during long term storage; but a loaded composition that contains shellac and paraffin or oil degenerates or shrinks slowly, and it sometimes causes an unexpected rapid burning through the gap created between the composition and the container.

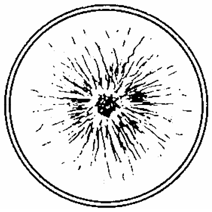


Figure 1. Decomposition of shellac on the surface of melted potassium nitrate.

Silicon, Si

Atomic weight: 28.06. Three forms of silicon are produced; amorphous, crystalline and graphite-type. The crystalline form has a black gray metallic luster; specific gravity: 2.4. The graphite-type form is black with a specific gravity of 2.7. All forms have the same crystal structure; melting point: 1420 °C; boiling point: 2335 °C; it is insoluble in water. The amount of heat generated upon oxidation is 7300 kcal per 1 kg of silicon, which is equal to 0.9 times the amount per 1 kg of carbon. This is almost the same as that of aluminum, but it is not used for reports because not much noise is produced. Silicon is stable against acid but is attacked by alkali, generating hydrogen gas. Silicon is used for red thermite in combination with red lead oxide (minium) (e.g., in a weight ratio Pb_3O_4:Si = 7:3).

Silicon conducts electric current as well as graphite; the electric resistance decreases as the temperature rises.

Starch, $(C_6H_{10}O_5)_n$

Starch is a white powder. If it is brownish, it may contain some impurities such as an iron salt, etc. Moisten the samples with a small amount of water or alcohol and observe it through a microscope, and it will be found that it consists of small grains that differ from each other in shape and size according to the kind of starch. For example the grains of potato starch are egg shaped, which is 0.06–0.1 mm in diameter (0.07 mm on average). The grains of wheat starch are spherical and 0.01–0.04 mm in diameter (0.028 mm on average). When heated, it burns without melting. It is insoluble in cold water, but soluble in hot water or hot alcohol to form a paste. The water temperature needed to dissolve starch is about 66–80 °C and higher, which varies based on the kind of starch.

There are many kinds of starch: potato, sweet potato, corn, wheat, rice, adder's tongue lily, bracken, etc. For fireworks, potato or wheat starch is used as a fuel, especially as the low temperature fuel for smoke compositions. (Rice starch is used as a binding agent.) It must be noted that commercial starch is sometimes mixed with a trace of ultramarine for a pure white appearance.

The heat of combustion of starch amounts to about 3400 kcal per 1 kg, which is almost equal to half of that of carbon or aluminum. Although the heat is quite low, it is favored for low temperature combustion (i.e., it allows smoke compositions to burn below about 500 °C to avoid the decomposition of dyes).

The amount of moisture contained in starch increases as the grain size of the starch increases; potato starch contains about 15% and wheat starch about 14% moisture. When the humidity increases, the moisture content increases further; 20–30% in potato starch and 18–27% in wheat starch at 80–90% relative humidity.[14]

Sucrose (Cane Sugar), $C_{12}H_{22}O_{11}$

Sucrose consists of colorless crystals with a monoclinic crystal structure; specific gravity: 1.558; it softens like wheat gluten at 160 °C and is caramelized at 200 °C. Sucrose contains about 1% moisture and at high humidity absorbs more moisture and can dissolve into a liquid state. It is very soluble in water; it dissolves in an amount of water of 1/3 of the weight of the sugar. Sucrose is insoluble in alcohol or acetone. When it comes in contact with heated potassium chlorate, it reacts with the chlorate at 307 °C, which is the lowest of all carbohydrates used at present for fireworks. Sucrose therefore is quite useful as a fuel for colored smoke compositions to produce good colored smoke. The only problem with sucrose lies in its hygroscopic nature, and at present it is used less than lactose.

Sulfur, S

Atomic weight: 32.06. There are two or three allotropes. The sulfur used at ordinary temperature and pressure is α, which is yellowish with a rhombic crystal structure; specific gravity: 2.07. The α form of sulfur makes a transition to β sulfur at 95.5 °C. The β form of sulfur is yellow brown with a monoclinic crystal structure; melting point: 118.95 °C; specific gravity: 1.96. There are two kinds of liquid state; λ and μ. Sulfur boils at 444.55 °C. The molecules of the vapor state are S_8, which change to S_2 at 1000 °C.

Sulfur does not conduct electricity, but it is easily charged by static electricity. For fireworks use the sulfuric acid content must be kept low especially if it is used in combination with chlorate. The acidity should be tested with blue litmus paper to see whether the wash water of the sulfur changes its color to red or not.

Sulfur ignites at 223 °C in the air. Because of this relatively low ignition temperature, sulfur is sometimes used for firework compositions due to its ease of ignition. Sulfur is used as a raw material for Black Powder in combination with potassium nitrate and charcoal, and it is also used for white smoke compositions.

A composition that contains sulfur and some oxidizer is generally sensitive to impact and friction. The highest degree of sensitivity is in combination with potassium chlorate; next is ammonium perchlorate; third is potassium perchlorate; and nitrates are even less sensitive. With any oxidizer sulfur gives a higher ignition sensitivity than charcoal. The combustion heat amounts to 2162 kcal per 1 kg of sulfur, which is 1/3 as large as that of carbon.

Titanium, Ti

Atomic weight: 47.90; melting point: about 1800 °C; boiling point: 3262 °C. Titanium filings are quite stable against water, moisture or the various other chemicals that are used in pyrotechnics. The filings are quite reactive at high temperatures (over a red heated state) and produce pretty yellowish white sparks when they are mixed with a Black Powder-type composition.

In Japan a Fe-Ti alloy in various mesh sizes, which contains more than 80% titanium, is currently used.

Titanium produces brilliant fire dust sparks having a relatively long life that cannot be obtained with other materials.

Wood Meal

Wood meal is a slightly yellowish powder which smells of wood; apparent specific gravity is about 0.18. The chemical composition is regarded as $C_7H_{11}O_5$, which is almost the same as that of cellulose or starch.

When heated, it is carbonized producing a combustible gas. It burns in combination with ammonium perchlorate at a fuel to oxidizer ratio of 2:10 producing a flame in which slight orange red lines are visible. The burning temperature is lower than that of shellac or rosin. Accordingly the brightness of the flame is not as great as with shellac or rosin. It somewhat reduces the caking of powdered compositions during storage.

Wood meal is used for industrial explosives and also as an anticaking agent, etc. It is quite inexpensive and does not interfere with the color of flames. It is used mainly for lance compositions. A standard test indicated: less than 13% moisture; 6.5–8.5 cm^3/g apparent specific volume; 97% of the meal passes 30 mesh; less than 1.4% ash.[15]

Zinc Dust, Zn

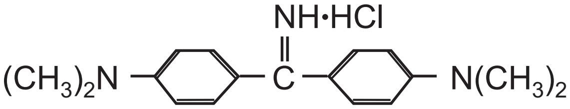
Atomic weight: 65.37; melting point: 419 °C; boiling point: 907 °C; specific gravity: 7.14. Zinc is a grey powder, the particles of which are somewhat oxidized at the surface.

Zinc dust is stable against water or moisture, because the film of zinc hydroxide, $Zn(OH)_2$ or basic zinc carbonate, $2ZnCO_3 \cdot 3Zn(OH)_2$, that forms on the particle surface protects the metal from corrosion. It is not easily soluble in sodium hydroxide solution in water, but it is soluble in a weak alkali solution such as sodium carbonate or bicarbonate generating hydrogen gas. It is also easily soluble in an ammonia solution to form a complex salt, $[Zn(NH_3)_4](OH)_2$. Zinc is attacked by chlorides, but not by ammonium perchlorate. The main use for zinc is in white smoke, which is created by zinc chloride particles. Zinc dust is quite reactive with hexachloroethane in the presence of moisture or water, and it often causes a fire when manufacturing smoke composition. It is thought that a trace of hydrochloric acid in the hexachloroethane causes the reaction.

Dyes

Dyes are used mainly for smoke. The dyes for smoke should be in a solid state at ordinary temperatures, have a relatively low boiling point (200–400 °C) and be thermally stable.

Auramine

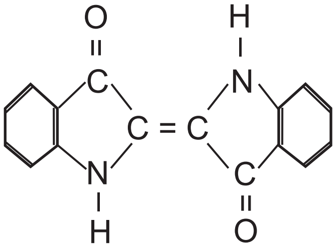


Auramine is a representative diphenylmethane dye; melting point: 250 °C; then begins to vaporize; boiling point: 290 °C where it is partly carbonized. The commercial material is generally hygroscopic.

Auramine produces smoke of pure yellow and is used alone or in combination with other dyes to obtain green or other colored smokes. When it is used alone for yellow smoke, it looks somewhat weaker than arsenic sulfide in yellowness. The HCl salt of auramine is soluble in water.

A smoke composition that contains auramine and potassium chlorate is said to cause spontaneous ignition,[16] but when the composition is in a well dried state, this should not be a problem. The reason is not clear, but it may come from the ammonium chloride that is used for manufacturing auramine and that remains in it as an impurity. As described above, the mixture of an ammonium salt and potassium chlorate creates ammonium chlorate, which easily decomposes.

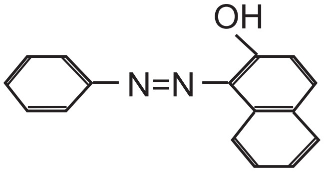
Indigo Pure



The designation “pure” means the artificial indigo rather than the natural one. This is a dark violet powder; specific gravity: 1.39; sublimes above 300 °C generating violet red vapor. In this case the commercial dye leaves a small amount of black residue. It is insoluble in acetone but soluble in benzene.

Indigo pure is a stable dye, which gives a blackish blue smoke, but when the burning temperature of the smoke composition is too high, it decomposes to generate yellow grey smoke.

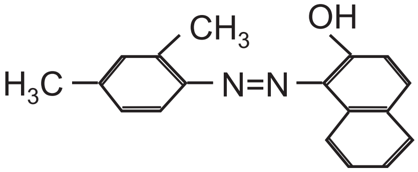
Oil Orange



Dyes that are soluble in oil are popularly prefixed with the word “oil” as part of the commercial name.

Oil orange is soluble in oil and belongs to the same class as para red or oil red. It is a reddish orange or dark orange powder, insoluble in water, soluble in alcohol producing an orange color, soluble also in acetone producing an orange color; melting point: 100 °C; begins to vaporize: 200 °C; boiling point: 270 °C. Oil orange is more stable with heat than para red. The substance sometimes causes an eruption on the skin. Perhaps this is because it dissolves into the fat of humans since other kinds of dyes, which dissolve in oil, generally have a similar property.

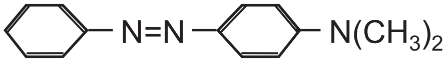
Oil Red



Oil red is a naphthol dye that contains one azo base, –N=N–, in the molecule like para red. It is a bright red powder, insoluble in water, soluble in alcohol and in acetone producing an orange red color; melting point: 165 °C; begins to vaporize: 270 °C; boiling point: 330 °C. Oil red is more stable with heat than para red and is not as easily damaged.

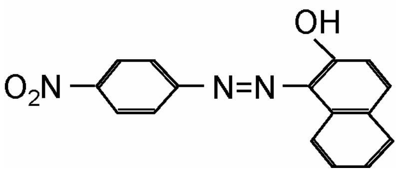
The color of the smoke of oil red is orange red and to obtain a good red smoke it is used in combination with rhodamine B.

Oil Yellow



Oil yellow is used for smoke and is somewhat reddish, but a pretty yellow, and is used in place of auramine. It is insoluble in water, but soluble in oil. The name “Butter Yellow” comes from the fact that it is used for coloring margarine. Soluble in alcohol or acetone; melting point: 105 °C; begins to vaporize: 200 °C; boiling point: 350 °C.

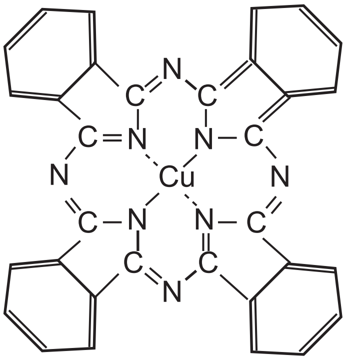
Para Red (p-nitroaniline red)



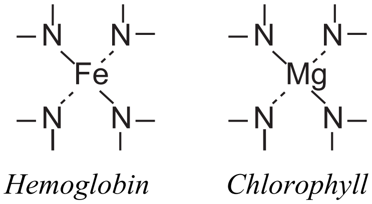
Para red is a type of naphthol dye that contains one azo base, –N=N–, in the molecule. It is a bright red powder; insoluble in water and alcohol; melting point: 210 °C; vaporizes from about 230 °C; boiling point: 280 °C, being partly carbonized. As a component of smoke compositions it is easily damaged by heat even at relatively low temperatures; this is a defect of this dye, and it may be caused by the NO_2 base contained in the molecule.

The smoke color of para red is orange red, and generally it is not used alone, but in combination with rhodamine B for red smoke.

Phthalocyanine Blue



Phthalocyanine blue resembles in molecular structure hemin, which is contained in hemoglobin and chlorophyll

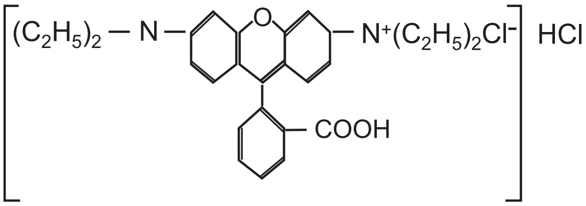


Phthalocyanine blue is a bright cobaltic blue powder; specific gravity: 1.6. It is quite stable and is generally used as a pigment. Insoluble in water or alcohol, very slightly soluble in acetone, producing a yellow color. When heated it does not easily decompose, but sublimes above 500 °C. When heated for a long time below 500 °C, it decomposes slowly to generate white smoke. This dye produces smoke of a very pretty bright cobaltic blue. The daylight firework display has become remarkably better from the use of this dye in place of indigo, which gives only a dark blue smoke.

Phthalocyanine blue is well vaporized by using only a strong heat producing agent (e.g., a mixture of carbohydrate and potassium chlorate) in quite a large quantity, because it is not very easily vaporized. Accordingly care must be taken because fire often remains in the ash after the smoke composition has burned out. If a weak heat producing agent such as celluloid is used in combination with this dye, it produces only a low temperature decomposition, which only generates white smoke.

This substance contains copper and burns in combination with ammonium perchlorate with a blue flame.

Rhodamine B



The base of Rhodamine B is a red powder, which is not soluble in water, but soluble in alcohol producing a red solution. The HCl salt, which is sold commercially as “Rhodamine B”, is a very fine violet black powder with yellow green fluorescence; soluble in water to produce a deep red violet color; also soluble in alcohol producing a red solution; melting point: 270 °C; boiling point: 310 °C, but it begins to smoke gradually with the temperature rise from the melting point and is carbonized partly without vaporizing. The smoke particles of rhodamine B from a smoke composition are insoluble in water.

The solution of rhodamine B is acidic, the pH value being 2.5–3.0 for a 1% solution in water, but its use in combination with potassium chlorate does not cause any trouble. This dye has a serious problem in that it stains everything that comes into contact with it.

The base, which is insoluble in water, can be used for smoke in place of the HCl salt, but it burns less easily than the smoke composition that contains the HCl salt. Moreover the base is not as cheap as the HCl salt because the manufacturing plant has to be modified for the purpose. The smoke color of rhodamine B is violet red.

Other Chemicals

Anthracene, $C_{14}H_{10}$

Molecular weight: 178.24; specific gravity: 1.250; melting point: 216.2 °C; boiling point: 342 °C; insoluble in water, and slightly soluble in alcohol (0.076 g per 100 g of ethanol at room temperature). Purified anthracene has pure white snow-like crystals, but is generally somewhat yellowish. In summer it sometimes causes trouble for workers because it produces a skin eruption, but this varies with the composition. It is used for compositions of black smoke.

Benzene Hexachloride (BHC), $C_6H_6Cl_6$

Six isomers are separated from industrial products; α, β, γ, δ, ε, ζ. They have slightly different physical characteristics. Only the γ BHC is effective as an insecticide. Industrial products generally contains 55–80% α BHC and only 8–15% γ BHC. The γ BHC, which is isolated from the industrial products to more than 99% purity is called "Lindane". It is best to use the by-product from the manufacture of Lindane for firework material.

BHC has white crystals; specific gravity is about 1.9; γ melting point: 112–113 °C, and β the highest: 309–310 °C. All the isomers are insoluble in water, but more or less soluble in alcohol, ether or acetone.

When BHC is heated, it vaporizes without carbonization. It is difficult to ignite BHC or its vapor in the air, but once ignited, it burns generating soot and HCl gas. Therefore it is used as an HCl producing agent and reducing agent for colored flames. But it is not as effective as PVC. However for strobe effects BHC is used in place of PVC, because BHC does not interfere with the strobing of the flame.

Boric Acid, H_3BO_3

Boric acid occurs as white flaky crystals. Molecular weight: 61.83; specific gravity: 1.4; melting point: 185 °C; solubility in water (2.70 g at 0 °C, 4.65 g at 20%, 12.96 g at 80 °C, 27.5 g at 100 °C in 100 g of water); solubility in ethanol (11.8 g at 25 °C in 100 g of ethanol); solubility in glycerin is 28 g at 20 °C in 100 g of glycerin. As described by Lancaster[8c] boric acid is quite effective in suppressing the decomposition of a composition that contains aluminum as a result of its buffer action, and it is superior to acetic acid or gum Arabic as shown in Table 3. However, it must be noted that boric acid corrodes magnesium.

Boron, B

Atomic weight: 10.811. Two kinds are produced; amorphous and crystalline, but only the amorphous boron is used for fireworks; specific gravity: 2.35; melting point: 2160 °C; boiling point: 3650 °C. When amorphous boron is touched, it feels as though it were somewhat hygroscopic. It absorbs moisture to about 6% so it is sometimes necessary to protect it against moisture. According to an American analysis[17] the purity of amorphous boron cannot exceed 92%. It is a dark brown powder of very fine particles.

Amorphous boron burns in oxygen and reacts with sulfur at 600 °C; however, it is stable with many chemicals. It does not react with concentrated HCl solution or HF even in a hot state. With concentrated nitric or sulfuric acid it reacts in small amounts to produce boric acid.

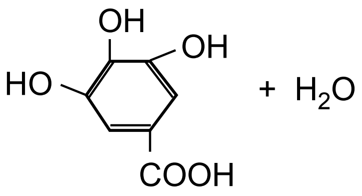
A mixture of amorphous boron and potassium nitrate in a ratio 75:25 burns rapidly with a brilliant green flame at very high temperature. The green color comes from the BO_2 band spectrum. The boron mixture is used as an igniter composition in place of thermit, and the difference between the two lies in that the boron mixture ignites other compositions with its high temperature flame whereas the thermit mainly ignites compositions with its high temperature liquid products. Amorphous boron is very expensive commercially, but it is very useful when the ignition surface of a composition cannot be pasted with thermit as in the case of a rocket propellant, which must start without a delay. The boron mixture ignites very well from a relatively weak ignition source such as a Black Powder flame.

Chlorinated Isoprene Rubber, Parlon® (in the USA), ADEKA Rubber (in Japan)

Chlorinated isoprene rubber is a white powder; known as a chlorine donor for producing colored flames; contains 66–67% chlorine.[8d]

Chlorinated isoprene rubber and PVC, which is described later, act not only as a chlorine donor, but also as a fuel. They are, however, different with regard to their ability to act as a fuel. Based on experiments, in practice, the rubber is only a chlorine donor, whereas PVC is both a chlorine donor and a fuel when it is used in chlorate or perchlorate based compositions.

Gallic Acid



Gallic acid consists of colorless needle-shaped crystals; molecular weight: 188.14; specific gravity: 1.694; melting point: 222 °C (decomposes to pyrogallol).

$C_6H_2(OH)_3COOH \rightarrow C_6H_3(OH)_3 + CO_2$

Gallic acid Pyrogallol

This is a raw material for blue-black ink, however in fireworks it has been used in combination with potassium chlorate as a whistle composition, which is very sensitive to impact and friction.

Guanidine Nitrate, $NH{:}C(NH_2)_2{\cdot}HNO_3$

Molecular weight: 122.09; colorless grainy crystals; specific gravity: 1.44; soluble in water (12.5 g at 20 °C, 41 g at 50 °C and 99 g at 80 °C in 100 g of water); soluble in methanol or ethanol in small amounts; insoluble in ether or acetone. Guanidine nitrate is an organic molecular compound of one molecule of guanidine and one molecule of nitric acid; the purity of commercial material is about 95% and white insoluble matter remains undissolved in water; melting point: 208 °C; begins to decompose at 235 °C, actively generating ammonia gas, leaving a yellowish substance that is insoluble in acid. It is difficult to ignite the gas, but when guanidine nitrate is suddenly heated to 400–500 °C, it ignites and burns furiously with an orange flame. Red phosphorus, charcoal powder, copper powder, copper compounds (copper oxide, copper sulfate, basic copper carbonate, etc.), and compounds of chromium or of manganese have a catalytic effect that decomposes guanidine nitrate into ammonia gas. The material on the market looks hygroscopic, but actually the moisture content is as small as 0.4%, which is observed at a relative humidity of 90% (left for 10 days).

Guanidine nitrate is stable to ordinary mechanical actions, impact and friction. But when it is initiated by a strong booster like RDX, it partially detonates, however perfect propagation of a detonation is difficult.[18] A mixture of guanidine nitrate and red phosphorus, antimony trisulfide or sulfur cannot be ignited or exploded by impact or friction and cannot continue burning, even when it is ignited by some heat source. A mixture of guanidine nitrate and potassium chlorate cannot continue burning.

Guanidine nitrate that is mixed with a catalyst and consolidated into small cylinders was sold in England as a fuel for toy airplanes under the name of “JETEX”. It is rather difficult to ignite this fuel, but once it is ignited, it burns at a much lower temperature than other rocket fuels; the gas burns at about 250–300 °C. Guanidine nitrate is also used for the compositions of some special smoke generators like insecticidal smoke or gas generators.

Hexachloroethane, C_2Cl_6

Molecular weight: 236.74; colorless crystals, which slowly sublime at room temperature producing an odor; melting point: 182–187 °C; insoluble in water, but soluble in ethyl alcohol, ether and acetone. This is a solid chlorine producing agent with 89.8% chlorine. It may be used as a color enhancing agent for flare compositions, but at present it is not used because of its volatility. It is used for white smoke composition, as described in zinc, which is sealed in a tin case.

A mixture hexachloroethane and zinc dust generates a large amount of heat when it is moistened. It is said that the reaction comes from a trace of acid contained in the hexachloroethane.

Iron Oxide, Red, Fe_2O_3

Molecular weight: 159.69; specific gravity: 5.24; melting point: 1550 °C. It is insoluble in water, soluble in hydrochloric acid reacting with it, but it is hardly soluble in other acids. Red iron oxide is a fine red powder. A mixture of red iron oxide and aluminum burns generating sparks at a high temperature (about 2400 °C), leaving melted iron and melted aluminum oxide.

Lead Oxide, Red (Minium), Pb_3O_4

Molecular weight: 685.57; clear yellowish red powder or crystals; specific gravity: 9.07; it decomposes generating oxygen above 500 °C; insoluble in water, but soluble in acetic acid, nitric acid and hot hydrochloric acid, reacting with them.

For pyrotechnic use it is combined with ferro silicon under the name of "Red Thermit", which is used as a first fire composition for compositions that are difficult to ignite. It is also used to display orange fire dust in combination with other compositions. The red thermit is said to generate no gas in the burning reaction, but truly a small quantity of gas is generated.

Red lead has an unusual characteristic in that it can produce "second burning". For example, if paper is dipped into a fire-proof solution, partly painted with red lead and dried, it will be found that when the paper is put into a flame it is at once carbonized and then the red lead alone burns leaving no carbon (i.e., the red lead causes the carbon to burn completely after a while).

Naphthalene (Tar Camphor, White Tar), $C_{10}H_8$

Molecular weight: 128.18; specific gravity: 1.168; melting point: 80.05 °C; boiling point: 217.96 °C. Colorless crystals that are insoluble in water, soluble in benzene, absolute alcohol and ether, and slowly sublimes at room temperature.

From early times it has been used for black smoke in combination with potassium chlorate. The composition cannot be stored for a long time, because the naphthalene sublimes. However the black color of the smoke is so dense that it is quite popular. Care must be taken because there is often a risk of changing the ratio of the components spontaneously to form a dangerous composition due to the sublimation of the naphthalene.

Picric Acid, Trinitrophenol, $C_6H_2(NO_2)_3OH$

Molecular weight: 229.11; specific gravity: 1.767; melting point: 122.5 °C. Picric acid is soluble in water (1.2 g in 100 g of cold water and 7.2 g in 100 g of hot water); soluble in alcohol, ether or benzene. It forms picrates, which are sensitive to impact and friction, in combination with lead, iron, copper or other salts.

Picric acid contains oxygen and is a strong explosive. It burns in the air with a flame that generates a small amount of soot, which is caused by insufficient oxygen. It can be used to increase the brilliancy of a flame due to the radiation of the carbon particles, but for this purpose it would be better to use lampblack or camphor. It is said that picric acid in combination with potassium chlorate or potassium nitrate produces chloric acid or nitric acid, which can cause spontaneous ignition.

Picric acid has been used for manufacturing potassium picrate for whistles. It is sometimes used as a combustion agent for black snakes. When handling picric acid, most metallic containers or tools must be avoided.

Polyvinyl Chloride (PVC), $CH_2{:}CHCl$

Polyvinyl chloride is a white powder, with a grain size that varies according to the manufacturing process; 0.2–2 μ with milk polymerization and 20–150 μ with grain polymerization; specific gravity: 1.35–1.45; softening point: 70–80 °C. It is not attacked by water, alkalis or strong acids; it dissolves in tetrahydrofuran, methyl ethyl ketone or cyclohexane. Polyvinyl chloride in its normal state degenerates slowly producing HCl gas and becoming discolored. This reaction is enhanced in the presence of air, more so with oxygen, or with exposure to the sun. Therefore, a stabilizer like the stearate of zinc or calcium is added to polyvinyl chloride when it is used for plastic. However, for colored flame compositions that contain magnesium and polyvinyl chloride that are shaped into stars, it was not possible to detect any generation of HCl even after a long storage period of two or three years. This may be a result of the suppressing effect of magnesium hydroxide, which is produced in small amounts in the composition, thus avoiding degeneration. (Regardless, such compositions show a strong alkalinity; pH values of about 10 in distilled water.)

When polyvinyl chloride is heated, it dissociates at about 170 °C being carbonized to generate gas, which is mainly HCl. Polyvinyl chloride, therefore, is used quite favorably as a HCl gas producing agent to deepen the color of flames. Too much polyvinyl chloride, however, causes the generation of soot, which decreases the light intensity and sometimes ruins the color of the flame. Therefore 10–15% by weight of polyvinyl chloride for compositions that contain magnesium and less than 4% by weight for other compositions may be most appropriate except when it is used as a fuel. Polyvinyl chloride contains carbon that allows the flame to become transparent due to the reduction of the metal oxide particles in the flame, so it is used also as a reducing agent.

Potassium Dichromate, $K_2Cr_2O_7$

Molecular weight: 294.21; orange red crystals; specific gravity: 2.7; melting point: 39 °C; decomposes at 500 °C; dissolves easily in water (4.8 g at 0 °C, 10.97 g at 20 °C, 20.83 g at 40 °C, 42.2 g at 80 °C, 94 g at 100 °C in 100 g of water); insoluble in ethanol. It is poisonous and corrosive to the skin and mucous membrane. When iron sulfate is added to the dichromate solution, the hexavalent chromium is reduced to the trivalent form with a loss of color, and the poisonous nature is decreased.

When potassium dichromate is heated to a high temperature, it decomposes as follows:

$$4\ K_2Cr_2O_7 \rightarrow 4\ K_2CrO_4 + 2\ Cr_2O_3 + 3\ O_2$$

Potassium dichromate can be used as an oxidizer, but its oxidizing power is very weak compared with other ordinary oxidizers.

Potassium dichromate enhances the burning reaction of a potassium perchlorate composition when it is added in small amounts. For example, a test showed that the burning rate of a composition, which consisted of potassium perchlorate and hemp coal in a weight ratio 75:25, increased 1.55 times when 4–5% potassium dichromate was added.

Potassium dichromate suppresses the corrosion of magnesium especially with ammonium perchlorate. Place a small amount of a magnesium powder into a test tube that contains potassium dichromate solution in water. Heat it for a short time, remove the solution and wash the powder with water several times. Add a saturated solution of ammonium perchlorate to the magnesium powder in the test tube, and it will be observed that no bubbles are generated. This phenomenon confirms that the magnesium powder is at least temporarily protected. After a while however it begins bubbling actively. Next add a small amount of the potassium dichromate solution to the mixture and shake it, and it will be seen that the bubbling suddenly stops and the reaction ceases. This shows that potassium dichromate suppresses the corrosion of magnesium powder against ammonium perchlorate.

It is difficult to ignite or to explode a mixture of potassium dichromate and red phosphorus or sulfur even by impact between iron surfaces.

Potassium dichromate is used in small amounts in match compositions. It may be to suppress the violent burning reaction caused by potassium chlorate.[19]

Ultramarine, $Na_2S_2{\cdot}3NaAlSiO_4$

Ultramarine is a beautiful blue powder. It is easily attacked by acids but has considerable resistance to alkalis. It is stable in the sun or in hydrogen sulfide, H_2S, and withstands heat.

As Lancaster wrote,[8e] there are very few ingredients that produce yellow flames without any storage problems. However, ultramarine is one of them, and it is suitable for ammonium perchlorate based compositions especially when they contain magnesium.[8f] An experiment showed that there was no degeneration when the composition was stored for two years in non-moisture proof containers. Under the same condition $NaNO_3$, Na_2SO_4, $Na_2C_2O_4$, cryolite, etc. caused degeneration due to moisture. The only problem with ultramarine is that the yellow of the flame is rather weak and when it is used with chlorate or perchlorate based compositions, it produces much ash.

Zinc Oxide, ZnO

Molecular weight: 81.37; white powder of quite small particles or hexagonal crystals; specific gravity: 5.47–5.78; occurs naturally as zincite in the district of Franklin Furnace in the USA; melting point: 1800 °C; sublimes: 1700 °C under normal atmospheric pressure; changes color to yellow at about 300 °C, but when it is cooled, becomes white again. Almost insoluble in water and alcohol, but soluble in dilute and concentrated alkalis.

This is used for white smoke composition in combination with zinc dust and hexachloroethane. It seems that the higher the purity, the whiter the smoke color. The smoke composition is generally packed in a tin can, and the apparent specific volume is important in manufacture; if it is too small, the can is not filled; and if it is too large, the can cannot be filled with the amount defined in the specification. The apparent specific gravity of this material on the market lies between about 0.5 and 1.0 kg per liter.

Binding Agents

Recently many synthetic resins have been developed as pastes or binding agents, unfortunately these are often damaged by heat. Further these resins or their vapor often permeate into compositions slowly during long storage to cause degeneration of the composition. When they are used as a binder, some compositions become difficult to ignite. The vapor of many of the synthetic resins can be harmful to one's health, and for this reason, the paste or binding materials naturally produced are still quite useful.

The characteristics of a good binding agent for fireworks use is that it:

a) Must have a strong cohesive power, but threading must be avoided if possible. When the cohesive power is great, even the smallest amount allows the composition to consolidate well, and it does not decrease the burning temperature very much.

b) Must provide the composition with strong water or solvent resistance when it is consolidated. Otherwise when the composition comes in contact with another slurry composition as in the case of the manufacture of round stars, the water or solvent in the slurry destroys the composition or it passes deeply into the layers of the composition and remains there to cause burning problems.

c) Must produce a composition that is very hard on consolidation. The hardness is necessary to protect from the impact caused by the bursting charge.

d) Must not interfere with the drying of shaped compositions.

e) Must not cause cavities in the composition when it is dried.

f) Should be soluble in water or solvent even at cold temperatures. If it is soluble at low temperatures, it can generally be added to the composition in an accurate ratio before consolidation.

g) Must allow a kneaded composition to be easily formed into a shape or cut with a knife.

h) Should be approximately neutral in an aqueous solution and cause no reaction with other chemicals in the composition.

i) Must not interfere with the ignition or burning of a composition.

j) Must not cause degeneration during long storage.

k) Should not be hygroscopic.

l) Must not interfere with the color of the flame of a composition.

Table 6 shows a comparison of various kinds of binding agents that are soluble in water and that were tested by manufacturing 10 mm cube stars.

Table 6. Comparison of the Characteristics of Water Soluble Binding Agents Used for 10 mm Cube Stars.

B.A.	Comp.	M.S.	C.P.	W.R.	H(kg)	DTR(h)	DT50(h)	C.F.	S.W.	Cut.	Acid.	B.P. (mm/s)	D.C
GRS	C	Pow.	○	○	6.0	61	—	○	○	△		2.1	X
		Pas.	⊙	⊙	9.0	64	—	○		△	△	2.3	X
	P	Pow.	○	○	7.5	—	5.9	○	○	△	△	1.5	X
		Pas.	⊙	⊙	7.7	120?	9.0?	○		△	△	—	X
ORS	C	Pas.	△	△	6.5	67	—	○	X	○	△	2.1	X
	P	Pas.	△	△	13.5	110?	2.4	○		○	△	1.2	X
WF (w)	C	Pas.	△	X	6.5	56	—	○	X	△	△	2.3	X
	P	Pas	△	X	10.0	41	1.2	△		△	△	1.0	X
WF (s)	C	Pas	△	X	8.0	75	—	○	X	△	△	2.1	X
	P	Pas	△	X	12.5	54	1.4	○		△	△	1.1	X
WS	C	Pas	△	○	—	50	—	○	○	△	△	2.0	X
	P	Pas	△	△	8.0	57	3.6	○		△	△	1.3	X
DEX	C	Pow.	X	X	8.0	42	—	X	○	X	X	△	X
	P	Pow.	X	△	18.0	31	1.9	X		X	X	△	X
GA	C	Pas.	X	X	3.0	42	—	X	○	X	X	○	X
	P	Pas.	X	X	14.5	27	0.9	X		X	X	○	X
CMC	C	Pow.	△	X	10.5	—	—	○	○	○	△	△	X
	P	Pow.	△	△	12.5	64	1.1	○		○	△	△	X

Table Notes:

Acid. = Acidity in water solution.
B.A. = Binding agent.
B.R. = Burning rate of composition in 1 atm.
C = Potassium chlorate base composition (67% potassium chlorate, 14% combustion agent BL, 13% strontium carbonate, 6% binding agent).
C.F. = Cavity formation in composition.
Comp. = Composition.
C.P. = Cohesive power of the kneaded mass.
Cut. = Ease of cutting kneaded composition.
D.C. = Interference with flame color.
DEX = Dextrin.
DTR(h) = Drying time at room temperature (hour).
DT50(h) = Drying time at 50 °C in a drier.
GA = Gum Arabic.
GRS = Glutinous rice starch.
H(kg) = Hardness in kg (the maximum loaded weight when a star is crushed between an iron anvil and a plastic pestle (ABS) with a flat head 3 mm diameter).
M.S. = Mixing state of the composition.
ORS = Ordinary rice starch.
P = Potassium perchlorate base composition (67% potassium perchlorate, 14% combustion agent BL, 13% strontium carbonate, 6% binding agent).
Pas. = Paste.
Pow. = Powder.
S.W. = Solubility of the raw material in cold water.
WF(s) = Wheat flour (strong).
WF(w) = Wheat flour (weak).
W.R. = Water resistance of the dried stars.
WS = Wheat starch.
⊙ = The largest or easiest of all.
○ = Large or easy.
△ = Middle or neutral.
X = Small, weak or difficult.

Casein

Casein is a phosphoprotein. It is the main protein of milk, and the name "casein" often refers to milk casein. Pure casein is white, but the commercially available product is creamy or slightly grayish brown grains. It is insoluble in water, alcohol or ether, but it slowly dissolves in alkali, carbonate and strong acid

Gelatin

Gelatin is generally used in match composition. The purpose may be to produce good ignition and to maintain fire.

Gelatin is colorless and forms transparent glass-like sheets or grains that are tasteless and swell absorbing 5 to 10 times as much cold water. It is easily soluble in hot water, but insoluble in alcohol or ether. The solution in water is neutral or slightly acidic. The solution sets as it cools like Japanese isinglass. The solution in water forms a white precipitate with tannic acid. The jelly, which is obtained by adding potassium dichromate to a hot gelatin solution in water, becomes insoluble in water when it is placed in the sun. When formalin is added to a gelatin solution in water, it increases the gelling power and makes the film tough after drying.

Successive heating and cooling of gelatin solutions decrease the gelling capacity, but they can be gelled again by adding formalin to them.

There is no clear distinction between gelatin and glue. There are also many products due to the varied raw materials and manufacturing processes. Gelatin is the name of a product of good quality produced by using good raw material and a rational process. The items are selected based on the purpose for which they are needed; cohesive power, the nature of the gelatin, or gelling power.

Nitrocellulose, Cellulose Nitrate, Nitrocotton

$[C_{12}H_{14}O_4(OH)_4(ONO_2)_2]_x$
$\sim[C_{12}H_{14}O_4(ONO_2)_6]_x$

Nitrocellulose is a white powder that is very fluffy in a dry state or a cottonwool-like material. Molecular weight: 426.4–594.3. In practice the nitrogen content varies from 9.0 to 13.4% with 11 to 12% being the most popular commercially for firework use. Nitrocellulose is soluble in acetone, ethyl acetate, amyl acetate, etc. Nitrocellulose that contains less than 12% nitrogen dissolves in a mixture of ether and ethanol in a ratio of 2:l by volume. This solution can produce a stronger film of nitrocellulose than one in acetone.

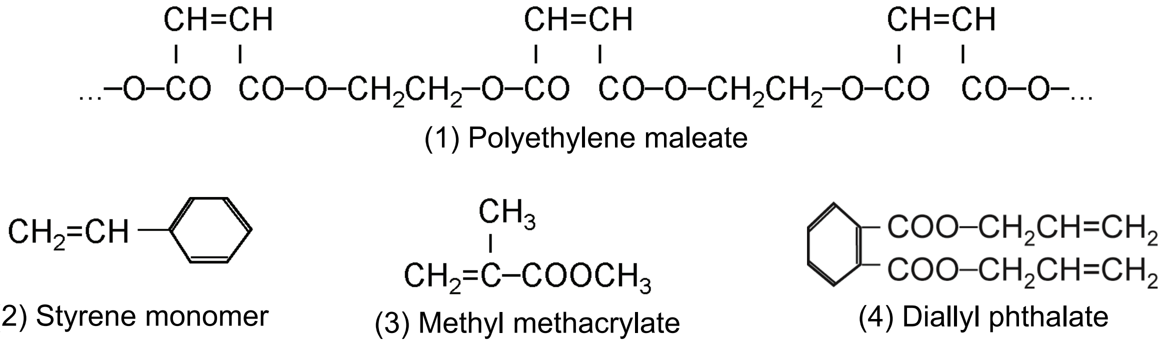
Nitrocellulose is a nitric ester. In a well dried state it ignites explosively at 160–180 °C; when burnt under 1 atm it produces a gas that consists of 25% NO_x, 42% CO, 18% CO_2, 8% H_2, 6% N_2, and 1% CH_4 by volume; it explodes on sudden heating or with a strong impact or friction. It is unstable and decomposes above 70 °C generating NO_x gas, even when the quality is good. It decomposes slowly even at room temperature especially if there is a trace of acid or an impurity. These characteristics increase as the nitrogen content increases. To suppress spontaneous decomposition a small amount of diphenylamine, about 1 g per 100 g of nitrocellulose, is added to a nitrocellulose solution.

It is important to keep it in a wet state with water or ethanol during storage. Never scatter it because it becomes a dangerous flammable dust floating in the air. It is used as a solution in acetone or amyl acetate and is known as "NC paste" for the consolidation of compositions that contain magnesium.

Polyester (Unsaturated Polyester)

The representative polyester on the market is a solution of polyethylene malate (ester) in styrene monomer in various ratios to obtain various hardnesses.

Polyethylene malate consists of very long molecules that contain many double bonds. Styrene monomer consists of short molecules that contain one double bond. (In place of the styrene monomer, methyl methacrylate or diallyl phthalate are also used.) (See Figure 2)


(1) Polyethylene maleate

(2) Styrene monomer

(3) Methyl methacrylate

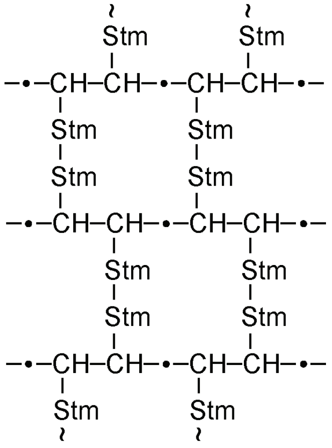
(4) Diallyl phthalate

Figure 2. The structure of various polyester components.

The melting and boiling points of the substances in Figure 2 are as follows:

Polyester Component	Melting Point (°C)	Boiling Point (°C)
(2) Styrene monomer	–31	146
(3) Methyl methacrylate	—	157
(4) Diallyl phthalate	–50	101

These long and short molecules combine with each other at the double bonds in three dimensions upon initiation by a catalyst to form a solid mass as follows:



Stm: is from styrene monomer and

–•–CH–CH–•–CH–CH–•–

is from polyethylene maleate.

When the proper catalyst is used, the reaction is initiated at room temperature, and it is accelerated by a temperature rise owing to the heat of reaction. Benzoyl peroxide, $C_6H_5CO–O–O–COC_6H_5$, or methyl ethyl ketone peroxide, $CH_3C_2H_5C(O–O)_2CC_2H_5CH_3$ is used as a catalyst. To initiate the reaction at room temperature it is necessary to add another substance such as cobalt naphthenate, $Co(C_{10}H_7COO)_2$, or dimethyl aniline, $C_6H_5N(CH_3)_2$, to produce an initiator [e.g., free radicals $C_6H_5NC:OO$ (benzoyl radical)].

Consolidated polyester shows different physical characteristics due to the ratio of the quantity of the ester to that of the monomer; specific gravity: 1.2–1.4; tensile strength: 350–700 kg/cm^2, compressive strength: 850–1700 kg/cm^2; generally hard and brittle. Its resistance to inorganic acids and alkalis is weak.

Polyester is used as a binder as well as a fuel. For example, a flare composition that does not contain magnesium can contain about 20% polyester by weight, and it can be cast into a container. In this case the composition shrinks in diameter upon consolidation, which can produce a gap between the composition and the container that often causes a quick fire problem. The diameter of the container is therefore generally limited to a maximum of about 25 cm. For a composition that contains magnesium, the quantity of polyester is kept to the minimum (about 2–5% by weight) to prevent the flame temperature from dropping. In this case the composition does not flow, and it is pressed into a container with quite high pressure. Stars that are consolidated with polyester as a binder have a high density, low ignitability and a slow burning rate. Naturally they cannot be used for shells that require the opposite characteristics.

A composition that contains magnesium and is consolidated with polyester is not really as waterproof or moisture proof as it is thought. Perhaps this may be due to the fact that the polyester has a weak resistance to acids and alkalis. The coating effect for magnesium powder is not as good as paraffin.

The amount of catalyst that is added to polyester for consolidation may vary based on its purpose, but for a commercial sample it is generally limited to a maximum of l% to avoid too great a temperature rise and rapid consolidation as these are both dangerous and produce an inferior quality product. It is thought that a small quantity of catalyst produces the best effect. Moreover the time of consolidation differs based on the brand, the quantity of the catalyst and the temperature.

Many substances that are used for firework compositions more or less have an influence upon the time of consolidation; sulfur, sulfide or organic fuels particularly delay the consolidation.

The toxicity of the polyester comes mainly from the vapor of the monomer, but it is said that the toxicity is slight or moderate and does not produce serious physical impairment.[20]

Soluble Glutinous Rice Starch (Mizinko)

There are two kinds of glutinous rice starch: one is parched and then ground into a powder and is called "quick starch"; the other one is steamed or further pounded into a cake, parched and ground into a powder and is called "parched starch". At present the material on the market is quick starch; however, for firework use parched starch is better than quick starch.

Glutinous rice starch contains approximately 80% carbohydrate, 7% albumin and 14% moisture. The carbohydrate consists of only amylopectin, which is a group of long branched chains of grape sugar molecules. On the contrary the group of long but unbranched chains of the sugar molecules is called amylose. These are detected by adding iodine solution in alcohol to the solution of these substances; amylopectin produces red violet, whereas amylose produces blue indigo color.

When a small amount of water is added to the glutinous rice starch and kneaded, it becomes like rice cake and is quite cohesive. But when a large amount of water is added to the starch and it is boiled for long time, the cohesive power of the starch decreases; this shows that the amylopectin changes to amylose.

The cohesive power of glutinous rice starch is very strong; this is clearly seen by comparing this starch with other binders like dextrin. Add ten times as much water to glutinous rice starch and stir well. Test it between the fingers, and it is clear how much more cohesive it is than a dextrin solution that is prepared in the same manner. This cohesive nature of glutinous rice starch is quite important, especially for preparing round stars, because the essential point of the process lies in that the composition must be pasted in a wet state on the core using as little paste as possible. Accordingly a paste that has a strong cohesive power satisfies the requirement well. For this reason glutinous rice starch is quite superior for manufacturing round stars because it causes the least amount of trouble.

However the cohesive power of the paste of glutinous rice starch generally changes as the time passes when it is mixed with chemicals or compositions. For example, an experiment in the summer season is set out in Table 7.

For this experiment, 20 mL of distilled water was added to mixtures of 2 g of glutinous rice starch and 20 g of other chemicals. The mixtures were stirred well and the viscosities were observed at definite time intervals.

Table 7 shows that only starch does not change in viscosity. Sodium carbonate and potassium chlorate increase the viscosity. Arsenic sulfide and aluminum have almost no influence upon the viscosity. Other substances generally decrease the viscosity. Sodium oxalate, barium nitrate, Black Powder, sulfur and in particular charcoal cause the starch to lose its viscosity. Ammonium perchlorate also has a large influence.

The decrease in the viscosity caused by sodium oxalate or Black Powder, which are the most extreme, was more precisely observed. In the first one or two hours it looks as though there is an increase in the viscosity, and then the viscosity slowly decreases; after five or six hours the viscosity is not much different than it was at the beginning. This property of glutinous rice starch does not cause any trouble in manufacturing stars, but the paste of a composition

Table 7. The Influence of Chemicals upon the Viscosity of Soluble Glutinous Rice Starch.

Chemical	After 15 hours	After 24 hours
— blank	s	s
$KClO_3$	ss	ss
$KClO_4$	w	ww
NH_4ClO_4	www	wwww
KNO_3	ww	www
$Sr(NO_3)_2$	ww	ww
$Ba(NO_3)_2$	o	o
$Na_2C_2O_4$	o	o
$CuSO_4$	ww	ww
Black Powder	o	o
S	o	o
Pine charcoal	o	o
Na_2CO_3	sss	sss
Arsenic sulfide	s	ss
Al (powder)	s	s
Sb_2S_3	w	o
Red phosphorus	w	ww
Shellac	s	ss
Rosin	w	ww
$NaNO_3$	ww	ww

Note: s = The mixture does not change in viscosity and somewhat flows.
ss = The viscosity increases and the mixture hardly flows.
sss = The viscosity increases greatly.
w = The viscosity somewhat decreases and the mixture flows fairly.
ww = Soft and flows well.
www = Quite soft and can be ruffled by shaking.
wwww = Quite low viscosity which is hardly felt.
o = Quite low viscosity like water.

that contains glutinous rice starch must not be left more than half a day.

Glutinous rice starch has the smallest hygroscopic degenerative nature of all the popular starches, but for long storage it is preferable to place products that contain glutinous rice starch in dry conditions as much as possible, and above 5 °C if possible, because the degeneration of starch occurs most easily at 30–60% moisture and a temperature of 2–3 °C. Careful kneading is also effective for avoiding degeneration.

Wheat Flour

Wheat flour varies in character based on the kind of wheat and the method of manufacture. For example, the soft wheat flour produced in the USA has a milling yield of 80%, contains 8.8% albumen, 88.6% carbohydrate, 1.4% fatty material, 0.5% cellulose, 0.7% ash and the effective heat of combustion value is 339 kcal per 100 g.[21] With lower yields the amount of carbohydrate increases. The particular character of wheat flour lies in that it contains a small amount of gluten, which corresponds more or less to the albumen content and it is insoluble in water, however it becomes elastic as water is absorbed. Wheat flour that contains a large amount of gluten is called “strong flour” and as the amount of gluten decreases it is called “middle flour” and then “weak flour”. Strong is a slightly yellow color and weak flour is white. For firework use, all can be used as fuels.

As a fuel, wheat flour generates a combustion heat of about 800 kcal per 1 kg of mixture of wheat flour and potassium chlorate; this value is the highest compared to other materials such as lactose, sucrose, dextrin, etc. Generally wheat flour contains about 14% moisture.

Wheat Starch

$[C_{12}H_{14}O_4(OH)_4(ONO_2)_2]_x \sim [C_{12}H_{14}O_4(ONO_2)_6]_x$

Wheat starch must not be confused with wheat flour. This starch is obtained by separating the gluten from wheat flour.

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Notes

An Introduction to Chemical Thermodynamics

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Introduction

Pyrotechnic devices use energy released by chemical reactions to produce a variety of effects including heat, light, sound and motion. The relationship between chemical change and energy is of central importance to a scientific approach to pyrotechnics. The branch of science that deals with this relationship is *chemical thermodynamics.* Thermodynamics can predict whether or not a chemical reaction is possible, and how much energy would be released or absorbed by that reaction. It cannot, however, predict how fast a reaction will be. That is the concern of *chemical kinetics.* The energy involved in chemical reactions and the speed of those reactions are both of obvious interest to the pyrotechnist. This chapter will give an introduction to chemical thermodynamics, with an emphasis on those aspects of relevance to pyrotechnics.

A Few Words about Mathematics

The following sections contain some mathematics. To a newcomer to science, it can be rather intimidating to see lines of mathematical symbols appearing in the middle of a discussion about some aspect of the physical world. It is by no means obvious how these symbols can have anything to do with what happens in the world outside. Some writers add to the confusion by claiming that the behavior of the real world is in some mysterious way “governed” by mathematics. What really happens is this: Scientists take some aspect of the real world and treat it *as if* it were one of the abstract objects dealt with by mathematics. The process of converting an aspect of the real world to a problem in mathematics is called making a *mathematical model.* The reason for making mathematical models is that mathematics provides a very powerful set of procedures for reasoning in a completely logical and consistent way. If the model is well chosen, a mathematical argument can reveal all sorts of relationships between aspects of the real world. If the results of the mathematical reasoning are consistent with what is observed, it is evidence that the mathematical model was indeed well chosen. Instead of saying that the behavior of the physical world is “governed” by mathematics, we should say that aspects of it can be *described* or *modeled* by mathematics.

The mathematical parts of this chapter are set out in more detail than is usual, in an effort to avoid the frustration that arises when one cannot follow a step that might be obvious to a more mathematically-minded reader.

Chemical Thermodynamics

Chemical thermodynamics can provide an understanding of what drives chemical change. It provides ways to calculate whether a particular reaction is possible and what energy changes would be associated with that reaction. Calculations, using tables of thermodynamic data, can reveal the maximum possible amount of energy that could be provided by a particular reaction, such as that between potassium perchlorate and aluminium in flash powder. A calculated value for the energy released in a pyrotechnic reaction can then be used to estimate the maximum possible temperature that could be reached. Such information can be useful when designing compositions for producing colored flames, for example. Thermodynamic calculations can provide useful information about the composition of chemical systems at equilibrium that would be difficult, or impossible, to obtain experimentally. Such information is useful in calculations for the design of efficient rocket motors.

Thermodynamics originated from efforts to understand the limitations of steam engines. Its application to chemistry happened at about the same time that the molecular theory of matter was being developed. Thermodynamics makes no assumptions about the structure of matter. It is much easier, however, to understand the application of thermodynamics to chemistry if the behavior of molecules is brought into the picture.

A Preamble about Matter

Since chemical thermodynamics is concerned with matter and energy, it is appropriate to review some relevant ideas about matter. The most obvious characteristic of matter is its complexity. Stars, planets, rocks, plants, people, cities—all are aggregates of matter in varying degrees of complexity. The task of understanding such complexity might seem impossible. Chemistry approaches the problem by focusing attention on the least complex types of matter. Over the past few centuries, chemists have subjected matter to various processes of chemical analysis, reducing structures and objects to materials, and then attempting to reduce each material to its simplest constituents. This led to the recognition of a relatively small number of *chemical elements*, materials that could not be decomposed into simpler substances by chemical analysis. The next level of complexity is the *chemical compound*. Chemical compounds are substances made up of chemical elements, in *constant proportions by mass*. Elements and compounds, because they are of constant chemical composition, are called *pure substances*. Compounds are formed from their elements (either directly or indirectly by way of intermediate compounds) by *chemical reactions*. During some chemical reactions, *energy* is released. In others, energy is absorbed from the surroundings by the reacting materials.

The Molecular Structure of Matter

Probably the most important idea in physical science is the notion that matter is made up of very small particles, called *molecules*. Each pure substance consists of molecules of the same kind. Molecules can be broken down into smaller particles, called *atoms*. The molecules of each of the chemical elements are made up of atoms having the same, unique set of chemical properties. They may vary in mass (atoms of the same chemical type but having different masses are called *isotopes*) but their chemical properties are essentially identical. The molecules of elements may consist of single atoms (helium, neon, argon and gaseous mercury are examples), or of two or more atoms bound together. Examples include oxygen (O_2, a pair of oxygen atoms), white phosphorus (P_4, a tetrahedron of phosphorus atoms) and sulfur (S_8, a ring of eight sulfur atoms). The word “atom” means “indivisible”, and at one time it was thought that the atom represented the limit to the breaking down of matter. These days, it is known that atoms consist of an extremely small, but massive, central *nucleus* surrounded by a rather complex outer structure of *electrons*. Chemical reactions occur when the outer electrons of atoms rearrange themselves. These rearrangements can result in atoms of various sorts becoming linked together by new electronic structures, forming molecules. Only the outermost electrons are involved the rearrangements that take place in chemical reactions. An arrangement of electrons that links two atoms together is referred to as a *chemical bond.*

Perhaps the simplest type of electronic rearrangement is the loss of a single electron from an atom. The electron-deficient atom left after this process is called a *positive ion*. Metals, such as sodium, iron and gold, are made up of positive ions, stacked in regular patterns, surrounded by a “sea” of loose electrons that can move around freely, provided they do not move too far from the ions. These mobile electrons are responsible for the high electrical conductivity of metals and for their characteristic metallic luster. Other atoms, such as those of non-metallic elements like oxygen and chlorine, can gain electrons and form *negative ions.* Compounds such as magnesium oxide (MgO) and sodium chloride (NaCl) consist of positive metal ions and negative non-metal ions stacked in regular patterns. These compounds are examples of *ionic compounds*. In substances such as elemental sulfur (S_8) and oxygen (O_2), and compounds such as water (H_2O) and alcohol (C_2H_5OH) and also in ions such as the ammonium ion (NH_4^+) and the nitrate ion (NO_3^-), the atoms are linked by pairs of electrons shared between the atoms. These shared pairs of electrons are called *covalent bonds*.

Molecular Structure of the States of Matter

Most pure substances can occur in three physical states: solid, liquid and gas. The three physical states differ in the way in which the molecules are arranged in space. Molecules in every state of matter are in constant motion. In a solid, molecules are close together and move mainly by vibrating about their rest positions. In a gas, molecules are relatively far apart and move at random through the entire volume available to be occupied by the gas. In a liquid, the molecules can move freely but tend to remain close to each other.

A Digression into Mechanics

Already in this discussion several *mechanical* concepts have been mentioned without definition or explanation. These concepts included motion, mass and energy. While these ideas might already be quite familiar, it is useful to review them. This requires a brief look at the classical Laws of Motion. It will be assumed that the ideas of space, distance and time can be taken for granted. The aim is to review the rules that describe how objects move; that is, how their position in space changes with time.

Displacement, Speed and Velocity

If you see an object at one place, and some time later you see it somewhere else, the object has undergone a *displacement*. Displacement is measured in units of length or distance, and in scientific work the unit of length is the *meter (m)*. By timing the object as it moves from one place to another, you can work out how far it travels in a unit of time, such as one second. That gives its *average speed* in *meters per second* (ms^{-1}). If the speed is the same from one instant to the next, and if the object is moving in a straight line, the object is travelling at constant *velocity*. Velocity has the same units as speed (meters per second), but speed is only one aspect of velocity. The other aspect is direction. Left to its self, an object will maintain its velocity. It will keep moving with the same speed, in the same direction, forever. This might seem an absurd statement, because everyday observation shows that moving objects usually stop moving unless something is done to keep them in motion. The point is that the objects in everyday life are not left to themselves but are always interacting with something else. Another way of looking at it is that a change in the velocity of an object requires an explanation, but a constant velocity does not.

Acceleration, Force and Newton's First Law

If the velocity of an object changes, either in speed or direction, the object has undergone *acceleration*. The units of acceleration *are meters per second per second* (ms^{-2})**.** In ordinary conversation, the term "acceleration" means an increase in speed. In physics, acceleration means any change in velocity. This can be an increase or decrease in the speed of an object, or a change in its direction of motion. Acceleration, being a change in velocity, requires an explanation. By definition, acceleration is the result of a *force***.** In everyday language the word force is associated with pushing, shoving, compelling, or making something happen. In physics, force is what causes acceleration. All the discussion of motion so far can be summarized in the statement: "An object will remain at rest, or in uniform motion in a straight line, unless acted on by a force". This is *Galileo's Law of Inertia* or *Newton's First Law of Motion*.

Mass and Newton's Second Law of Motion

It is obvious from everyday experience that a push or shove that produces a certain change in the motion of one object will not necessarily have the same effect on a different object. By definition, the ratio of the force on an object to the resulting acceleration is the *mass* of the object.

$$\text{mass} = \frac{\text{force}}{\text{acceleration}}$$

or force = mass × acceleration.

This relationship is *Newton's Second Law of Motion.*

It is known from experiment that in the absence of air, objects near the surface of the earth fall towards the ground at the same speed. That means that they all experience the same acceleration, known as the *gravitational acceleration, g* in meters per second per second. The force that acts on bodies near the earth's surface is therefore $m \times g$, where m is the mass (units not yet defined). The mass of an object can most easily be described by comparing the gravitational force acting on it to that acting on some reference object. The comparison is readily carried out using a *balance*.

For historical reasons, the reference object for mass is a piece platinum-iridium alloy called the standard *kilogram*.

In scientific work, mass is measured in *kilograms (kg)*. Force is measured by the acceleration that it produces in an object of unit mass. A force that produces an acceleration of one meter per second per second when acting on an object having a mass of one kilogram is called a *newton (N)*.

Mass and Weight

It is worth recalling that mass is a fundamental property of an object and does not vary from place to place. In contrast, the *weight* of an object is the force exerted by the gravitational interaction between the object and the earth (or the moon, if the object happens to be on the moon). Because the gravitational acceleration near the earth's surface is constant, it is convenient to describe weight in units of mass, when really we should use units of force. If the day ever comes when people regularly travel between the earth and the moon, the distinction between mass and weight will be common knowledge. Spring balances and electronic balances would need to be re-calibrated for use on the moon. A beam balance, of course, would be accurate in either location.

Pressure

Having introduced the concept of force, it is appropriate to mention *pressure*, which is the force applied per unit area of a surface. Pressure is extremely important in discussing the behavior of gases. It is measured in *pascals (Pa).* A pressure of one pascal corresponds to a force of one newton per square meter. Living as we do at the bottom of a vast ocean of air, we are subjected to a relatively constant pressure of around 100 kilopascals (kPa). A pressure of 101.33 kilopascals is defined as one *atmosphere* and is often used as a unit of pressure in thermodynamics. This usage, though well-established, is not consistent with the SI system of units, in which pressure is always measured in pascals. Accordingly, thermodynamic properties are preferably specified not at 101.3 kPa but at 100 kPa. This pressure is given the name one *bar*.

It should be mentioned, too, that pressure gauges, even though they might be calibrated in pascals, often take their zero point as one atmosphere. Such gauges actually read the difference between the measured pressure and one atmosphere, the so-called *gauge pressure*. In thermodynamic calculations, pressure must be measured from a true zero point of zero newtons per square meter.

Newton's Third Law of Motion

Most of the discussion so far has really been giving definitions. Now it is time to introduce some results of experiments and observations. One important result is that acceleration always involves the interaction of at least two objects. There is a general rule that summarizes the results of many experiments and observations. "If two isolated objects interact in a manner that results in their acceleration, the accelerations of the two objects will be in opposite directions". The objects are described as "isolated" to indicate that the only force acting on them is the one involved in the interaction. If the two interacting objects are identical, the accelerations will not only be in opposite directions but of the same magnitude. If the two interacting objects are different, their accelerations will be inversely proportional to their masses. In other words, when two objects interact, the force acting on one object will be of the same magnitude, but in the opposite direction, as the force acting on the other. This is *Newton's Third Law of Motion.* The traditional statement of that Law is "For every action, there is an equal but opposite reaction".

Work

When a force acts on an object and accelerates it, the force is said to have done *work*. The amount of work is obtained by multiplying the force by the distance over which it acts. The units of work are *newton meters (Nm).* A good example of work is the lifting of a weight. To raise a weight of mass m kilograms, you must apply a force of ($m \times g$) newtons to overcome the gravitational force of mg newtons acting on the object. If you lift the object h meters, you will have exerted a force of mg newtons over a distance of h meters. You will have done mgh newton meters of work.

Energy

Energy is one of the most important concepts in physical science. Perhaps because of its central role in scientific explanation, it is also one of the most difficult concepts to define. Fortunately, the ultimate nature of energy is irrelevant for the purposes of this discussion. In mechanics, energy can be defined as the *capacity to do work,* and it is expressed in the same units as work; the amount of energy required to do one newton meter of work is the *joule (J)*. Conversely, the joule can be used as a unit of work, exactly equivalent to the newton meter.

This definition of energy as the capacity to do work is not entirely satisfactory, because in thermodynamics situations arise where energy is not available to do work. It could be argued that to speak of a "capacity to do work" that is not available to do work is not particularly meaningful. As will be seen, however, this idea of "unavailable energy" is of fundamental importance in thermodynamics and is easy to understand from the molecular perspective.

For the moment, it is necessary only to review energy in simple mechanical systems.

Potential Energy

Imagine a small heavy object, of mass m_1 kilograms, at rest on the floor, attached to a string threaded through a pulley fixed to the ceiling. See Figure 1. Imagine, too, that the pulley is absolutely perfect, offering no resistance whatsoever to the motion of the string. If you pull downwards on the other end of the string, the string will eventually become tight and will exert a force on the object. If you increase the force until it exceeds the weight of the object (m_1g newtons, where g is the gravitational acceleration), the object will be accelerated and will rise toward the ceiling. If you keep pulling the string until the object is h meters above the ground, you will have exerted a force of m_1g newtons over a distance of h meters and you will have done m_1gh newton meters (i.e., joules) of work in lifting the object.

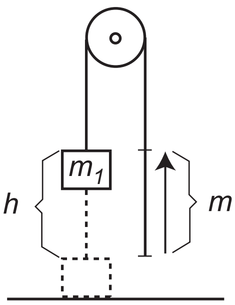

Figure 1. Potential energy illustration when a downward force is exerted on the pulley rope, m_1 is raised h meters and exerts a force of m_1g in the opposite direction.

Suppose now that you tie your end of the string to another object and release it. See Figure 2. The string will exert an upward force on the second object equal to the weight m_1g newtons of the first object. The earth's gravity will exert a downward force m_2g newtons on the second object. If m_2 is less than m_1, then the second object will be subjected to a net upward force of ($m_1g - m_2g$) newtons. It will accelerate upwards. Meanwhile, the first object, experiencing a net downward force of *($m_1g - m_2g$)* newtons, will accelerate towards the floor. It will fall a distance of h meters before it crashes into the floor. The second object, having been accelerated to a certain upward velocity, will now experience only the downward force of gravity m_2g. If it has reached a sufficiently high upward velocity, it may hit the ceiling or reach the end of the string, but ultimately it will come to rest hanging h meters above the floor. The overall effect has been to lift a weight of mass m_2 kilograms to a distance h meters above the floor. The net work that has been done is m_2gh newton meters (joules). Notice that the work done in lifting the second object (m_2gh newton meters) is *less* than the work done in raising the first object (m_1gh newton meters) because m_2 was less than m_1.

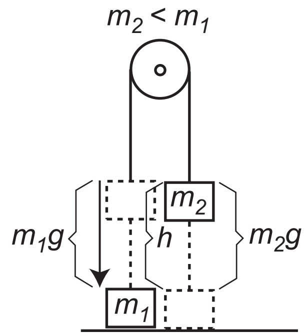

Figure 2. Potential energy illustration where m_2 is less than m_1. The work done by raising m_2 though the distance h is force x distance = m_2gh. This situation will be true even if the difference in mass between m_1 and m_2 is very small. In the limit, the maximum work would be done if m_2 were only a negligibly small amount less than m_1. A mass m_1 at a height h therefore has the ability to do no more than m_1gh units of work. It has a potential energy of m_1gh.

Suppose now that the mass m_2 of the second object is only a few milligrams less than that of the first object. The second object will experience a very small upward force, and it will accelerate upwards very slowly. At the same time the first object will accelerate downwards very slowly until it lands gently on the floor. The second object, having reached only a very small velocity, will very quickly come to rest at a height h meters above the floor. The net work that has been done is again m_2gh newton meters. Notice that the work done in lifting the second object (m_2gh newton meters) is again less than the work done in raising the first object (m_1gh newton meters) because m_2 was less than m_1.

Carrying this line of argument to its limit, as the mass of the second object approaches that of the first, the net force acting on each object will approach zero. When the second object is only a tiny amount less massive than the first, the second object will take an extremely long time to rise to its ultimate height of h meters above the floor and will overshoot its rest position by only a minute distance. The work done will be m_2gh newton meters, which in this case is very close to the work m_1gh newton meters that was done when the first object was lifted h meters above the ground.

Ultimately, a weight of mass m kilograms hanging h meters above the floor has the capacity to do mgh newton meters of work in falling to the floor. It therefore possesses a *potential energy* of mgh joules. In this example, the object possesses potential energy because of its *position* in the gravitational field of the earth. Potential energy is also possessed by objects such as compressed springs, to which a force has been applied over a distance to distort the shape of the object.

Equilibrium

When the masses of two objects hanging from a string on either side of a pulley are exactly equal, the upward and downward forces acting on each object are exactly balanced. The forces are said to be in *equilibrium.* Once a system is in equilibrium, there are no net forces available to do work. *A system in equilibrium can do no work. The available energy is zero.*

When the masses of the two objects are unequal, the system will come to rest with one weight on the floor and the other hanging in the air. Again, the forces acting on each weight are exactly balanced, the available energy is zero, and the system can do no work. The system has come to equilibrium, but the equilibrium is clearly very different from that achieved when the two weights were equal. In that case, a tiny change in the mass of either weight would upset the equilibrium. This leads to the idea of a *reversible* process. A process is *reversible* if its direction can be reversed by an infinitesimally small change.

Equilibrium and Reversibility

The imaginary experiment with the hanging weights provides a useful mechanical example of a reversible process.

Imagine that the two weights are of exactly equal mass, and that they are hanging at equilibrium on either side of a perfect pulley that offers absolutely no resistance to motion. Now, imagine that the mass of one object is increased by a very small amount. Perhaps a very tiny speck of dust falls on it. The forces on the two weights are no longer equal. The heavier weight will start to accelerate downward, with an extremely small acceleration. Now suppose that the speck of dust is blown off the weight with a gentle puff of air that imparts no vertical acceleration to either weight. The net forces acting on each object will again be zero, and acceleration will cease. According to Newton's First Law, each body will keep moving upward or downward at the very tiny velocity that it had acquired after its very small acceleration. After an extremely long time, the system will come to equilibrium with one object on the floor and the other object h meters above the ground. At any instant, the addition of a very small mass to the rising object would cause it to experience a net downward force so the direction of motion would reverse. Such a process, that can be set into reverse by an infinitesimally small change, is an example of a *reversible* process.

Notice that when this reversible process eventually comes to equilibrium, the system will have done the maximum possible amount of work.

In thermodynamics, a process carried out reversibly will always perform the maximum possible amount of work, but will take an infinitely long time to do so. All natural processes take place in a finite amount of time and are therefore irreversible. Nonetheless, the concept of a reversible process is important in thermodynamics because of the link between reversibility and maximum work. This will be discussed further in the section dealing with the Second Law of Thermodynamics.

Kinetic Energy

Kinetic energy is the energy possessed by a body because of its *state of motion*.

A thought experiment can show how a moving body can do work in being brought to rest. See Figure 3. Imagine a body of mass m_1 kilograms moving with a uniform velocity of v meters per second over the surface of an ideal, friction-free table. At the edge of the table is a perfect pulley, over which passes a string attached to a small object of mass m_2 kilograms sitting on the floor. The moving object is travelling away from the pulley. At a certain point the string is suddenly attached to the moving object. It pulls tight, and lifts the second object off the ground. The string exerts a force on the moving object, causing it to accelerate in the opposite direction to its direction of motion. Eventually the moving object comes momentarily to a stop after having moved through a distance of h meters. The small object has been raised a height of h meters above the ground, so the moving object has done m_2gh newton meters of work.

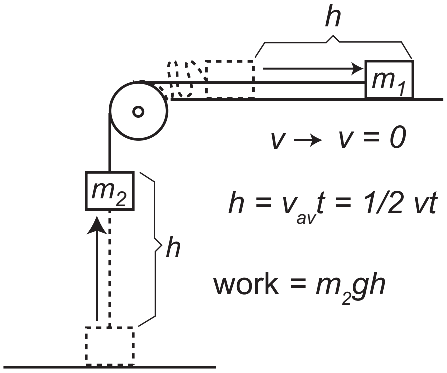

Figure 3. Kinetic energy illustration. Mass m_1 was originally moving with constant velocity v but was brought to a halt by raising mass m_2 through a vertical distance h. During this time m_1 travels through a horizontal distance h and undergoes a negative acceleration a. The average velocity of m_1 while it is being slowed down is v/2, the time taken for this process is v/a. The distance h is given by average velocity × time (i.e., v/2 × v/a). The force acting on m_1 is mass × acceleration (i.e., m_1 × a). The work done is force × distance (i.e., $\frac{1}{2}m_1v^2$). See text for details.

In bringing the moving object to a halt, the force m_2g newtons has been applied over a distance of h meters. This force was applied to an object of mass m_1 kilograms and accelerated it from an initial velocity of v meters per second to a final velocity of zero meters per second.

The distance h over which the force acted is given by the average velocity v_{av} multiplied by the time t:

$$h = v_{av}t$$

The average velocity v_{av} is half the sum of the initial velocity (v) and the final velocity (0 meters per second), so the distance h is given by

$$h = \frac{1}{2}(v + 0)t$$

$$= \frac{1}{2}vt$$

The final velocity (0 meters per second) is given by the initial velocity (v) plus the acceleration $-a$ multiplied by the time t. Notice that the acceleration is given a negative sign, because it is acting in the opposite direction to the initial velocity v.

$$0 = v - at$$

so $$t = \frac{v}{a}$$

$$h = \frac{1}{2}vt$$

and $$= \frac{1}{2}v\left(\frac{v}{a}\right)$$

$$= \frac{1}{2}\left(\frac{v^2}{a}\right)$$

But

force = mass × acceleration

$$= m_1a$$

and work = force × distance

$$= m_1ah$$

$$= m_1a\left(\frac{1}{2}\frac{v^2}{a}\right)$$

$$= \frac{1}{2}m_1v^2 \text{ Nm}$$

The work done by a body of mass m_1 kg *being brought to rest* from an initial velocity of v meters per second is ½ m_1v^2 newton meters. A body of mass m kg moving with a velocity v meters per second has a kinetic energy of ½ mv^2 joules.

Conservation of Energy

In the thought experiment just described, the moving body on the table top was brought momentarily to rest, while the small body suspended from the pulley was raised a distance h meters above the floor. The potential energy of the suspended body became m_2gh joules, while the kinetic energy of the body on the table became zero joules. Obviously this situation can only last for an instant. The stationary body, under the influence of the force m_2g in the string, will begin to accelerate in the opposite direction as the suspended object falls towards the floor. The falling object will end up on the floor, having fallen through a distance h meters, and its potential energy will again be zero. By reversing the arguments in the previous section, it is easy to show that the object on the table will end up with a velocity of v meters per second, in the opposite direction to that of its initial velocity. Its kinetic energy is again ½ m_1v^2 joules. Energy has been converted from kinetic energy to potential energy and back again.

In some mechanical devices, conversion from potential to kinetic energy and back again can (at least in theory) proceed indefinitely. An example is the pendulum. At the top of its swing, the pendulum is momentarily at rest, so its kinetic energy is zero and its potential energy is at a maximum. At the bottom of its swing, the pendulum is moving at its maximum velocity, its kinetic energy is at a maximum and its potential energy is at a minimum. As the pendulum swings to the top at the other side, the kinetic energy decreases to zero and the potential energy rises back to the maximum value. In principle, if there were no losses of energy, this process could repeat indefinitely. Such a system is called a *conservative system*, because the total mechanical energy is conserved. A real pendulum does not keep swinging indefinitely but eventually comes to a halt. This indicates that the transformation of potential energy to kinetic energy and back again is not 100% efficient. What happens to the lost energy? Part of it goes to stir up the air through which the pendulum moves, and some is used in moving the parts of the suspension device past each other. Ultimately, this energy is converted to *heat*. The air and the suspension device are a little bit warmer at the end of the process than they were at the beginning.

In the last century the British scientist James P. Joule carried out careful experiments that showed that mechanical work could be converted entirely into heat. Before then, heat and work were measured in different units. Now, (at least in scientific work), the same units are used for both.

The conversion of mechanical work into heat is important in pyrotechnics. Devices such as the friction match, the party popper, the pull-wire igniter and the percussion cap all rely on the conversion of mechanical work into heat that subsequently ignites a pyrotechnic composition. Unintended initiation of pyrotechnic mixtures during manufacturing and processing can result from the mechanical work associated with friction, shock or impact being transformed into heat. The heat produced in such processes is highly localized and can be very effective in initiating certain sensitive mixtures.

It is a fundamental postulate of thermodynamics that when heat is taken into account, the total amount of energy in the universe is constant. This is the *Law of Conservation of Energy.*

Heat as a Form of Energy

As outlined in the preceding sections, energy is transferred between mechanical systems as work. The Law of Conservation of Energy is based on the recognition that energy can also be transferred as heat. There are several other processes that can transfer energy. Electric currents and various types of radiation are two examples. In this discussion of chemical thermodynamics, however, it will be sufficient to consider only heat and work.

Classical chemical thermodynamics made no reference to the molecular structure of matter. It is, however, very useful to interpret thermodynamic properties by relating them to the behavior of molecules. Heat can be thought of as the energy associated with *the random motion of molecules*. This makes the connection between mechanical work and heat much easier to understand. In Joule's experiments, water stirred by mechanically driven paddles became hotter. From a molecular perspective one can imagine the uniform motion of the molecules in the paddles moving nearby water molecules, initially in a rather uniform way. The motion of the water molecules would quickly become randomized as one molecule collided with another, so ultimately the effect of the stirring paddles would be to increase the random motion of the molecules—in other words, to heat the water. Each molecule has a certain mass m, and at any instant of time has a certain velocity v. At that instant the molecule has a kinetic energy $\frac{1}{2}mv^2$. The average kinetic energy of the molecules is directly related to the *temperature* of the material.

As well as energy being transferred between molecules by direct mechanical impact, it can also be transferred by *electromagnetic radiation.* A proper discussion of this would take up considerable space. It is sufficient to note that this radiation is familiar to us as *light* and *radiant heat* (or *infra-red* radiation), the only fundamental difference between these being the energy with which the radiation is associated. The energy of electromagnetic radiation can be thought of as being packaged into particles called *photons.* The energy of a photon is related to the wave properties of the radiation through *Planck's relationship*:

$$E = h\nu = \frac{hc}{\lambda}$$

where ν (Greek letter *nu*) is the *frequency* in cycles per second (units**:** *inverse seconds,* s^{-1}, often called *hertz, Hz*), c the velocity of light (2.9979×10^8 meters per second in vacuum) and λ the wavelength in meters. The constant of proportionality h is *Planck's constant* (6.6262×10^{-34} joule seconds). Radiation emitted by a molecule travels through space and can be absorbed by another, resulting in a transfer of energy from one molecule to another without any direct contact between them.

Temperature

The idea of temperature is familiar from everyday life, as an indicator of 'hotness' or 'coldness'. Historically, people have chosen some property of matter that varies with 'hotness' or 'coldness' and used it as the basis of a system for measuring temperature. Such a property is the volume of a fixed mass of gas or liquid. A fixed mass of gas or liquid, arranged in such a way that changes in volume can be readily measured, can be used as a temperature measuring instrument or *thermometer*. The thermometer is calibrated by placing it in environments where the temperature is reproducible. One such environment is a mixture of pure water and ice. The temperature of this mixture has been assigned the value of 0 degrees Celsius (ºC). The temperature of pure water boiling at atmospheric pressure has been assigned the value of 100 °C. The liquid or gas in the thermometer has a certain volume in the melting ice, and another, larger volume in the boiling water. This range of volumes is divided into 100 equal parts, and a change of one of these units of volume is defined to correspond to a change in temperature of 1 degree Celsius. It is found experimentally for gases that 1 degree Celsius corresponds to a change of 1/273 of the volume at 0 °C. This suggests that if the temperature were reduced to –273 °C, the volume of the gas would shrink to zero. While this is only a "thought experiment", because all real gases turn into liquids before the temperature reaches –273 °C, it suggests the very important idea of an absolute zero of temperature at –273 °C. More accurate estimates give the value as –273.15 °C. The temperature scale used in scientific work, the kelvin (or absolute) scale, uses the same degrees as the Celsius scale but starts at absolute zero. The kelvin temperature is obtained by adding 273.15 to the Celsius temperature. The unit of temperature on the absolute scale is the *kelvin (K).*

The Zeroth Law of Thermodynamics

Temperature could be defined as "the property that is measured by thermometers". This is expressed in a formal way as follows:

Two bodies that are in thermal equilibrium with a third body are in thermal equilibrium with each other. They share a common property called "temperature".

This statement is the *Zeroth Law of Thermodynamics.*

The 'third body' referred to in the Zeroth Law is the thermometer. Being in thermal equilibrium means that the transfer of heat from the body to the thermometer is exactly balanced by the transfer of heat from the thermometer to the body. This situation is easily recognized, because the reading of the thermometer is then constant.

Molecular Interpretation of Temperature

Temperature is a measure of the *average kinetic energy* associated with the *random motion of molecules.* A detailed discussion of the relationship between molecular motion, energy and temperature is not appropriate here; useful references are provided later, in the section on the molecular interpretation of entropy.

Heat Capacity

It is found experimentally that different amounts of energy are required to change the temperature of the same mass of different substances by the same amount. The *heat capacity* of a substance is the quantity of energy required to raise the temperature of a specified amount of the substance by one kelvin. In thermodynamics, particularly when dealing with gases, it is necessary to distinguish between C_v, the heat capacity at constant volume, and C_p, the heat capacity at constant pressure.

Amount of a Substance

In chemical thermodynamics the *amount of a substance* is specified in *moles (mol).* One mole of any substance is the molecular weight of that substance expressed in grams. The molecular weight is simply the sum of the atomic weights of all the atoms in one molecule of the substance. The atomic weight is the ratio of the mass of that atom to the mass of an atom of the most common type of carbon atom, which has been assigned a mass of exactly 12 *unified atomic mass units (symbol u)*. One mole of a substance contains 6.022×10^{23} molecules. This enormous number

602,200,000,000,000,000,000,000

molecules per mole is called *Avogadro's Number.*

Thermodynamic Systems

Thermodynamics attempts to gain some understanding of the incredibly complex world by focusing attention on relatively simple aspects of it. In any thermodynamics experiment, whether done in the laboratory or in the imagination, the objects that are being studied are very carefully defined and are called the *system***.** Everything else in the world is called the *surroundings.* The system may interact with the surroundings, or it may be kept separate from the surroundings so that there is no interchange of matter or energy between it and the surroundings. The system is then said to be *isolated*. A system that cannot exchange matter with its surroundings, but that may exchange energy, is called a *closed* system. A system that can exchange both matter and energy with its surroundings is called an *open* system. The combination of system and surroundings is called the *universe*.

Thermodynamic States and State Functions

Having decided what the system of interest is, the next step is to describe it as completely, yet as concisely, as possible. The aim is that anyone given the description should be able to reproduce the system in all its relevant aspects. Thermodynamics does not concern itself with the molecular structure of matter, so the position and energy of all the individual molecules in the system are not relevant. That is just as well. On the molecular level, the world is in a state of constant change. If the position and energy of all the molecules in the system (*the microscopic state* of the system) could ever be described, the description would be correct only for an instant. It could be reproduced only by pure chance, and then only for an instant.

Thermodynamics deals only with those aspects of a system that can be measured by large-scale devices such as thermometers, measuring rods and pressure gauges. Such properties are called *macroscopic* properties. A complete description of the macroscopic properties of a system is called the *thermodynamic state* of the system. The thermodynamic state can be described by a relatively small number of properties, called *state functions*. State functions are *chosen* so that their values depend only on the thermodynamic state of the system and not on the path that was taken to reach that state. There are two sorts of state functions: *intensive functions*, such as temperature and pressure that do not depend on the amount of matter in the system; and *extensive functions,* such as mass and volume that depend on the amount of matter (number of moles) present. It is obvious that mass must be an extensive function. One can, however, imagine a system of fixed volume, into which any quantity of gas might be compressed. In such a system, volume would not be an extensive function, but a constant. For volume to be an extensive function, the *volume of the system must be variable*. Such systems are often modeled as a cylinder closed with a perfectly sealed, massless piston that offers no resistance to motion.

State functions are always indicated by capital letters, but not all quantities indicated by capital letters are state functions. A quantity indicated by a lower-case letter will not be a state function, and its value may depend on the path that was taken by the system to arrive at its present state.

The algebraic relationship between the state functions is called the *equation of state* of the system. An example is the *equation of state for a perfect (or ideal) gas.* A perfect gas is simply one in which the physical volume of the molecules is negligible in comparison to the volume of the gas, and in which forces between the molecules are negligible. The system to which the equation of state for a perfect gas applies is a fixed amount of perfect gas in a container of variable volume, such as a cylinder sealed with a perfect, frictionless, massless piston. The container is equipped with a thermometer and a pressure gauge. The volume can be calculated from the position of the piston. The equation of state is

$$PV = n\mathrm{R}T$$

P is the pressure in pascals, V is the volume in cubic meters, n is the number of moles of the gas, R is the *universal gas constant* (8.3143 joules per mole per kelvin) and T is the temperature in kelvin.

Each side of this equation can be expressed in units of energy:

- The left-hand side is the energy associated with the *mechanical* properties of the system:

$$PV = \text{newtons per meter}^2 \times \text{meter}^3$$

$$= \text{newton meters} = \text{joules}.$$

- The right hand side is the energy associated with the thermal properties:

$$n\mathrm{R}T = \text{number of moles} \times \text{joules per mole per kelvin} \times \text{kelvins}$$

$$= \text{joules}.$$

- The equation of state is simply the Law of Conservation of Energy applied to a perfect gas.

The equation indicates that for a fixed amount (n moles) of gas, there are only *two* properties that need to be specified. For example, if the pressure and the temperature are specified, the volume of the gas is fixed. This is a consequence of the Law of Conservation of Energy, as expressed in the equation of state.

The equation of state can be re-arranged to indicate how the volume varies with the other parameters.

- $V = \dfrac{nRT}{P} = nRT\left(\dfrac{1}{P}\right)$

  indicates that the volume (V) of a fixed amount (n moles) of gas at a constant temperature T is inversely proportional to the pressure P. This relationship was established experimentally in the 17th century and is known as *Boyle's Law.*

- $V = \dfrac{nRT}{P}$ also shows that the volume of a fixed amount (n moles) of gas at a fixed pressure P is proportional to the absolute temperature T. This relationship, also first established experimentally, is known as Charles' Law.

- Finally, $V = \dfrac{nRT}{P}$ shows that a fixed volume of any perfect gas under the same conditions of temperature and pressure contains the same number of moles, and hence the same number of molecules. This was first proposed by Avogadro, and is called Avogadro's hypothesis.

A great deal of information about the behavior of gases is summarized in the simple equation $PV = n\mathrm{R}T$.

Changes in State Functions

If a system undergoes a change from one thermodynamic state to another, the new state will, by definition, be described by a new set of values of the state functions. The values of the state function after the change will depend only on the properties of the new state. They will not be influenced in any way by any properties that the system might have had while it was in the process of undergoing the change. Many thermodynamic calculations deal with changes in state functions. Such changes are always calculated by subtracting the value of the initial state function from that of the final one. For example, for a temperature change from a starting temperature T_1 to a final temperature T_2 the change of temperature ΔT is given by

$$\Delta T = T_2 - T_1$$

The symbol Δ that indicates "change of" is the capital form of the Greek letter delta. The symbol *"*ΔT*"* is read "delta tee".

State Functions and Equilibrium

A system is in equilibrium when the values of the state functions are constant in all parts of the system. In other words, for a system at equilibrium

$$\Delta X = 0$$

where X is *any* state function. This is one definition of thermodynamic equilibrium.

Internal Energy and the First Law of Thermodynamics

So far, three state functions have been introduced. These are the temperature T, the volume V, and the pressure P. All of these can be measured easily. There are other state functions that are not measured directly. Such a state function is the *internal energy* of a system, denoted by the symbol U. This is the sum total of the energy, in whatever form, stored in a system. The total energy will obviously vary according to the amount of substance in the system, so internal energy is an extensive function. The absolute value of the internal energy of a system is not of concern to thermodynamics, but changes in internal energy are of central importance. Suppose a system undergoes a change in internal energy from an initial (unknown) value of U_1 joules to a final value (unknown) value of U_2 joules. Then the change in internal energy ΔU is

$$\Delta U = U_2 - U_1$$

This might not seem very useful, since U_2 and U_1 are both unknown. The equation is nothing more than another statement of the Law of Conservation of Energy. The change in internal energy ΔU represents the net energy that has come into the system from the surroundings or that the system has lost to the surroundings. For the purposes of this discussion, only two ways of a system exchanging energy with the surroundings are relevant. Energy can be transferred *mechanically*, as *work*, denoted by w. For example, if a gas expands against an external pressure, the gas does work. Energy can also be transferred as *heat*, denoted by q. The change in internal energy can now be written:

$$\Delta U = q - w$$

This states that the change in internal energy ΔU of a system is given by the heat q *absorbed by the system* minus the work w *done by the system* on its surroundings.

This statement, which is again a statement of the Law of Conservation of Energy, is the *First Law of Thermodynamics.*

Heat or work going *into* the system from the surroundings increases the internal energy of the system, and heat or work leaving the system *decreases* the internal energy.

Enthalpy

The four state functions introduced so far are the intensive functions temperature, T, and pressure, P, and the extensive functions volume, V, and internal energy U.

It is convenient to define another state function, called *enthalpy*, H. This is given by

$$H = U + PV$$

Notice that H has units of energy. Since U, P and V are all state functions, H is necessarily one as well. Notice, too, that U and V are extensive functions, and consequently H is also an extensive function. Since the purpose of state functions is to give the most concise description of a system, it might seem counterproductive to introduce another function that combines three others. Why use five when four would be enough?

The reason will emerge from the following discussion. The change in enthalpy when a system with an original enthalpy H_1 changes to a final enthalpy H_2 is given by

$$\begin{aligned} \Delta H &= H_2 - H_1 \\ &= U_2 + P_2V_2 - (U_1 + P_1V_1) \\ &= U_2 - U_1 + P_2V_2 - P_1V_1 \\ &= \Delta U + \Delta(PV) \\ &= q - w + \Delta(PV) \end{aligned}$$

Chemical reactions are often carried out in systems open to the atmosphere, that is, under conditions of constant pressure. Then,

$\Delta(PV) = P\Delta V$, and

$$\Delta H = q - w + P\Delta V$$

At constant pressure the work w done by the system on the surroundings is simply the pressure P multiplied by the change in volume ΔV.

$$w = P\Delta V$$

Therefore, at constant pressure,

$$\begin{aligned} \Delta H &= q - w + P\Delta V \\ &= q - P\Delta V + P\Delta V \\ &= q \end{aligned}$$

The change in enthalpy is a measure of the heat transferred between the system and the surroundings at conditions of constant pressure. This is what makes the enthalpy such a useful function in chemical thermodynamics. If the enthalpy change is positive, the system will absorb heat from the surroundings. An example is ammonium nitrate dissolving in water. Such a process is *endothermic* (heat taken in). If the enthalpy change is negative, the system will release heat into the surroundings. Such a process is *exothermic* (heat given out). An example is sodium hydroxide dissolving in water.

Thermochemistry

To find the heat emitted or absorbed in a chemical reaction at constant pressure, all that is required is the enthalpy change associated with that reaction. Enthalpy changes are very easily calculated from tables of *the standard enthalpy of formation* $\Delta H_f°$, of various substances (see Table 1 at end of this chapter). The superscript (°) indicates that the change in state function is calculated for reactants and products in their "standard states" (i.e., solid, liquid or gas) at "standard conditions" of pressure, usually one bar. Note that the superscript (°) does not imply any particular temperature. The temperature must be specified; the values in Table 1 are for 298.15 K.

Recall that enthalpy is an extensive property, that is, it is proportional to the amount of substance present. Recall, too, that only *changes* in enthalpy are relevant. For convenience, *the standard enthalpy of formation of the most stable form of any chemical element at a pressure of one bar and at a temperature of 298.15 K is given the value of zero joules per mole*. The standard enthalpy of formation of any compound that can be formed by direct reaction of the elements is then very easily obtained, at least in principle. Experimental details may well be quite difficult. All that is required is to measure the heat emitted or absorbed when a known amount of the compound is formed from the elements at 1 bar and 298.15 K. Since enthalpy is a state function, the intermediate values of temperature and pressure during the reaction are irrelevant. As long as the reactants start and the products end at 1 bar and 298.15 K, the heat emitted or absorbed will correspond to the change in enthalpy.

Hess' Law of Heat Summation

The fact that the enthalpy change in a chemical reaction does not depend on the path was first stated by G. H. Hess in 1840 and is often referred to as *Hess' Law*. Its usefulness can be illustrated by the classic example of how it can be used to calculate a quantity that would be impossible to measure experimentally: the standard enthalpy of formation of carbon monoxide.

$$C + \frac{1}{2} O_2 \rightarrow CO \qquad \Delta H° = x \text{ kJ/mol}$$

The *standard enthalpy of formation* of carbon dioxide is easily calculated from the *molar heat of combustion*, the heat released when one mole of carbon is burned in an excess of oxygen:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H° = –393.5 \text{ kJ/mol}$$

The same approach is not possible for carbon monoxide, because it is impossible to burn carbon in oxygen to produce only carbon monoxide.

Carbon monoxide can, however, be burned in excess oxygen to produce carbon dioxide:

$$CO + \frac{1}{2} O_2 \rightarrow CO_2 \qquad \Delta H° = –283.0 \text{ kJ/mol}$$

The combustion of carbon to carbon dioxide can now be *imagined* to take place in two steps:

Step 1:

$$C + \frac{1}{2} O_2 \rightarrow CO \qquad \Delta H° = x \text{ kJ/mol}$$

Step 2:

$$CO + \frac{1}{2} O_2 \rightarrow CO_2 \qquad \Delta H° = –283.0 \text{ kJ/mol}$$

By addition:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H° = (x – 283.0) \text{ kJ/mol}$$

For this reaction $\Delta H° = –393.5$ kJ/mol, so

$$(x – 283.0) \text{ kJ/mol} = –393.5 \text{ kJ/mol}$$

$$x = –393.5 \text{ kJ/mol} + 283.0 \text{ kJ/mol}$$

$$= –110.5 \text{ kJ/mol}$$

For the reaction to form carbon monoxide, then,

$$C + \frac{1}{2} O_2 \rightarrow CO \qquad \Delta H° = –110.5 \text{ kJ/mol}$$

Application to Pyrotechnics

As an example, consider the thermochemistry involved in a *flash powder* consisting of a mixture of powdered aluminium and potassium perchlorate.

Potassium perchlorate decomposes on heating to form potassium chloride and oxygen:

$$KClO_4 \rightarrow KCl + 2\,O_2$$

This reaction can be *imagined* to take part in two stages:

$$KClO_4 \rightarrow K + \tfrac{1}{2}\,Cl_2 + 2\,O_2$$

$$K + \tfrac{1}{2}\,Cl_2 \rightarrow KCl$$

Of course the reaction certainly does not take place by these two steps. The enthalpy of the reaction must, however, equal the sum of the enthalpy changes of these two reactions. The enthalpy changes of these reactions can be obtained from tables of thermochemical data, such as Table 1.

The first reaction is the decomposition of one mole of potassium perchlorate into its elements. The enthalpy change is, therefore, *minus* the standard enthalpy of formation of potassium perchlorate, –(–433 kJ/mol) = 433 kJ/mol.

The second reaction is the formation of one mole of potassium chloride from its elements, and the enthalpy change is the standard enthalpy of formation of potassium chloride, –437 kJ/mol.

The total enthalpy change for the decomposition of one mole of potassium perchlorate is the sum of these two enthalpy changes:

$$KClO_4 \rightarrow K + \tfrac{1}{2}\,Cl_2 + 2\,O_2 \qquad \Delta H° = 433 \text{ kJ/mol}$$

$$K + \tfrac{1}{2}\,Cl_2 \rightarrow KCl \qquad \Delta H° = –437 \text{ kJ/mol}$$

$$KClO_4 \rightarrow KCl + 2\,O_2 \qquad \Delta H° = –7 \text{ kJ/mol}$$

The decomposition of one mole of potassium perchlorate releases 7 kilojoules of heat.

Now consider the combustion of aluminium in oxygen to form one mole of aluminium oxide:

$$2\,Al + 3/2\,O_2 \rightarrow Al_2O_3 \qquad \Delta H° = –1676 \text{ kJ/mol}$$

The enthalpy change for this reaction is, of course, the standard enthalpy of formation of aluminium oxide.

The net reaction of aluminium with potassium perchlorate in flash powder is

$$3\,KClO_4 + 8\,Al \rightarrow 3\,KCl + 4\,Al_2O_3$$

This can be imagined as taking place in two steps:

Step 1: decomposition of three moles of potassium perchlorate:

$$3 \times (KClO_4 \rightarrow KCl + 2\,O_2 \qquad \Delta H° = –7 \text{ kJ/mol})$$

or

$$3\,KClO_4 \rightarrow 3\,KCl + 6\,O_2 \qquad \Delta H° = –21 \text{ kJ}$$

and

Step 2: Combustion of aluminium in oxygen to form four moles of aluminium oxide:

$$4 \times (2\,Al + 3/2\,O_2 \rightarrow Al_2O_3 \qquad \Delta H° = –1676 \text{ kJ/mol})$$

or

$$8\,Al + 6\,O_2 \rightarrow 4\,Al_2O_3 \qquad \Delta H° = –\,6704 \text{ kJ}$$

The total enthalpy change for the reaction is the sum of the enthalpy changes for the two steps:

$$3\,KClO_4 \rightarrow 3\,KCl + 6\,O_2 \qquad \Delta H° = –21\text{kJ}$$

$$8\,Al + 6\,O_2 \rightarrow 4\,Al_2O_3 \qquad \Delta H° = –\,6704 \text{ kJ}$$

$$3\,KClO_4 + 8\,Al \rightarrow 3\,KCl + 4\,Al_2O_3 \qquad \Delta H° = –\,6725 \text{ kJ}$$

The reaction of three moles of potassium perchlorate with eight moles of aluminium releases 6725 kilojoules of heat.

It is useful to convert the units of measure of the amounts of the chemicals from moles to grams, because pyrotechnic mixtures are not usually specified in moles.

One mole of aluminium weighs 26.98 grams, and one mole of potassium perchlorate weighs 138.55 grams. These values are obtained from the formula weights of these materials, listed in Table 1.

Three moles of potassium perchlorate weigh

$$3 \times 138.55\ \text{g} = 415.65\ \text{g}$$

Eight moles of aluminium weigh

$$8 \times 26.98\ \text{g} = 215.84\ \text{g}$$

Three moles of potassium perchlorate plus eight moles of aluminium weigh

$$(415.65 + 215.84)\ \text{g} = 631.49\ \text{g}$$

This quantity of mixture releases 6725 kilojoules, so the heat released per gram is:

$$\frac{6716\ \text{kJ}}{631.49\ \text{g}} = 10.69\ \text{kJ/g}$$

The percentage composition of this mixture is:

potassium perchlorate:

$$\frac{415.65\ \text{g}}{631.49\ \text{g}} \times 100\% = 65.8\%$$

aluminium:

$$\frac{215.84\ \text{g}}{631.49\ \text{g}} \times 100\% = 34.2\%$$

Lancaster[1] quotes two mixtures for European style flash composition. One of these (66% potassium perchlorate and 34% aluminium) is almost identical to the mixture just discussed.

Such a mixture, in which the ratio of the components is exactly as required for the balanced chemical reaction, is called a *stoichiometric* mixture.

Lancaster[1] also lists some flash mixtures that contain sulfur. One of the mixtures he quotes is 67% potassium perchlorate, 17% aluminium and 16% sulfur. It is instructive to calculate the heat output of this composition.

First, the percentage by weight is converted to moles per 100 grams, by dividing the percentage of each component by its formula weight:

potassium perchlorate:

$$\frac{67.00}{138.55} = 0.4836\ \text{mol/100 g}$$

aluminium:

$$\frac{17.00}{26.98} = 0.6301\ \text{mol/100 g}$$

sulfur:

$$\frac{16.00}{32.06} = 0.4991\ \text{mol/100 g}$$

From the previous discussion, every eight moles of aluminium require three moles of potassium perchlorate. To find the amount of potassium perchlorate needed to burn the aluminium, divide the number of moles of aluminium by 8 and multiply by 3.

Amount of potassium perchlorate required to burn the aluminium:

$$\frac{0.6301}{8} \times 3 = 0.2363\ \text{mol}$$

Amount left to burn the sulfur:

$$0.4836 - 0.2363 = 0.2473\ \text{mol}$$

From the reaction

$$KClO_4 \rightarrow KCl + 2\ O_2$$

each mole of potassium perchlorate releases two moles of oxygen. The 0.2473 moles of potassium perchlorate left after burning the aluminium therefore release $2 \times 0.2473 = 0.4946$ moles of oxygen. This is available to burn the 0.499 moles of sulfur. The ratio of oxygen to sulfur is

$$\frac{0.4946}{0.4991} = 0.991$$

which is very close to 1. The chemical equation for the burning of sulfur in oxygen is

$$S + O_2 \rightarrow SO_2$$

with a ratio of one mole of oxygen to one mole of sulfur. This composition is therefore very close indeed to having exactly enough potassium perchlorate to burn the aluminium and sulfur to their oxides. It is another example of a stoichiometric mixture.

The heat released when aluminium burns with a stoichiometric quantity of potassium perchlorate has already been shown to be 10.69 kJ/g. It now remains to calculate the heat released when sulfur burns with a stoichiometric quantity of potassium perchlorate. The reaction for the decomposition of potassium perchlorate has already been discussed:

$$KClO_4 \rightarrow KCl + 2\ O_2 \qquad \Delta H^\circ = -7\ \text{kJ/mol}$$

The burning of sulfur to sulfur dioxide

$S + O_2 \rightarrow SO_2$

is the formation of one mole of sulfur dioxide from its elements, so the enthalpy change is the standard enthalpy of formation of sulfur dioxide, which from Table 1 is –297 kJ/mol.

The total reaction can be thought of as proceeding as follows:

Step 1: Decomposition of half a mole of potassium perchlorate to release a mole of oxygen:

$$\tfrac{1}{2} \times (KClO_4 \rightarrow KCl + 2\,O_2 \qquad \Delta H° = -7\text{ kJ/mol})$$

or

$$\tfrac{1}{2}\,KClO_4 \rightarrow \tfrac{1}{2}\,KCl + O_2 \qquad \Delta H° = -3.5\text{ kJ}$$

Step 2: Combustion of one mole of sulfur in one mole of oxygen to form one mole of sulfur dioxide:

$$S + O_2 \rightarrow SO_2 \qquad \Delta H° = -297\text{ kJ}$$

The total enthalpy change for the reaction is the sum of the enthalpy changes for the two steps:

$$\tfrac{1}{2}\,KClO_4 \rightarrow \tfrac{1}{2}\,KCl + O_2 \qquad \Delta H° = -3.5\text{ kJ}$$

$$S + O_2 \rightarrow SO_2 \qquad \Delta H° = -297\text{ kJ}$$

$$\tfrac{1}{2}\,KClO_4 + S \rightarrow \tfrac{1}{2}\,KCl + SO_2 \qquad \Delta H° = -300\text{ kJ}$$

The next step is to convert the units from moles to grams. Half a mole of potassium perchlorate weighs

$$\tfrac{1}{2} \times 138.55\text{ g} = 69.275\text{ g}$$

One mole of sulfur weighs 32.06 grams. Half a mole of potassium perchlorate plus one mole of sulfur weighs

$$(69.275 + 32.06)\text{ g} = 101.34\text{ g}$$

This quantity of mixture releases 300.5 kilojoules, so the heat released per gram is:

$$\frac{300.5}{101.34} = 2.965\text{ kJ/g}$$

One hundred grams of the original mixture can be thought of as being made up of two stoichiometric mixtures:

Mixture A: A mixture of 17.00 grams (0.6301 moles) of aluminium with the stoichiometric amount of potassium perchlorate (0.2363 moles or 32.74 grams). Total amount of mixture A:

$$17.00 + 32.74 = 49.74\text{ g}$$

Mixture B: A mixture of 16.00 grams (0.499 moles) of sulfur with the stoichiometric amount of potassium perchlorate (0.2495 moles or 34.57 grams). Total amount of mixture B:

$$16.00 + 34.57 = 50.57\text{ g}$$

Total (Mixture A + Mixture B) = (49.74 + 50.57) grams = 100.31 grams per 100 grams. The mixture is clearly very close to a 50:50 mix of mixtures A and B. The heat output per gram is therefore:

$$\begin{aligned}&\tfrac{1}{2}\text{ heat output per gram Mixture A} + \\ &\quad \tfrac{1}{2}\text{ heat output per gram Mixture B}\\ &= \tfrac{1}{2}\,(10.69\text{ kJ/g}) + \tfrac{1}{2}\,(2.965\text{ kJ/g})\\ &= (5.345 + 1.483)\text{ kJ/g}\\ &= 6.828\text{ kJ/g}\end{aligned}$$

The heat output per gram of the flash mix containing sulfur is 6.828 kJ/g, while that of the mix containing no sulfur is 10.69 kJ/g.

This shows that the heat output is only one aspect of a pyrotechnic mixture. Another very important factor is the speed or rate of the reaction. While adding sulfur to the flash mix reduces the heat output, it might (and the evidence is that it does) increase the rate of the reaction. A discussion of how this might be so is outside the scope of this discussion, as it relates to chemical kinetics, not thermodynamics.

Another relevant difference between the two mixtures is that the one with no sulfur generates products that are solids at room temperature. The conversion of these to liquids and/or gases at the temperature of the reaction absorbs large amounts of heat. The only way that the reaction can do mechanical work is by the heat of the reaction causing the expansion of a gas. This gas can include vaporized products (if there is sufficient heat to vaporize them) and the surrounding air that gets raised to high temperatures by the heat released in the reaction.

Suppose one gram of each mixture is ignited in a closed container of fixed volume V. An estimate of the maximum pressure reached in the container can be obtained from the equation $PV = nRT$. This gives the pressure as

$$P = \frac{nRT}{V}$$

For a fixed volume V this equation predicts that the pressure will be proportional to the temperature T and to the number of moles of gas n.

For the mixture of aluminium and potassium perchlorate, the chemical equation

$$3\ KClO_4 + 8\ Al \rightarrow 3\ KCl + 4\ Al_2O_3$$

shows that three moles of potassium perchlorate react with eight moles of aluminium to produce three moles of potassium chloride plus four moles of aluminium oxide. Potassium chloride boils at 1437 K at atmospheric pressure, while aluminium oxide does not boil until 2950 K. The procedure for calculating the maximum temperature in a reaction will be explained in a later section. For the moment, it can be assumed that the temperature of the reaction is sufficient to vaporize the potassium chloride but not the aluminium oxide. From the equation, three moles of potassium perchlorate react with eight moles of aluminium to produce three moles of potassium chloride vapor. As shown previously, three moles of potassium perchlorate and eight moles of aluminium correspond to 613.48 grams of mixture. The amount of potassium chloride vapor produced by one gram of mixture is therefore

$$\frac{3}{613.48}\ \text{mol/g} = 4.89 \times 10^{-3}\ \text{mol/g}$$

Now, for the reaction of sulfur and potassium perchlorate

$$½\ KClO_4 + S \rightarrow ½\ KCl + SO_2$$

it has been shown previously that one-half a mole of potassium perchlorate and one mole of sulfur corresponds to 101.34 grams of mixture. The amount of potassium chloride produced is therefore

$$\frac{1/2}{101.34} = 4.93 \times 10^{-3}\ \text{mol/g}$$

The amount of sulfur dioxide produced is

$$\frac{1}{101.34} = 9.86 \times 10^{-3}\ \text{mol/g}$$

As shown previously, the aluminium/sulfur/potassium perchlorate flash mixture was close to one part by weight of the aluminium/potassium perchlorate mixture and one part by weight of the sulfur/potassium perchlorate mixture.

The aluminium/potassium perchlorate mixture produces 4.89×10^{-3} moles of potassium chloride per gram. Half a gram of this mixture will contribute 2.445×10^{-3} moles of potassium chloride to the reaction products.

The sulfur/potassium perchlorate mixture produces 4.93×10^{-3} moles of potassium chloride per gram. Half a gram of this mixture will contribute 2.465×10^{-3} moles of potassium chloride to the reaction products. The total amount of potassium chloride produced per gram of mixture is therefore

$$(2.445 + 2.465) \times 10^{-3}\ \text{moles} = 4.91 \times 10^{-3}\ \text{moles.}$$

This is very similar to the amount of potassium chloride (4.89×10^{-3} moles) produced by one gram of the aluminium/potassium perchlorate mix. However the sulfur/potassium perchlorate mix also generates 9.86×10^{-3} moles of sulfur dioxide per gram of mixture. Half a gram of mixture will therefore contribute 4.93×10^{-3} moles of sulfur dioxide to the reaction products. The total number of moles of gas at the temperature of reaction is 4.91×10^{-3} moles (KCl) plus 4.93×10^{-3} moles (SO_2) = 9.84×10^{-3} moles of gas per gram of mixture. This is close to twice the number of moles of gaseous products formed by the aluminium/potassium perchlorate mixture. So, while the mixture that contains sulfur produces less heat per gram, it produces much more gas per gram.

An estimation of the total pressure produced by the same mass of each mixture in a fixed volume would require an estimation of the maximum temperature. At the maximum temperature reached in these highly exothermic reactions the reaction products would not be the same as the final products at room temperature, so the preceding discussion of the amount of gas is at best a very rough approximation. A more realistic analysis would require thermodynamic modeling of the reactions on a computer, to be discussed later.

It is worth emphasizing that the enthalpy of a reaction depends only on the reactants and products and not on the path taken to go from one to the other. Consequently the possible formation of aluminium sulfide by reaction of the sulfur and aluminium can contribute nothing to the enthalpy of the reaction. While the reaction of aluminium and sulfur is indeed highly exothermic:

$$2\ \mathrm{Al} + 3\ \mathrm{S} \rightarrow \mathrm{Al_2S_3} \qquad \Delta H^\circ = -724\ \mathrm{kJ/mol}$$

the heat released in this reaction would be exactly balanced by the heat absorbed when the aluminium sulfide was (conceptually, if not in reality) broken down into its elements before they were oxidized to form aluminium oxide and sulfur dioxide.

Effect of Temperature on the Enthalpy

Tables of standard enthalpies of formation usually list values at 298.15 K (25 ºC).[2,3] Barin's tables[4] list enthalpies of formation at intervals of 100 K, so it is easy to calculate enthalpy changes at any desired temperature in the range listed.

It is useful to understand how enthalpy changes for reactions at other temperatures can be calculated from the standard enthalpies of formation of the reactants and products at 298.15 K.

Suppose you wanted to calculate the enthalpy change for some reaction at 500 K:

Reactants at 500 K → Products at 500 K

From tables, you have the enthalpy change for the reaction at 298.15 K.

Step 1. Imagine the reactants at 500 K are brought to 298.15 K; then calculate the enthalpy change for this process. For the simplest cases, this will be the heat capacity at constant pressure of the reactants multiplied by the temperature change. This is complicated by the fact that the heat capacity varies with temperature; formulas are available for some materials that give the heat capacity as a function of temperature. If one or more of the reactants undergoes a phase change (melts, for example) over the temperature range of interest, the enthalpy change for that process must also be included.

Step 2. Imagine that the reaction takes place at 298.15 K and that it forms products at that temperature. Calculate the enthalpy change from tables.

Step 3. Imagine that the products at 298.15 K are heated to 500 K. The enthalpy change for this process is at least the heat capacities at constant pressure of the products multiplied by the temperature change. Again, it is necessary to account for the variation of heat capacity of each substance with temperature. The enthalpy changes associated with any melting or vaporization of the products must also be included.

The enthalpy change for the reaction at 500 K is simply the sum of the enthalpy changes for steps 1, 2 and 3.

For reactions with large enthalpy changes, the contributions of steps 1 and 3 can be small compared with that of step 2. In such cases, and for relatively small temperature changes, the enthalpy change of the reaction will vary to only a small extent with temperature.

Spontaneous Processes

In chemical thermodynamics a "spontaneous" process means one that will continue to equilibrium *once it has been started*, without further input of external work. This is different from the usage in ordinary speech, where something is said to be "spontaneous" if it happens "of its own accord". The reaction of aluminium with hydrochloric acid is spontaneous in both the conventional and the thermodynamic senses. The reaction between aluminium and potassium perchlorate is spontaneous in the thermodynamic sense, but not in the conventional. The reasons why many thermodynamically spontaneous processes are not spontaneous in the conventional sense are dealt with by *chemical kinetics*.

A New State Function: Entropy

The First Law summarizes the experience of many generations of scientists and engineers that energy cannot be created or destroyed, but is merely *transferred* in one form or another. If you watch a movie that is being run in reverse, you will see examples of energy being transferred in ways that are completely consistent with the First Law, but which never happen in the real world. Something that could happen in such a movie, but not in the real world, would be a balloon inflating by itself as air rushes into it from the room. A block of ice might emerge from a bucket of hot water, with the water coming to the boil as the ice freezes. Neither one of these processes conflicts with the First Law, but neither has ever been observed. There is clearly a preferred direction of change in the real world.

In the real world, gas at high pressure will spontaneously flow to a region of low pressure, until the pressure in both regions is the same. A cold object and a hot object in contact will come to an intermediate temperature. In each case, the system has come to equilibrium. It has also lost the ability to perform work. A system with gas at different pressures could do work through a fan or turbine placed between the two regions. A system with two bodies at different temperatures could do work through a heat engine placed between the two bodies. In coming to equilibrium*, the system has lost the ability to do work, but the internal energy of the system has not changed*. No work has been done, and no heat has been exchanged with the surroundings, so the internal energy must be the same. Energy that was once available to do work has somehow become unavailable as the system has come to equilibrium.

In the examples just given, at the beginning of the process, a thermodynamic state function was different in various parts of the system. In one case, the pressure was different. In another, the temperature was different. To reach equilibrium, the system changed in such a way that the state functions became equal in all parts of the system. This leads to an important question. Is there a state function that can be used to indicate whether or not a *chemical* system is in thermodynamic equilibrium? Clearly pressure and temperature will not suffice. A mixture of potassium perchlorate and powdered aluminium might well be at uniform temperature and pressure, but it is certainly very far from a state of thermodynamic equilibrium. A new state function is needed. To arrive at it, however, requires a measure of the loss of ability to perform work that accompanied the attainment of equilibrium in the two simple examples just discussed.

In the nineteenth century Clausius[2a] introduced a thermodynamic state function called *entropy* (symbol S) that provides just such a measure. The word comes from a Greek word meaning “transformation” or “change”.

Recall that for any process the change in internal energy is

$$\Delta U = q - w$$

where ΔU is the change in the internal energy of the system, q is the heat absorbed by the system and w is the work done by the system.

Recall, too, that the *maximum* work done by a system in coming to equilibrium is w_{rev}, the work that is done when equilibrium is reached in a *reversible* process. A reversible, or *quasistatic,* process is one in which all change takes place infinitely slowly, so that the system is in equilibrium at each step in the process. The concept of a reversible process is important because it allows powerful mathematical tools (the calculus) to be applied to problems that would otherwise be extremely difficult or impossible to model mathematically. For the present discussion, the important point is that the work done and the heat absorbed, in the reversible process taking a system from one state to another, is the *maximum* possible for that change in internal energy.

For each very small step in a reversible process, the First Law of thermodynamics becomes

$$\mathrm{d}U = \mathrm{d}q_{rev} - \mathrm{d}w_{rev}$$

The symbol “d” can be taken to mean “an extremely small change in”.

The heat absorbed by the system ($\mathrm{d}q_{rev}$) during this very small change was absorbed at a particular temperature T. Because $\mathrm{d}q_{rev}$ is extremely small, T can be taken as constant over the time taken for the change. The ratio $\mathrm{d}q_{rev}/T$, taken at every step during a change from a first state 1 to a second state 2 leads to a new state function called the *entropy***.** The change in entropy ΔS is *defined* by

$$\Delta S = S_2 - S_1 = \int_1^2 \mathrm{d}\frac{q_{rev}}{T}$$

The integral sign $\int$ (an elongated "S") in this equation is simply an instruction to add up ("sum") the quantities that follow. Stated in words, the right hand side of the equation means "the sum of the ratio $\mathrm{d}q_{rev}/T$ for every step in the process, starting at State 1 and ending at State 2".

The direction of change in the physical world can be predicted from the entropy change. Change will always occur in such a way that the *entropy of the universe increases*. This is one way of expressing the *Second Law of Thermodynamics.* Recall that in thermodynamics the word "universe" means the system of interest plus its surroundings, and that the system and its surroundings are assumed to be totally isolated from external influences. A thermodynamic "universe" could be, for example, a piece of experimental apparatus enclosed in a perfectly insulated box.

Molecular Interpretation of Entropy

The entropy, as introduced in classical thermodynamics, is a rather abstract concept. It is not obvious why the ratio of heat absorbed in a reversible process to the temperature at which the absorption occurs should be associated with the direction of change in the physical world. The situation becomes completely different when we think about what the molecules are doing. It is then possible to express the Second Law very crudely, but accurately, as "moving molecules get into a mess".

The Natural Tendency To Get into a Mess

It is a matter of personal experience that there is a natural tendency for things to get into a mess.

Everybody knows how difficult it is to keep a kitchen or workshop tidy. Unless you take care to put everything back where it belongs, the place soon gets messed up. Why? Simply because there are *millions upon millions* of ways of putting things in a room that make it look a mess, but *relatively few* ways of arranging things that make it look tidy. That is consistent with the old adage "a place for everything, and everything in its place". According to that rule, there is only *one* arrangement of things that is consistent with the room being tidy. At the other extreme, who could say how many ways there are of putting things in a room that would make the room look untidy?

Sometimes an untidy room is described as "disordered". In thermodynamics "disorder" has a particular technical meaning that is consistent with the common usage of the word but is more rigorously defined. The amount of disorder (in the thermodynamic sense) associated with a particular state of a room is simply an indication of how many ways of arranging things in the room are consistent with that state. For example, the state described by "a perfectly tidy room" might be consistent with just one possible arrangement; the "degree of disorder" of "a perfectly tidy room" is low; indeed, it could be no lower. At the other extreme, because the description "a very untidy room" would be consistent with countless possible arrangements, the degree of disorder of "a very untidy room" is very high.

Messiness among the Molecules

Go into a tidy room, pick something up, and then put it down without thinking about where you are putting it, and chances are that it will not land in a place that will make the room tidy. Do that with two or three or more things, and the degree of disorder begins to increase significantly.

Exactly the same sort of thing happens on the molecular scale. With molecules, however, it is necessary to think of different *velocities* as well as different *positions*. To begin with, it's useful to imagine what would happen if molecules had no tendency whatsoever to stick to each other. At a given temperature (room temperature, for example) such molecules would be continually jostling around, incessantly colliding with each other and rebounding to collide over and over again. Left to themselves, they would spontaneously distribute themselves over a vast number of different arrangements of position and velocity. This is the same as saying that a collection of these imaginary molecules would naturally get into a state of disorder. Having no inherent stickiness, they would have no impediment to getting themselves well and truly mixed up. They would be in that chaotic state that we call a *gas*.

The Effect of Temperature on Molecular Disorder

What would happen if the temperature were to increase? Recall the Equation of State of a Perfect Gas. If the pressure were constant, the gas would expand. More space would be available for the molecules to move around, and they could take up even more different arrangements of their positions. What about their velocities? Obviously, if temperature is a measure of the average molecular kinetic energy, and kinetic energy is proportional to the square of the velocity, the average velocity of the molecules would be greater at the higher temperature. Detailed analysis of the behavior of large collections of randomly colliding molecules[3a] shows that the molecules can have a huge range of velocities, and the way in which they distribute themselves over that range depends on the temperature. At low temperatures most molecules have velocities that are rather close to the average velocity. At high temperatures the distribution of velocities is much broader, with more molecules having velocities very different from the average. A proper treatment of the relationship between molecular velocity and temperature[3b,5] is beyond the scope of this discussion. The important point is that an *increase in temperature* means an increase in the *spread of molecular velocities* and consequently an *increase in disorder*.[6]

Attractions between Mixing Molecules

So far, the molecules have been imagined to have no tendency to stick to each other. They would spontaneously mix themselves into a state of disorder by their random motion. A world made of such molecules would be completely disordered on the molecular level but completely uniform on the large scale. It would be a very dull place. Fortunately, real molecules always have a tendency to stick together because of attractive forces arising from electrostatic interactions. If molecules have opposite electrical charges, as for example gaseous sodium and chloride ions (Na^+ and Cl^-) these attractive forces can be very strong indeed. Even the most simple and symmetrical molecules (atoms of helium or argon, for example) have a slight tendency to stick together. The distribution of electrons in each atom is continually changing, and when the atoms are very close, the electrons in each atom come under the influence of the nuclear charge of the other. This results in a small attractive force between the atoms.

These attractive forces make a great difference to the behavior of atoms and molecules at low temperatures. Imagine a collection of atoms, all of the same kind, with each atom having a rather high average kinetic energy. For example, this could be a quantity of argon gas in a container at room temperature. The atoms are continually colliding; as they collide, they have a slight tendency to stick together. The attractive force is very weak, however, and at high temperatures is negligible. Now suppose that the sample of argon is cooled by some sort of refrigerator, to the point where the average kinetic energy of the atoms is so low that colliding atoms can start to stick together and form clumps. If the temperature is low enough, some of the gas will condense into a *liquid*. A more ordered state of matter (liquid) has spontaneously appeared from a more disordered one (gas).

Order Here, Disorder There

It seems that cooling the gas has made the world a more orderly place. This conclusion would seem even more valid if the cooling process were to continue to the point where all the argon condensed to a crystalline solid, with the atoms neatly arranged in a beautifully regular array. That is certainly a more ordered arrangement of atoms than the original chaotic swarm of atoms filling the whole container. There is no doubt that the degree of molecular disorder in the container has been reduced.

In thermodynamics, however, what happens in the container is only part of the story. What about the surroundings? Recall that the sample of gas was originally at room temperature, and a refrigerator was used to cool it. For argument's sake, the refrigerator can be assumed to be perfectly efficient: it simply takes a quantity of energy from the gas, and dumps it into the outside world. On the molecular level, this means that the molecules of the outside world can now move more rapidly and are therefore able to become even more disordered.

As will be shown later, the increase in molecular disorder in the outside world must at the very least equal the decrease in molecular disorder that happened when the gas condensed into a liquid, or when the liquid condensed into a solid. Because of the natural tendency of randomly moving molecules to get mixed up, *the entire physical world tends to become more disordered on the molecular scale*. Parts of the world can be made very orderly, but the ordering process inevitably results in some other part of the world becoming even more disordered.

To return to the example of the untidy room, imagine you are in a small room that is so full of stuff that you are up to your elbows in objects. You try to tidy the room, but as you pick up things and put them where they need to go, your movements stir up all the objects around you, and they get into more of a mess than they were originally. In a room, and in the world at large, there is no way around the fact that objects moved at random are inevitably going to end up in a mess.

It must be admitted, of course, that continuous random rearrangement of a set of objects does have some chance of putting the objects into one of the rare orderly arrangements. That chance would be greater if there were only a few objects being moved around, but even then the objects would remain ordered for only an instant. As the number of objects increases, the number of possible arrangements increases tremendously, and the fraction of time that the objects spend in orderly arrangements becomes completely insignificant compared to the time that they spend in disordered arrangements.

The statement that the world becomes more disordered on the molecular scale is another way of stating the Second Law of Thermodynamics.

The Consequences of Molecular Disorder

What are the consequences of this tendency to disorder? To answer this, it is necessary to look at how molecular disorder shows itself in the everyday world. All substances and systems have their own characteristic properties, which can stay the same only if the positions and velocities of the molecules that make up the substance or system are restricted to a certain range. If that range is reduced or exceeded, the properties of the substance or system will change. For example, the molecules of a crystalline solid must remain arranged in a regular array if the crystal is to retain its hardness and rigidity. To remain in a regular array, the molecules can have only a rather restricted range of positions and velocities.

The degree of disorder depends on the number of possible combinations of position and velocity that are available to the molecules. A substance (or system) has a low degree of molecular disorder if the molecules that make it up can arrange themselves over only a relatively restricted number of positions and velocities. The degree of disorder in a crystalline solid is therefore low. In a liquid, the molecules can distribute themselves over a much greater range of positions and velocities than they can in a crystalline solid. The degree of disorder of a liquid is therefore higher than that of a crystalline solid. The molecules in a gas can spread themselves over a vast range of positions and velocities. The degree of disorder in a gas is very high.

The natural tendency towards molecular disorder would suggest that a crystalline solid should spontaneously melt, and the liquid should then evaporate and turn into a gas. This certainly happens, but only if the temperature is sufficiently high. Energy has to be absorbed from the surroundings to overcome the forces that hold the molecules together in the solid. The loss of that energy from the surroundings reduces the molecular disorder there. The solid cannot melt until the increase in disorder resulting from its melting at least equals the decrease in disorder in the outside world that comes about by the transfer of energy from the outside to the melting solid.

How something changes, or whether it changes at all, is constrained by two factors: *the total amount of energy in the universe must stay the same*, and *the total amount of molecular disorder in the universe must increase*. The first of these constraints is a statement of the First Law of Thermodynamics, while the second is a statement of the Second Law. The Second Law was previously stated as the *entropy of the universe increases*. This implies that the *entropy is a measure of the amount of molecular disorder*.

The Relationship between Entropy and Molecular Disorder

Recall that in thermodynamics, the disorder of a system is simply the number of molecular arrangements that are consistent with the properties of that system. This number is sometimes called the thermodynamic probability of the system, and is given the symbol W.

In the nineteenth century Ludwig Boltzmann[3c] showed that the entropy S of a system is given by

$$S = k \ln W$$

where k is a constant (Boltzmann's constant, 1.381×10^{-23} joules per kelvin), and $\ln W$ is the *natural logarithm* of W (The natural logarithm of any number x is defined as follows: if $x = e^y$, where e is the number 2.71828…, then $y = \ln x$).

A Justification of the Entropy Formula

A properly detailed discussion of the mathematical relationship between entropy and molecular disorder[5] is beyond the scope of this chapter. Nonetheless, it is worth offering a brief justification of the formula for the *change* in entropy.

According to this formula, the entropy change ΔS for a reversible process at constant temperature, such as the melting of ice at 273 kelvin at a pressure of 1 bar, is given by

$$\Delta S = \frac{q}{T}$$

where q is the heat absorbed and T is the absolute temperature.

It is easy to see that the absorption of heat would increase molecular disorder, because the extra energy would help to overcome attractive forces that tend to keep molecules close together. Even when attractive forces are negligible, the addition of extra energy gives molecules a broader range of velocities and this makes the system more disordered.

Why is the absorbed heat divided by the absolute temperature? That implies that the same amount of energy produces a greater change in the disorder of a collection of molecules at a low temperature than it does at a higher temperature. Does that seem reasonable? Recall that collections of molecules become more *disordered* as the temperature increases. The same amount of disruption (i.e., added energy) produces a greater *change* in the degree of disorder in a group of molecules that was *less* disordered to start with than it does in one that was more disordered. The analogy with a tidy room is useful. Imagine that you go into a perfectly neat and tidy room, and you throw ten objects about and leave them where they fall. Is it obvious how the state of order in the room has changed? Now go into a really untidy room and do exactly the same thing. Pick up ten objects at random, throw them into the air and leave them where they fall. Are you aware of much difference in the tidiness of the room? The change in orderliness produced by the same amount of disruption (i.e., randomly changing the positions of ten objects) is clearly much greater in a tidy room than in a room that was already in a mess.

It has already been stated that entropy is a state function; that is, its value does not depend on the path that was taken to arrive at the final state. That makes sense, given that entropy is basically a measure of how many arrangements of molecules are consistent with the properties of the system. A system is characterized by a particular set of state functions, all of which are independent of the path taken to get to that state. Only a certain number of arrangements of molecules is consistent with that set of state functions; there is no reason to think that that number is in any way dependent on the way in which the system came to have that particular set of state functions.

Now, temperature is also a state function, but the heat absorbed is not. The heat absorbed by a system in going from one state to another is not well defined at all. It depends on how much work was done in the process, and this clearly depends on the path taken. However, imagine that the change from one state to another is carried out infinitely slowly, in other words, it is carried out *reversibly.* Then the amount of heat absorbed is well defined and is the maximum that is consistent with the change in internal energy. The proper definition of the entropy change is therefore

$$\Delta S = \frac{q_{rev}}{T}$$

What happens if the temperature is not constant during the change from one state to the next? In such a case, the process must be thought of as taking place in very small steps. The tiny amount of heat absorbed reversibly by the system during this very small step is $\mathrm{d}q_{rev}$. The temperature at each step is effectively constant for that step. The value of q_{rev}/T is calculated for each step, and then all the values are added to give the entropy change. This is written as

$$\Delta S = \int_1^2 \frac{\mathrm{d}\,q_{rev}}{T}$$

This, of course, is the formula presented in a previous section as the definition of the entropy change that takes place when a system in one state (state 1) changes to another state (state 2).

Entropy Changes in Reversible Processes at Constant Temperature

It is useful to think about entropy changes taking place at a constant temperature. This can be done if the surroundings are imagined to be some sort of huge thermostat, kept at the same temperature *T*.

In a reversible process, the entropy change *in the system* is given by

$$\Delta S_{system} = \frac{q_{rev}}{T}$$

The heat absorbed came from the surroundings, so the heat "absorbed" by the surroundings is $-q_{rev}$ (the negative sign mean that heat is lost by the surroundings) and the entropy change *in the surroundings* is

$$\Delta S_{surroundings} = \frac{-q_{rev}}{T}$$

The entropy change in the universe is the sum of the entropy changes in the system and the surroundings:

$$\begin{aligned}\Delta S_{universe} &= \Delta S_{system} + \Delta S_{surroundings} \\ &= \frac{q_{rev}}{T} - \frac{q_{rev}}{T} \\ &= 0\end{aligned}$$

The entropy change in the universe in a reversible process at constant temperature is therefore zero. This is consistent with the definition of a reversible process as one in which the system and its surroundings are always in equilibrium. Recall that for a system in equilibrium, the change in *any* state function is zero.

Entropy Changes in Real Processes

Real processes, except those in very carefully controlled electrochemical cells, occur irreversibly. The entropy changes are easily calculated if we imagine that the surroundings are at a constant temperature *T*, as in the previous example. First, consider the entropy change in the system. Entropy is a state function, so the entropy change in the system is exactly the same as it would have been if the change had been carried out reversibly.

$$\Delta S_{system} = \frac{q_{rev}}{T}$$

The heat absorbed in the real process, however, would have been *less* than q_{rev}. This is because q_{rev} is the maximum amount of heat that can be absorbed for a given change in internal energy. The quantity of heat absorbed by the system in an irreversible process can be labeled q_{irrev}.

Now consider the entropy change in the surroundings. The heat absorbed by the system, q_{irrev} came from the surroundings, so the heat "absorbed" by the surroundings is $-q_{irrev}$ and the entropy change *in the surroundings* is

$$\Delta S_{surroundings} = \frac{-q_{irrev}}{T}$$

As previously, the entropy change in the universe is the sum of the entropy changes in the system and the surroundings:

$$\begin{aligned}\Delta S_{universe} &= \Delta S_{system} + \Delta S_{surroundings} \\ &= \frac{q_{rev}}{T} - \frac{q_{irrev}}{T} \\ &> 0\end{aligned}$$

because q_{irrev} is always less than q_{rev}.

The entropy change in the universe in a real, irreversible process is always greater than zero.

Entropy Change in the Expansion of a Perfect Gas

Suppose one mole of a perfect gas with an initial volume V_1 and an initial temperature T_1 reversibly absorbs a small quantity of heat $\mathrm{d}q_{rev}$ and expands by a very small volume $\mathrm{d}V$ against an external pressure P. The final volume is V_2; the final temperature is T_2. The work done by the gas will then be $\mathrm{d}w_{rev} = P\mathrm{d}V$

From the First Law,

$$\begin{aligned}\mathrm{d}U &= \mathrm{d}q_{rev} - \mathrm{d}w_{rev} \\ \mathrm{d}U &= \mathrm{d}q_{rev} - P\ \mathrm{d}V \\ \mathrm{d}q_{rev} &= \mathrm{d}U + P\ \mathrm{d}V\end{aligned}$$

From the Equation of State of a Perfect Gas, for one mole of the gas $P = RT/V$

$$\mathrm{d}q_{rev} = \mathrm{d}U + \frac{RT\ \mathrm{d}V}{V}$$

Also for one mole of gas, the internal energy U is given by the product of the heat capacity at constant volume C_V and the temperature T,

$$\mathrm{d}q_{rev} = C_V\ \mathrm{d}T + \frac{RT\ \mathrm{d}V}{V}$$

Dividing both sides by the temperature T

$$\frac{\mathrm{d}q_{rev}}{T} = C_V \frac{\mathrm{d}T}{T} + R\frac{\mathrm{d}V}{V}$$

This equation can now be integrated to give

$$\Delta S = (C_V\ \ln T_2 + R\ \ln V_2) - (C_V\ \ln T_1 + R\ \ln V_1)$$

because the integral of $\mathrm{d}x/x = \ln x$ (the natural logarithm of x).

Since $\ln x - \ln y = \ln x/y$

$$\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{V_2}{V_1}\right)$$

This equation defines the entropy change in terms that are either constants (C_V and R) or state functions (V and T). This shows that entropy is a state function for a perfect gas.

Entropy and the Direction of Change in Isolated Systems

Expansion of a Gas at Constant Temperature

The equation for the entropy change that results from the absorption of heat by a perfect gas allows one to calculate the entropy change associated with the expansion of a certain quantity of gas in an isolated system at constant temperature. As previously,

$$\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{V_2}{V_1}\right)$$

but in this case $T_2 = T_1$ so $T_2/T_1 = 1$. From the definition of the natural logarithm, ln 1 = 0 and so

$$\Delta S = R\ln\left(\frac{V_2}{V_1}\right)$$

From this equation, if V_2 is greater than V_1, V_2/V_1 will be greater than 1 and $\ln(V_2/V_1)$ (and consequently ΔS) will be positive. If $V_1 = V_2$, then $V_2/V_1 = 1$ and $\ln(V_2/V_1)$ (and consequently ΔS) will be zero. If V_2 is less than V_1, then V_2/V_1 will be less than 1 and $\ln(V_2/V_1)$ (and consequently ΔS) will be negative.

In the real world, a gas in an isolated system at constant temperature always expands to fill the maximum volume available. This corresponds to an increase in entropy. The process whereby a gas at constant temperature spontaneously collects in a small volume of such a system leaving the rest of the system empty has never been reported. Such a process would correspond to a decrease in the entropy of an isolated system.

Transfer of Heat between Two Objects at Different Temperatures

Suppose that an isolated system contains two separate objects, one of which is at a temperature T_1 and the other is at some different temperature T_2. Now suppose that, by some unspecified process, a very small quantity of heat dq is transferred from the object of temperature T_1 to the object of temperature T_2. The change in entropy of the first object is $-\mathrm{d}q/T_1$ (negative, because heat is lost from the object) while the change in entropy of the second object is $\mathrm{d}q/T_2$ (positive, because heat is absorbed by the object). The change in entropy for the whole system is the sum of the individual changes, that is,

$$\frac{\mathrm{d}q}{T_2}-\frac{\mathrm{d}q}{T_1}=\mathrm{d}q\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

If T_2 is smaller than T_1, then $1/T_2$ will be greater than $1/T_1$ and the entropy change will be positive. If T_2 equals T_1, the entropy change will be zero. If T_2 is greater than T_1, the entropy change for the process will be negative.

Comparing these results to what happens in the real world, one sees again that in an isolated system *the process that results in an increase in entropy happens spontaneously*. Put an object in contact with one at a lower temperature, and energy will be transferred as heat from the object at the higher temperature to that at the lower temperature. If the temperature of the two objects is the same, then they are by definition in thermal equilibrium. If a minute quantity of heat is transferred reversibly from one object to the other, the entropy change is zero. The process for which the entropy change is negative, namely the transfer of heat from an object at a lower temperature to one at a higher temperature, never happens spontaneously in an isolated system. If such a process is to occur, external work must be done to transfer the heat. This is what happens in a refrigerator, where the net effect of the work being done by the electric motor is to cool the inside of the refrigerator and make the air outside warmer.

The Second Law Restated

The statement that "in isolated systems, processes for which the entropy change is negative are not spontaneous" is yet another form of the *Second Law of Thermodynamics.* Perhaps the most general statement of the Second Law is that "the entropy of the Universe increases". In this instance, where the word "Universe" has a capital letter, the meaning is the conventional one: *everything there is*. This is very different from the thermodynamic meaning of the word "universe" (no capital). As indicated earlier, a thermodynamic "universe" is simply the system of interest plus its surroundings, assumed to be totally isolated from external influences.

The statement of the Second Law with reference to the Universe indicates that there is an inevitable progression in time towards a state of higher entropy *for the Universe as a whole*. When one sees a movie being played backwards, one sees a world in which the entropy of the Universe is decreasing with time. Some processes, such as the swinging of a pendulum, do not look any different. Other processes, such as the dropping of a glass of water onto the floor, look remarkably different. Randomly scattered globs of water and shards of glass miraculously re-assemble themselves into a glass of water. Why, one might ask, is that such an amazing process? Why has such an event never been reported in the entire history of the human race? After all, on the molecular level all that has to happen is for the molecular motions that took place when the glass was shattered and the water scattered to be precisely reversed. Having stated that, it is immediately obvious why such a process would be amazing. It is not that it is impossible. It is just wildly improbable. Of all the ways that the molecules making up a smashed glass of water have of arranging themselves, very, very few correspond to the multitude of successive re-arrangements that would be required to re-assemble the original glass of water.

The Driving Force of Change

The Second Law of Thermodynamics states that for a spontaneous process, the entropy of the system and its surroundings must increase. In other words, ΔS *for the system and its surroundings* must be positive.

Suppose a process takes place in a system for which the entropy change *in the system* is ΔS_{system} and the enthalpy change *in the system* is ΔH_{system}. The heat evolved or absorbed by the system in the enthalpy change ΔH_{system} obviously goes into, or comes from, the *surroundings*. This heat will be absorbed (or lost) by the surroundings at a temperature T and the *entropy of the surroundings* will change by an amount $(-\Delta H_{system}/T)$. The negative sign is there because heat *emitted* by the system is *absorbed* by the surroundings.

The total entropy change for the system plus the surroundings is therefore

$$\Delta S_{system\ +\ surroundings} = \Delta S_{system} - \frac{\Delta H_{system}}{T}$$

This equation is very important because it provides a way of finding *the total entropy change for the system and surroundings* using only the calculated changes in the entropy and enthalpy *of the system*.

For a process to be spontaneous, the total entropy change must be positive. Now, ΔS_{system} and ΔH_{system} can be either positive or negative, but the temperature T is always positive. Multiplying the equation by T,

$$T\Delta S_{system\ +\ surroundings} = T\Delta S_{system} - \Delta H_{system}$$

Again, a process will be spontaneous if this quantity is positive or, equivalently, if the quantity $\Delta H - T\Delta S$ is *negative*.

Another State Function: the Gibbs Free Energy

The quantity $\Delta H - T\Delta S$ has the units of energy. Recall that ΔH represents the energy change after allowance has been made for the work ($P\Delta V$) done in volume changes at constant pressure. The quantity $T\Delta S$ can be thought of as the energy that has been dispersed as random molecular motion and is unavailable to do useful work. The remaining energy, $\Delta H - T\Delta S$, is referred to as the *free energy*, because it is available to perform useful work. An example of the conversion of free energy into useful work is provided by electrochemical cells. This interesting and important area of thermodynamics is not, however, of direct relevance to pyrotechnics and will not be discussed here.

The free energy is of such great importance that it is convenient to define a new quantity $G = H - TS$ for which, at constant temperature, (from the definition of Δ)

$$\Delta G = \Delta H - T\Delta S$$

Notice that this quantity G, being made up of the state functions H, T and S, is itself a state function. That is to say, changes in its value depend only on the state of the system before and after a process, and are independent of any intermediate states that the system might have assumed during the process. This new state function is called the *Gibbs free energy* (after J. Willard Gibbs).[2b]

This, at last, is the state function that can be used to predict the direction of change in a chemical system.

At equilibrium, the Gibbs free energy of the reactants will equal the Gibbs free energy of the products. If the Gibbs free energy change (ΔG) for a process is *negative*, the *entropy change for the universe will be positive*, and the process will be thermodynamically spontaneous.

The sign of ΔG indicates only whether or not the process will be spontaneous. It does *not* indicate whether the transfer of energy during the process will be from the system to the surroundings, or in the opposite direction. That information is given by the sign of the *enthalpy* change. A process with a negative ΔG may result in the spontaneous transfer of energy *from the system to the surroundings* (i.e., ΔH is negative). Examples of such a process include the freezing of water in the freezer compartment of a refrigerator, and the combustion of magnesium in a burning pyrotechnic composition. On the other hand, another process, also having a negative ΔG, might result in the spontaneous transfer of energy *from the surroundings to the system* (i.e., ΔH is positive). Examples of such a process include the melting of a lump of ice in a glass of water, and the decomposition of a particle of strontium carbonate in a burning red star.

The Third Law

The entropy of a system, as noted previously, is a measure of the number of molecular arrangements that are consistent with the properties of the system.

Recall that the relationship between the entropy S of a system and the number W of molecular arrangements consistent with the properties of the system was shown by Boltzmann[3c] to be

$$S = k \ln W$$

This relationship means that the entropy of a system that is consistent with only *one* arrangement of its molecules will be zero, because for such a system $W = 1$ and the natural logarithm of 1 is zero. In other words, Boltzmann's equation implies that *the entropy of a perfectly ordered system is zero.*

If this is correct, then the entropy of a perfect crystalline solid should approach zero as the temperature approaches absolute zero. This trend has been demonstrated experimentally by measurements of heat capacities at very low temperatures.[7] The statement that "the entropy of a perfect crystalline solid is zero at the absolute zero of temperature" is one form of the *Third Law of Thermodynamics*. The importance of this law is that it allows an absolute value to be assigned to the *molar entropy* of a substance. The molar entropy is calculated from heat capacity measurements, starting from zero at 0 K. For example, the molar entropy of a gas at room temperature would include contributions from the heat capacity of one mole of the solid from 0 K to the melting point, including any heat absorbed in any changes between different crystalline states. It would also include the latent heat of fusion of the solid, the heat capacity of the liquid from the melting point to the boiling point, the latent heat of vaporization and the heat capacity of the gas from the boiling point to room temperature. At each stage the entropy would by calculated from $dS = dq/T$ and the total molar entropy would be obtained by summing all these increments dS.

The Standard Free Energy of Formation

All pure substances have a Standard Free Energy of Formation, ΔG_f°. This is the free energy change when one mole of the compound is formed from its elements in their standard states at a pressure of 1 bar and a specified temperature, normally 298.15 K. The free energy of formation of the chemical elements at standard conditions is by definition zero; values for the free energies of formation of many compounds are available in tables of thermodynamic data. Standard Free Energy changes can be added and subtracted just like enthalpy changes.

For a chemical reaction

$$w\,\mathrm{A} + x\,\mathrm{B} \rightarrow y\,\mathrm{C} + z\,\mathrm{D}$$

the Standard Free Energy change ΔG° associated with the reaction is given by

$$\Delta G^{\circ} = \left[y\ \Delta G^{o}_{f\,C} + z\ G^{o}_{f\,D} \right] - \left[w\ G^{o}_{f\,A} + x\ G^{o}_{f\,B} \right]$$

where $G^{o}_{f\,A}$ is the Standard Free Energy of Formation of the species A, etc.

Like the enthalpy and the entropy, the Gibbs free energy is an *extensive* function; that is, it varies depending on the amount of substance in a system. The Gibbs free energy of formation of *one mole* of a substance is called the *molar free energy* of that substance. If a number of different substances are introduced into a system, with no chemical reactions, the total free energy change can be calculated by multiplying the number of moles of each substance by its molar free energy and adding up the results. To reach chemical and thermodynamic equilibrium, substances undergo chemical reactions until the free energy is at a minimum. The reason for this is that minimizing the free energy in a system is the same as maximizing the entropy of the system and its surroundings.

Variation of the Gibbs Free Energy with Pressure, Temperature and Volume

Tabulated values of the molar free energy of various substances at specified conditions of temperature and pressure can be used to calculate the free energy changes involved in chemical reactions. To do this, it is necessary to know how free energy varies with temperature, pressure and volume.

By definition

$$G = H - TS$$

and

$$H = U + PV$$

Therefore

$$G = U + PV - TS$$

where U is the internal energy and V is the volume.

For the purposes of this discussion it can be assumed that the only work done by, or on, the system is the work involved in changing the volume of the system in response to pressure, or vice versa. That is, the only work to be taken into account is "pressure-volume" or "expansion" work. Electrochemical effects, for instance, are not considered. For very small (i.e., differential) changes in internal energy, pressure, volume, temperature and entropy, the corresponding change in Gibbs free energy is

$$dG = dU + PdV + VdP - TdS - SdT$$

But for a closed system, doing only "expansion" work,

$$dU = TdS - PdV$$

and these terms drop out of the equation, so

$$dG = VdP - SdT$$

At constant temperature, $dT = 0$, and consequently $dG = VdP$. At constant pressure, $dP = 0$, so $dG = -SdT$.

Variation of Gibbs Free Energy with Pressure, at Constant Temperature

At constant temperature

$$dG = VdP$$

and by integration

$$\Delta G = G_2 - G_1 = \int_1^2 VdP$$

For a perfect gas,

$$V = \frac{nRT}{P}$$

and for n moles at a constant temperature nRT is constant. For a pressure change from P_1 to P_2,

$$\Delta G = G_2 - G_1 = \int_1^2 \left(\frac{nRT}{P}\right) dP$$

$$= nRT \int_1^2 \frac{dP}{P} = nRT \ln\left(\frac{P_2}{P_1}\right)$$

This gives the change in Gibbs free energy with pressure at constant temperature for a perfect gas.

For one mole of gas at standard pressure, $G_1 = G°$, so the molar free energy G at some other pressure P is given by

$$G = G° + RT \ln\left(\frac{P}{P°}\right)$$

where $G°$ is the free energy of one mole of the gas at standard pressure ($P°$).

What about a liquid or solid? As previously,

$$dG = VdP$$

and by integration

$$\Delta G = G_2 - G_1 = \int_1^2 VdP$$

In the pressure ranges of interest to pyrotechnics, the volume of a liquid or solid changes very little with pressure. The volume can usually be treated as constant, and in this case

$$\Delta G = V\Delta P$$

This equation applies only for pressure ranges over which the substance can be considered incompressible.

The change in free energy with pressure for one mole of a solid or liquid is very much smaller than that for one mole of a gas, and it can usually be ignored. For example, suppose the pressure of one mole of a substance is increased from 1 to 10 bars, at room temperature (298 K). If the substance is a gas, the free energy change is given by

$$\begin{aligned}\Delta G &= nRT\ln\left(\frac{P_2}{P_1}\right)\\ &= 1\text{ mol}\times\frac{8.3145\text{ J}}{\text{K}\cdot\text{mol}}\times 298\text{ K}\times\ln\left(\frac{10}{1}\right)\\ &= 8.3145\times 298\times\ln 10\text{ J}\\ &= 5705.2\text{ J}\\ &= 5.71\text{ kJ (3 significant figures)}\end{aligned}$$

On the other hand, taking water as an example of a liquid, the volume of one mole of water (18 grams) is around 18 cubic centimetres or 1.8×10^{-5} cubic metres. For a change in pressure from 1 to 10 bars, the free energy change is

$$\begin{aligned}\Delta G &= V\Delta P\\ &= 1.8\times 10^{-5}\,\text{m}^3\times 9\text{ atm}\times 1.013\times\frac{10^5\text{N}}{\text{m}^2\cdot\text{atm}}\\ &= 16.4\text{ Nm}\\ &= 16.4\text{ J}\\ &= 0.016\text{ kJ (2 significant figures)}\end{aligned}$$

This is a bit less than 0.3% of the free energy change that the same pressure change would bring about in the same quantity of gas.

Variation of Gibbs Free Energy with Temperature, at Constant Pressure

At constant pressure

$$dG = -SdT$$

and so

$$\frac{dG}{dT} = -S$$

This is only true for constant pressure; to emphasize this, it is customary to write it in the form

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

where the symbol ∂ indicates "partial differentiation" and that the variable indicated by the subscript P (i.e., the pressure) must be held constant.

This simple equation is one version of the Gibbs-Helmholtz equation. There is another version that can be derived with the help of the differential calculus.

By definition,

$$G = H - TS = H + T\left(\frac{\partial G}{\partial T}\right)_P$$

$$\left(\frac{\partial G}{\partial T}\right)_P T - G = -H$$

Divide this equation by T^2

$$\frac{\left(\frac{\partial G}{\partial T}\right)_P}{T} - \frac{G}{T^2} = \frac{H}{T^2}$$

It can be shown that

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = \frac{\left(\frac{\partial G}{\partial T}\right)_P}{T} - \frac{G}{T^2}$$

The right hand side of this equation is the same as the left-hand side of the previous equation, therefore

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = \frac{H}{T^2}$$

This is the other form of the Gibbs-Helmholtz equation. Notice that it shows how G/T (rather than G) varies with temperature at constant pressure. Another variation of this equation is

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P = \frac{\Delta H}{T^2}$$

Variation of Gibbs Free Energy with Chemical Composition, at Constant Temperature and Pressure

The free energy of a reacting mixture will change with pressure and temperature, and it will also change as the amount of each substance in the mixture changes. For a very small change in the number of moles of a substance in a mixture at constant temperature and pressure there will be a corresponding free energy change. The ratio of these changes, given by the partial derivative,

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \mu_i$$

is called the *chemical potential* of the substance *i*. The chemical potential is usually given the symbol μ (mu, the Greek equivalent of the letter 'm'). *The chemical potential of a pure substance is numerically equal to the molar free energy of that substance*. The chemical potential of a substance has units of joules per mole. It is an *intensive* quantity – that is, it does not depend on the amount of substance.

In reaching equilibrium, systems move from conditions of high chemical potential to the lowest possible chemical potential. This is a bit like the tendency of objects in a gravitational field to move from a position of high potential energy to one of low potential energy, or of electric currents to flow from a high electrical potential to a low one. The reason for the movement from a state of high chemical potential to one of low chemical potential is simply that such a movement corresponds to an increase in the total entropy of the system and its surroundings. In other words, it is nothing more (or less) than the natural tendency of molecules to get into a mess.

If *n* moles of a substance of chemical potential μ are added to a system, the change in Gibbs free energy is given by

$$\Delta G = n\mu$$

More generally, if substances *a, b, c,…* are added to a system, the change in Gibbs free energy is given by

$$\begin{aligned}\Delta G &= n_a\mu_a + n_b\mu_b + n_c\mu_c + \ \dots \\ &= \Sigma n_i\mu_i\end{aligned}$$

where n_i is the number of moles of substance *i,* and μ_i is the chemical potential of substance *i.*

Free Energy Changes and Chemical Reactions: Effect of Temperature

Recall that a process will be spontaneous (will continue to equilibrium once it has been started) if its Gibbs free energy change is negative. The equation for the Gibbs free energy change

$$\Delta G = \Delta H - T\Delta S$$

leads to some useful generalizations about chemical reactions. For example, if the entropy change is positive, there will *always* be a temperature at which $T\Delta S$ becomes greater than ΔH. Processes for which the entropy change is positive are those in which the molecular disorder increases. These include the melting of solids, the evaporation of liquids, and the decomposition of complex molecules into simpler ones and ultimately into atoms. The equation for the Gibbs free energy change indicates that as a solid is heated it will eventually melt, if it does not decompose first, and that a liquid will evaporate. Moreover, at a sufficiently high temperature every substance will be decomposed into its constituent atoms.

Free Energy Changes and Phase Changes: Freezing and Melting of Solids

If the enthalpy change (ΔH) is large and negative, the Gibbs free energy change is likely to be negative. Consequently, exothermic processes are often spontaneous. The exceptions are those for which the change in the entropy is negative. The freezing of a liquid is always exothermic, but also involves a decrease in entropy. The freezing of a liquid becomes spontaneous only when the temperature is low enough for $T\Delta S$ to be less than ΔH.

When $\Delta H = T\Delta S$, and there is no driving force for the change in either direction, the solid and the liquid are in equilibrium. At constant pressure, this occurs at just one temperature. This temperature is the freezing point (or melting point) of the substance. The Gibbs free energy change accounts for the fact that pure substances at constant pressure have fixed melting points.

Free Energy Changes and Phase Changes: Evaporation of Liquids

At the melting point, the solid and liquid are in equilibrium. The free energy change is zero. In other words, at the melting point the free energy of the liquid is exactly equal to the free energy of the solid. As long as both liquid and solid are present, the temperature remains precisely at the melting point, no matter how much heat is supplied to the system. At any given pressure there is one, and only one, temperature at which the two phases can exist in equilibrium.

Contrast this situation with that of a liquid and its vapor. As shown previously, at constant temperature, the free energy of a gas varies with pressure:

$$G = G^\circ + RT\ln\left(\frac{P}{P^\circ}\right)$$

At any temperature, a certain pressure of gas will have a free energy equal to that of the liquid at that temperature, so the gas and liquid will be in equilibrium. The corresponding gas pressure is called the *vapor pressure* of the substance at that temperature. When the vapor pressure becomes equal to the atmospheric pressure, the liquid and vapor are in equilibrium at atmospheric pressure. The corresponding temperature is the *boiling point* of the substance. The Gibbs free energy change predicts that a pure substance will have a fixed vapor pressure at any given temperature and a fixed boiling point at any given pressure, in accordance with experiment.

Free Energy and Chemical Reactions in Gases

If two gases undergo a *chemical reaction* to form two new gases, the reactants and products will be in equilibrium when the free energy of the products equals the free energy of the reactants. For each gas involved in the reaction, the free energy is given by

$$G_i = n_i\left(G_i{}^\circ + RT\ln\left(\frac{P_i}{P^\circ}\right)\right)$$

where n_i is the number of moles of that gas, P_i is the *partial pressure* of gas$_i$ and P° is the pressure to which the Standard Free Energy G_i° corresponds. The term "partial pressure" simply means the pressure that each gas contributes to the total pressure.

For a constant pressure system, as in the present discussion, the partial pressure P_i of each gas is given by the total pressure multiplied by the *mole fraction* of the gas X_i.

$$P_i = PX_i$$

The mole fraction $X_i = n_i/n$ is the ratio of the number of moles n_i of the gas i divided by the total number of moles of gas in the system.

Suppose the reaction is a moles of gas A reacting with b moles of gas B to form c moles of gas C and d moles of gas D:

$$a\,\mathrm{A} + b\,\mathrm{B} \rightarrow c\,\mathrm{C} + d\,\mathrm{D}$$

The free energy of the reactants will be

$$a\left(G_A^\circ + RT\ln\left(\frac{P_A}{P^\circ}\right)\right) +$$
$$b\left(G_B^\circ + RT\ln\left(\frac{P_B}{P^\circ}\right)\right)$$

and the free energy of the products will be

$$c\left(G_C^\circ + RT\ln\left(\frac{P_C}{P^\circ}\right)\right) +$$
$$d\left(G_D^\circ + RT\ln\left(\frac{P_D}{P^\circ}\right)\right)$$

where P_A, P_B, P_C and P_D are the partial pressures of gases A, B, C and D.

The free energy change of the reaction will be the free energy of the products minus the free energy of the reactants.

$$\begin{aligned}\Delta G = {} & c\left(\overset{\circ}{G}_C + RT\ln\left(\frac{P_C}{P^\circ}\right)\right) + \\ & d\left(\overset{\circ}{G}_D + RT\ln\left(\frac{P_D}{P^\circ}\right)\right) - \\ & a\left(\overset{\circ}{G}_A + RT\ln\left(\frac{P_A}{P^\circ}\right)\right) - \\ & b\left(\overset{\circ}{G}_B + RT\ln\left(\frac{P_B}{P^\circ}\right)\right) \\ = {} & \left(c\overset{\circ}{G}_C + d\overset{\circ}{G}_D - a\overset{\circ}{G}_A - b\overset{\circ}{G}_B\right) + \\ & cRT\ln\left(\frac{P_C}{P^\circ}\right) + dRT\ln\left(\frac{P_D}{P^\circ}\right) - \\ & aRT\ln\left(\frac{P_A}{P^\circ}\right) - bRT\ln\left(\frac{P_B}{P^\circ}\right)\end{aligned}$$

$$\begin{aligned}& c\overset{\circ}{G}_C + d\overset{\circ}{G}_D - a\overset{\circ}{G}_A - b\overset{\circ}{G}_B \\ & = \left(c\overset{\circ}{G}_C + d\overset{\circ}{G}_D\right) - \left(a\overset{\circ}{G}_A + b\overset{\circ}{G}_B\right) \\ & = \Delta G^\circ\end{aligned}$$

Therefore

$$\begin{aligned}\Delta G = \Delta G^\circ + cRT\ln\left(\frac{P_C}{P^\circ}\right) + dRT\ln\left(\frac{P_D}{P^\circ}\right) - \\ aRT\ln\left(\frac{P_A}{P^\circ}\right) - bRT\ln\left(\frac{P_B}{P^\circ}\right)\end{aligned}$$

Now, because $x \ln X = \ln X^x$

$$\begin{aligned}\Delta G = \Delta G^\circ + RT\ln\left(\frac{P_C}{P^\circ}\right)^c + RT\ln\left(\frac{P_D}{P^\circ}\right)^d - \\ RT\ln\left(\frac{P_A}{P^\circ}\right)^a - RT\ln\left(\frac{P_B}{P^\circ}\right)^b\end{aligned}$$

and, because $\ln X + \ln Y = \ln XY$

$$\begin{aligned}\Delta G = \Delta G^\circ + RT\ln\left(\frac{P_C}{P^\circ}\right)^c \times \left(\frac{P_D}{P^\circ}\right)^d - \\ RT\ln\left(\frac{P_A}{P^\circ}\right)^a \times \left(\frac{P_B}{P^\circ}\right)^b\end{aligned}$$

Finally, because $-\ln X = \ln(1/X)$:

$$\Delta G = \Delta G^\circ + RT\ \ln\left(\frac{\left(\frac{P_C}{P^\circ}\right)^c\left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a\left(\frac{P_B}{P^\circ}\right)^b}\right)$$

This equation shows how the free energy change relates to the pressures of gaseous reactants and products at constant temperature. It is called the van't Hoff isotherm.

At equilibrium, the free energy of the reactants equals the free energy of the products, so $\Delta G = 0$ and

$$0 = \Delta G = \Delta G^\circ + RT\ \ln\left(\frac{\left(\frac{P_C}{P^\circ}\right)^c\left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a\left(\frac{P_B}{P^\circ}\right)^b}\right)$$

or

$$\Delta G^\circ = -RT\ \ln\left(\frac{\left(\frac{P_C}{P^\circ}\right)^c\left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a\left(\frac{P_B}{P^\circ}\right)^b}\right)$$

where P_A, P_B, P_C and P_D are the pressures of gases A, B, C and D *at equilibrium*.

The right hand side of this equation can be written as $-RT \ln K$, where

$$K = \left(\frac{\left(\frac{P_C}{P^\circ}\right)^c\left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a\left(\frac{P_B}{P^\circ}\right)^b}\right)$$

K is called the *equilibrium constant* for the reaction, and therefore

$$\Delta G^\circ = -RT \ln K$$

Relative Activities

As shown previously, at constant temperature the free energy of a gas varies with pressure according to:

$$G = G^\circ + RT\ln\left(\frac{P}{P^\circ}\right)$$

where P is the partial pressure of the gas and $G°$ is the free energy of one mole of the gas at pressure $P°$. This can be expressed in chemical potentials:

$$\mu = \mu° + RT\ln\left(\frac{P}{P°}\right)$$

where $\mu° = G°$

This applies only to perfect gases. For other substances, it is useful to *define* a property called the *relative activity* such that the chemical potential is given by

$$\mu = \mu° + RT\ln(a_A)$$

where a_A is the relative activity of the substance A. The equation requires the logarithm of the relative activity, a_A, which means that a_A must be a pure number—it cannot be some quantity requiring units. It has to be a ratio of some property of A, at the conditions of interest, to the value of that property in the standard state corresponding to $\mu°$. The relative activity of a perfect gas is obviously $P/P°$. For a real gas (that is, a gas that does not conform exactly to the ideal relationship $PV = nRT$) the relative activity can be defined by assigning an "effective pressure" f to the gas such that

$$\mu = \mu° + RT\ln\left(\frac{f}{P°}\right)$$

This "effective pressure" f varies with temperature and has to be determined for each gas. It is called the *fugacity* of the gas. What is the relative activity for a pure solid or liquid?

As discussed previously, the free energy per mole of a pure solid or liquid changes very little with pressure, and it is usually sufficiently accurate to treat the chemical potential of a pure solid or liquid as constant. That simplifies matters greatly, because if the chemical potential is constant, then for one mole of a pure solid or liquid

$$\mu = \mu° + RT\ln(a) = \mu°$$

from which $RT\ln(a) = 0$ and so $a = 1$. The relative activity of pure solids and liquids is 1.

For perfect (or ideal) solutions, the chemical potential of a component i is given by

$$\mu_i = \mu_i° + RT\ln X_i$$

where X_i is the mole fraction of i and $\mu_i°$ is the chemical potential of pure i in the same physical state as the solution.

Relative Activities and Equilibrium Constants

The definition of relative activity was chosen so that for *any* reaction

$$a\,\mathrm{A} + b\,\mathrm{B} + c\,\mathrm{C} + \dots \rightarrow$$
$$w\,\mathrm{W} + x\,\mathrm{X} + y\,\mathrm{Y} + \dots$$

there is an equilibrium constant K of the form

$$K = \frac{(a_W)^w (a_X)^x (a_Y)^y \dots}{(a_A)^a (a_B)^b (a_C)^c \dots}$$

where a_W is the relative activity of W, etc.

The equilibrium constant is related to the Standard Free Energy change for the reaction by

$$\Delta G° = -RT\ln K$$

This equation can be rearranged to give

$$K = e^{-\frac{\Delta G°}{RT}}$$

Equilibrium Constant, Free Energy and the Stability of Compounds

The relationship $K = e^{-\frac{\Delta G°}{RT}}$ can be used to explain the stability of compounds by reference to their free energy of formation.

For the general reaction for the formation of a compound from its elements,

$$a\,\mathrm{A} + b\,\mathrm{B} \rightarrow \mathrm{A}_a\mathrm{B}_b$$

the equilibrium constant is given by

$$K = \frac{[A_aB_b]}{[A]^a[B]^b}$$

If the Standard Free Energy of Formation $\Delta G°$ is large and negative, then $-\Delta G°/\mathrm{RT}$ will be large and positive, so K will be large and the equilibrium concentration of the product will be large. As the temperature T increases, the value of –ΔG°/RT will become smaller, K will decrease and the equilibrium concentration of the product will decrease. In general, the equilibrium will shift more and more towards the reactants as the temperature increases. Substances for which the Standard Free Energy of Formation is larger and more negative will withstand a higher temperature before the equilibrium lies in favor of the products. *The Standard Free Energy of Formation is a quantitative indicator of the thermal stability of a substance*.

Notice that if the reactants and products of a reaction are all solids, then the relative activity of each is 1, and the equilibrium constant is also 1. This means that $\Delta G° = -RT \ln 1 = 0$. The solid reactants and products can be in equilibrium at one, and only one, temperature: that at which $\Delta G° = 0$ (*i.e.*, $T = \Delta H°/\Delta S°$). At all other temperatures, the system consists either *entirely* of reactants or *entirely* of products. This might seem odd, but it is no different from the familiar example of a pure solid being in equilibrium with its liquid at one and only one temperature.

Variation of Equilibrium Constants with Temperature

Recall

$$\Delta G° = -RT \ln K$$

$$\ln K = -\frac{\left(\frac{\Delta G°}{T}\right)}{R}$$

The partial derivative of this equation with respect to temperature, assuming constant pressure, is

$$\left(\frac{\partial(\ln K)}{\partial T}\right)_P = -\frac{\left(\frac{\partial\left(\frac{\Delta G°}{T}\right)}{\partial T}\right)_P}{R}$$

Then, by the Gibbs-Helmholtz equation:

$$\left(\frac{\partial(\ln K)}{\partial T}\right)_P = -\frac{\left(\frac{\partial\left(\frac{\Delta G°}{T}\right)}{\partial T}\right)_P}{R} = \frac{\Delta H°}{RT^2}$$

It is not necessary to restrict this relationship to constant pressure, because neither ΔG° nor ΔH° vary with pressure. By definition they are the values of ΔG or ΔH at some standard pressure, usually one bar. Therefore,

$$\frac{\mathrm{d}(\ln K)}{\mathrm{d}T} = \frac{\Delta H°}{RT^2}$$

This gives the relationship between the equilibrium constant and the temperature.

The equation can be rearranged to

$$\mathrm{d}(\ln K) = \frac{\Delta H°}{R}\left(\frac{dT}{T^2}\right)$$

Now, $\mathrm{d}\frac{T}{T^2} = -\mathrm{d}\left(\frac{1}{T}\right)$, so

$$\mathrm{d}(\ln K) = -\frac{\Delta H°}{R}\mathrm{d}\left(\frac{1}{T}\right)$$

This can now be integrated, assuming ΔH° is constant with temperature, to give

$$\Delta(\ln K) = \frac{-\Delta H°}{R}\Delta\left(\frac{1}{T}\right)$$

If the equilibrium constant is known at one temperature, this equation provides a way to calculate the equilibrium constant at any other temperature, provided that the relationship between ΔH° and temperature is known, and that the pressure is constant. The effect of temperature on ΔH° can be calculated from the heat capacities of the reactants and products over the temperature range of interest. If the equilibrium constant at one temperature T_1 is K_1, what can be said about the equilibrium constant (K_2) at a higher temperature T_2?

Rearrange the previous equation to obtain

$$\ln K_2 - \ln K_1 = \frac{-\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Since T_2 is greater than T_1, $(1/T_2 - 1/T_1)$ will be negative. If ΔH° is also negative (that is, if the reaction is exothermic), $\ln K_2 - \ln K_1$ must be negative and K_1 must be greater than K_2. Recall that a larger equilibrium constant corresponds to more products. Since the equilibrium constant is larger at the lower temperature, the equilibrium at the lower temperature favors the products. For an exothermic reaction, an increase in temperature results in the equilibrium shifting in favor of the reactants.

The same line of reasoning can also show that for an endothermic reaction an increase in temperature will result in the equilibrium shifting in favor of the products. This is the thermodynamic explanation of *Le Châtelier's Principle*, as applied to the effect of temperature on chemical equilibrium. Le Châtelier's Principle can be stated in various ways, for example: *if a system at equilibrium is subjected to a stress, it will respond in such a manner that tends to relieve the stress*. This is a useful guide to the behavior of chemical systems and is often all that is needed for a qualitative explanation.

Variation of Equilibrium Constants with Pressure

The discussion of equilibrium constants so far has referred to conditions of constant pressure. The next step is to show how the composition of the equilibrium mixture can change with pressure. Recall that the composition can be expressed in mole fractions given by

$$X_i = \frac{P_i}{P}$$

where P is the total pressure and P_i is the partial pressure of the particular gas.

For the reaction of *a* moles of gas A reacting with *b* moles of gas B to form *c* moles of gas C and *d* moles of gas D

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$$

$$K = \frac{\left(\frac{P_C}{P^\circ}\right)^c \left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b}$$

Now,

$$P_i = X_i P$$

If the pressure P is expressed in bars, and $P^\circ = 1$ then

$$K = \frac{\left(P_C\right)^c \left(P_D\right)^d}{\left(P_A\right)^a \left(P_B\right)^b}$$

$$= \frac{\left(X_C P\right)^c \left(X_D P\right)^d}{\left(X_A P\right)^a \left(X_B P\right)^b}$$

$$= \frac{\left(X_C^c X_D^d\right)}{\left(X_A^a X_B^b\right)} \frac{\left(P^c P^d\right)}{\left(P^a P^b\right)}$$

But $\dfrac{\left(P^c P^d\right)}{\left(P^a P^b\right)} = \dfrac{P^{(c+d)}}{P^{(a+b)}} = P^{(c+d)-(a+b)}$

and $(c + d) - (a + b) = \Delta n$

where Δn is the change in the number of moles. So

$$K = \frac{\left(X_C^c X_D^d\right) P^{\Delta n}}{\left(X_A^a X_B^b\right)}$$

$$\frac{\left(X_C^c X_D^d\right)}{\left(X_A^a X_B^b\right)} = K P^{-\Delta n}$$

If Δn is positive, that is, if there are more moles of products than of reactants, the right-hand side of the equation becomes smaller as the pressure P increases. This means that the equilibrium must shift in favor of the reactants. Similarly, if Δn is negative, the equilibrium will shift in favor of the products as the pressure P increases. This is the thermodynamic explanation for Le Châtelier's Principle, as it applies to the effect of pressure on the equilibrium composition of a reacting mixture.

Application to Pyrotechnics

Two useful pieces of information about reacting pyrotechnic mixtures are the maximum temperature reached and the chemical species present at that temperature. In principle, both can be calculated from thermodynamics.

The process for calculating the temperature is conceptually very simple:

1) Calculate the enthalpy change ΔH° for the reaction at standard temperature and pressure.

2) Assume that all the released heat is available to raise the temperature of the products.

3) Calculate the final temperature from the relationship:

$$\Delta T = \frac{-\Delta H^\circ}{\Sigma n_i C_{p,i}}$$

where ΔT is the temperature rise in kelvin, ΔH° is the enthalpy change in joules, n_i is the number of moles of product i, $C_{p,i}$ is the molar heat capacity (at constant pressure) of product i and the symbol Σ means "the sum of". Dolata[8] has shown that this method can be used to predict the temperatures of the flames of burning pyrotechnic mixtures that burn at relatively low temperatures.

It has been known for a long time that such calculations work quite well for the flame temperatures of certain gas mixtures that burn at moderate temperatures. Examples of such mixtures include coal gas and air or hydrogen and air with either gas in excess.[9a] In these calculations the "products" are the real end products of the reaction: carbon dioxide, water, nitrogen and argon in the case of an air and coal gas flame. There is no need to consider any intermediate products that might be formed along the way. For gas flames that burn at higher temperatures, however, these calculations yield flame temperatures that are much higher than the real flame temperatures.

This discrepancy can be understood if it is imagined that the energy released by the formation of the reaction's final products heats those products to such a high temperature that they start to break down again. This decomposition absorbs energy that would otherwise raise the temperature of the flame.

To calculate the temperature of high-temperature flames one must consider not only the ultimate products (those that are stable at room temperature) but also those intermediate products that are stable at high temperatures. For example, ethylene (C_2H_4) burns in oxygen to form carbon dioxide and water. At the temperature of an ethylene-oxygen flame, however, the following species are in equilibrium: H_2O, O_2, O, H_2, H, OH, CO, and CO_2. The enthalpies of formation of these are known, but the amount of each substance present is not. Nevertheless, the amount of each *element* is obviously constant, and the equilibrium constants of the various dissociation reactions can be calculated for any temperature. Consequently, the problem can be solved by trial and error. One makes a reasonable guess at the temperature and of the partial pressures of two of the substances. With the aid of the equilibrium constants, one can then calculate the partial pressures of all the other products. The sum of these partial pressures should be 1; if it is not, the calculation is repeated. After a few trials, the values for the next trial are chosen by carefully examining the results of the first few and choosing values that are likely to lead in the right direction. With care, the method can yield a result after five or six iterations. The method, which is explained in detail by Gaydon and Wolfhard,[9a] can yield remarkably accurate results. For example, Snelleman[10] measured the temperature of a carefully controlled, pre-mixed air-acetylene flame to be 2554 ± 3 K. The calculated temperature was 2600 ± 3 K. Energy losses from the flame were measured, and when these were taken into account, the calculated flame temperature was 2559 ± 4 K, in agreement with the measured value.

The calculation of flame temperatures of a burning pyrotechnic mixture is much more complicated. For a start, the reaction might never reach thermodynamic equilibrium. Certain reactions might take place at relatively low temperatures, and volatile products of those reactions might be lost before the system can come to equilibrium. Even if equilibrium is reached, unless the mixture is an unusually simple one, the exact composition of the products might not be known. Then, the enthalpies of formation of many common ingredients are not known, or if they are known, they may be difficult to find. Examples of such ingredients are the natural products that are used as binders and fuels in fireworks. A compilation of *estimated* values for these has been published by Meyerriecks.[11–13]

Furthermore, the molar heat capacity of each product is not constant but varies with temperature. As a result, the products change with temperature: solids melt, liquids vaporize, and compounds decompose. The energy consumed in all these processes has to be taken into account. If all these problems can be overcome, eventually a combination of temperature and chemical composition is reached at which the enthalpy of the products exactly equals the enthalpy of the reactants. If the enthalpy of the products as a function of temperature is available, the maximum possible temperature reached in a reaction can be obtained graphically. One plots the enthalpy of the products versus temperature and then finds the temperature at which the graph intersects the line representing the enthalpy of the reactants.

For example, consider the formation of iron(II) sulfide from powdered iron and sulfur:

$$\mathrm{Fe} + \mathrm{S} \rightarrow \mathrm{FeS} \qquad \Delta H_f^\circ = -102 \text{ kJ}$$

The reactants are pure elements, so their enthalpies of formation are (by definition) zero. Therefore, the enthalpy of the reaction is simply the enthalpy of formation of FeS. What is the maximum possible temperature that can be reached in this reaction?

Figure 4 is a graph of the molar enthalpy of formation of iron(II) sulfide as a function of temperature (data from reference 4). The graph cuts the zero line at 1463 K. This is the temperature at which the molar enthalpy of formation of iron(II) sulfide equals the room-temperature molar enthalpies of formation of iron and sulfur, and it is the maximum possible temperature that could be achieved in this reaction. The sharp rise in the curve at 1463 K corresponds to the melting of the solid. The maximum temperature reached is the temperature at which the solid product melts. This is consistent with experimental results. A stoichiometric mixture of powdered iron and sulfur glows bright red when heated to reaction, and the product is found to be partially melted. It is quite common for the maximum temperature of a pyrotechnic reaction to be determined by a phase change in the products. For example, the maximum temperature reached in the combustion of many metals in air corresponds to the boiling point of the metal oxide.[9b]

The example just given was very simple because the possibility of some of the product decomposing at the maximum temperature of the reaction was ignored. In most cases the decomposition of the product must be taken into account. As discussed previously, the increase in entropy associated with the formation of gases favors the decomposition of compounds at high temperatures. The problem is to find the equilibrium composition and the temperature, keeping the elemental composition and total energy constant.

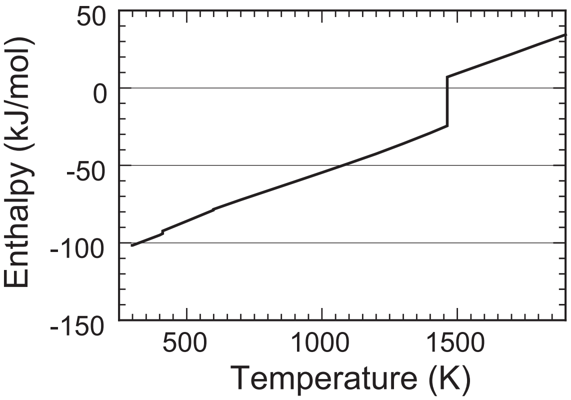

Figure 4. Molar enthalpy of iron(II) sulfide as a function of temperature.[10]

Thermodynamic Modeling

Numerous computer programs have been developed to calculate high-temperature equilibria.[14–16] As noted by Belov,[14] the incentive for developing these programs came from the requirement for better rocket engines.

The calculation most useful for pyrotechnics is the determination of the temperature and chemical composition at constant pressure. This is done by minimizing the Gibbs free energy, with the constraint that the total number of moles of each element remains unchanged. The details of these calculations are given by McBride and Gordon.[16] The calculations are least complicated when the equilibrium products are all gases. If solids or liquids (condensed phases) are predicted, the calculations have to be revised to take into account the fact that the relative activity of a condensed phase of a pure substance is essentially constant and equal to 1. The results of thermodynamic modeling can be rather surprising. For example, a simple pyrotechnic mixture of a pure metal fuel with potassium perchlorate might be expected to produce nothing more than potassium chloride and the oxide of the metal. That is certainly what would be produced if the products were at room temperature, but at the high temperatures of the reaction the chemical composition will be very different. Powers and Gonthier[17] analyzed the operation of a pyrotechnically actuated pin-puller device that used a burning mixture of zirconium and potassium perchlorate to move a piston. The mixture was fuel-deficient: $Zr:KClO_4$ is 1.4:1, compared to the 2:1 molar ratio required for the reaction

$$2\ Zr + KClO_4 \rightarrow 2\ ZrO_2 + KCl$$

Presumably, this fuel-deficient composition was chosen to increase the amount of gas generated on combustion. On the basis of the properties of the products at room temperature, one would expect the reaction products to have been solid zirconium dioxide, solid potassium chloride and oxygen gas from the excess oxidizer. The calculations showed, however, that at the high temperature of the reaction even the highly refractory zirconium dioxide was partially vaporized. All the potassium chloride was vaporized, and the following species were calculated also to be present as gases: atomic oxygen (O), atomic chlorine (Cl), atomic potassium (K), atomic zirconium (Zr), diatomic oxygen (O_2), diatomic chlorine (Cl_2), diatomic potassium (K_2), potassium monoxide (KO), zirconium monoxide (ZrO), chlorine monoxide (ClO) and dipotassium dichloride (K_2Cl_2). As the hot products cooled to room temperature, this diverse collection of atoms and molecules would react to produce the three products (solid zirconium dioxide, solid potassium chloride and diatomic oxygen gas) that are thermodynamically stable at room temperature. The chemical nature of the products at the high temperatures prevailing during the very rapid operation of the device could not have been determined by conventional chemical analysis.

Farren et al.[18] used thermodynamic modeling to simulate the combustion of pyrotechnic compositions including those used in US Navy colored flares. Their results showed that only about 18% of the strontium in the flame of the red flare was present as strontium monochloride (SrCl), the species that emits the desired red light. Most (~65%) was present as strontium dichloride ($SrCl_2$), while some (~15%) was there as strontium (Sr) vapor. Similarly, in the flame of the green flare less than 5% of the barium was present as the barium monochloride (BaCl) color emitter; most (~93%) was barium dichloride ($BaCl_2$), with a little (~1.5%) barium (Ba) vapor and the rest as barium monohydroxide (BaOH) (~0.7%) and barium dihydroxide ($Ba(OH)_2$) (~0.5%). The authors concluded that thermodynamic modeling "can be recommended as a useful tool to survey prospective pyrotechnic compositions as to their likely product distributions and their likely maximum achievable reaction temperature. However, those compositions showing potential usefulness should certainly be mixed, burned and analyzed in the laboratory before being recommended for use in any new or improved pyrotechnic device".[18] In other words, the predictions of modeling must be verified by practical experiments.

Thermodynamic modeling was used by Koch[19] to support his analysis of the reasons why lithium compounds have so far been ineffective as color-producing agents in pyrotechnics. His calculations showed that very little atomic lithium was expected to be present in the flame of a published composition that gave a pink flame instead of the anticipated scarlet red. Furthermore, Koch showed—by thermodynamic modeling—that appropriately formulated compositions should be capable of generating much higher concentrations of atomic lithium and ought to be effective emitters of red light. Recognizing that thermodynamic modeling always requires practical validation, Koch wrote, "it is hoped that an *experimental* proof will be found soon".[19]

Successful efforts to produce the beautiful deep violet-blue atomic emission of indium in pyrotechnic flames have not yet been reported, although, like lithium, indium imparts an intense color to laboratory flames. Perhaps thermodynamic modeling can point the way to achieving a deep blue flame with indium. The cost of indium compounds would inhibit practical applications, but it would be an interesting exercise all the same.

The basic requirements of an effective colored light composition are straightforward: a high concentration of the color-emitting species, minimum concentration of other light-emitting species and maximum temperature. Since these requirements can be in conflict, to achieve optimum results by formulating, manufacturing and testing can be time-consuming and expensive. In general, the requirements of a pyrotechnic composition can be stated by specifying:

1) the chemical composition of the products (either at room temperature or at the temperature of the reaction) and
2) the maximum temperature of the reaction.

Thermodynamic modeling provides the possibility of developing close-to-optimum compositions on the computer. This should greatly reduce the burden of formulation and testing.

Summary and Conclusion

Chemical systems can be described by a few properties called *state functions*. These include temperature T, pressure P, volume V, internal energy U, enthalpy H, entropy S and Gibbs free energy G.

A system is at *equilibrium* when the state functions have constant values throughout the system.

The change in any state function depends only on the initial and final states of the system, not on the intermediate steps.

Energy can be transferred between a system and its surroundings *mechanically*, as *work*, and *thermally*, as *heat*. The change in the *enthalpy* of a system is the heat absorbed or emitted by the system at constant pressure.

Entropy is related to the degree of molecular disorder in a system. An increase in disorder corresponds to an increase in entropy.

A system plus its surroundings is called the *universe*.

- The energy of the universe is constant (First Law of Thermodynamics).
- The entropy of the universe increases. (Second Law of Thermodynamics).

Consequently,

- For a spontaneous process, the Gibbs free energy change is negative. That is,

$$\Delta G = \Delta H - T\Delta S$$

is negative for a spontaneous process.

Consequently:

- If ΔH is negative (heat is released) and ΔS is positive (molecular disorder increases), the process will *always* be spontaneous.
- If ΔH is negative (heat is released) and ΔS is negative (molecular disorder decreases) the process will be spontaneous at a sufficiently low temperature.
- If ΔH is positive (heat is absorbed) and ΔS is positive (molecular disorder increases), the process will be spontaneous at a sufficiently high temperature.
- If ΔH is positive (heat is absorbed) and ΔS is negative (molecular disorder decreases), the process will *never* be spontaneous.

The entropy change ΔS is positive for any process that results in an increase in the molecular disorder. Consequently, if the temperature is increased sufficiently

- Solids will melt.
- Liquids will vaporize.
- Compounds will decompose.
- Gases will ionize.

For a system in equilibrium, the Gibbs free energy change is zero. Consequently, at constant pressure

- Pure substances have fixed freezing (melting) points.
- Pure substances have fixed boiling points.
- There is an equilibrium constant K for chemical reactions, given by

$$\Delta G^\circ = -RT \ln K$$

The variation of the equilibrium constant with temperature and pressure can be calculated from thermodynamics. This variation accounts for Le Châtelier's Principle *(if a system at equilibrium is subjected to a stress, it will respond in such a manner that tends to relieve the stress)* as it applies to the effect of pressure and temperature on the equilibrium composition of a reacting mixture.

Thermodynamic modeling allows the maximum temperature and chemical composition of reacting pyrotechnic mixtures to be estimated from the thermodynamic properties of the reactants and possible products.

Table 1 (at the end of this chapter) shows, for illustrative purposes only, thermodynamic properties of some substances relevant to pyrotechnics. Much more complete data are available in Reference 4, for example.

Acknowledgements

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General References and Suggestions for Further Reading

In addition to the text-specific references, this chapter includes information from a number of sources, including the following, cited in order of publication. More recent editions of some of the books may be available; others may be out of print.

For further reading, there are many books that deal with this subject. The simplest treatments are to be found in the general chemistry texts, followed by the physical chemistry texts and then the specialized texts on chemical thermodynamics. There are also many texts on engineering thermodynamics that contain little of direct relevance to chemical thermodynamics. Of the books listed, that by E. B. Smith and the two books by B. H. Mahan are particularly recommended. The work by P. W. Atkins is a comprehensive physical chemistry textbook with an excellent treatment of chemical thermodynamics. The first volume of I. Barin’s superb 2-volume collection of thermochemical data contains a concise overview of chemical thermodynamics and some useful worked examples.

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Table 1. Formula Weights and Thermodynamic Properties for Some Substances Relevant to Pyrotechnics.

Chemical Name	Chemical Formula [a]	Formula Weight	ΔH_f° [b]	ΔG_f° [b]	S° [b]	C_p° [b]
Aluminium	Al	26.98	0	0	0.028	0.024
carbide	Al_4C_3	143.96	–209	–196	0.089	0.117
oxide	Al_2O_3	101.96	–1676	–1582	0.051	0.079
sulfide	Al_2S_3	150.16	–724	—	—	—
Ammonium						
chloride	NH_4Cl	53.49	–314	–203	0.095	0.084
nitrate	NH_4NO_3	80.04	–366	–184	0.151	0.139
perchlorate	NH_4ClO_4	117.49	–295	–89	0.186	—
Antimony	Sb	121.75	0	0	0.046	0.025
oxide	Sb_2O_3	291.50	–720	–634	0.110	0.101
sulfide	Sb_2S_3	339.69	–175	–174	0.182	0.120
Arsenic	As	74.92	0	0	0.035	0.025
oxide	As_2O_3	197.84	–657	–576	0.107	0.096
sulfide	As_2S_3	246.04	–169	–169	0.164	0.116
Barium	Ba	137.34	0	0	0.063	0.028
carbonate	$BaCO_3$	197.35	–1216	–1138	0.112	0.085
chlorate	$Ba(ClO_3)_2$	304.24	–772	—	—	—
chlorate monohydrate	$Ba(ClO_3)_2{\cdot}H_2O$	322.24	–1067	—	—	—
chloride	$BaCl_2$	208.25	–859	–810	0.124	0.075
nitrate	$Ba(NO_3)_2$	261.35	–992	–797	0.214	0.151
oxide	BaO	153.34	–554	–525	0.070	0.048
peroxide	BaO_2	169.34	–634	—	—	0.067
sulfate	$BaSO_4$	233.40	–1473	–1362	0.132	0.102
sulfide	BaS	169.40	–460	–456	0.078	0.049
Boron	B	10.81	0	–141	0.200	0.122
oxide	B_2O_3	69.62	–1273	–1194	0.054	0.063
Calcium	Ca	40.08	0	0	0.041	0.025
carbonate	$CaCO_3$	100.09	–1207	–1129	0.093	0.082
oxide	CaO	56.08	–635	–604	0.040	0.043
sulfate	$CaSO_4$	136.14	–1434	–1332	0.107	0.092
Carbon	C (graphite)	12.01	0	0	0.006	0.009
monoxide	CO(g)	28.01	–111	–137	0.198	0.029
dioxide	$CO_2(g)$	44.01	–394	–394	0.214	0.037
Chlorine	$Cl_2(g)$	70.91	0	0	0.223	0.034
atomic chlorine	Cl(g)	35.45	122	106	0.165	0.022
Copper	Cu	63.54	0	0	0.033	0.024
(I) chloride	CuCl	98.99	–137	–120	0.086	0.049
(II) chloride	$CuCl_2$	134.45	–220	–176	0.108	0.072
(I) oxide	Cu_2O	143.08	–169	–146	0.093	0.064
(II) oxide	CuO	79.54	–157	–130	0.043	0.042
carbonate, basic	$CuCO_3{\cdot}Cu(OH)_2{\cdot}H_2O$	221.10	–1051	–894	0.186	—
Hydrogen	$H_2(g)$	2.02	0	0	0.131	0.029
chloride	HCl(g)	36.46	–92	–95	0.187	0.029
sulfide	$H_2S(g)$	34.08	–21	–34	0.206	0.034
(water)	$H_2O(l)$	18.02	–286	–237	0.070	0.075

Table 1. Formula Weights and Thermodynamic Properties for Some Substances Relevant to Pyrotechnics (continued).

Chemical Name	Chemical Formula [a]	Formula Weight	ΔH_f° [b]	ΔG_f° [b]	S° [b]	C_p° [b]
Iron	Fe	55.85	0	0	0.027	0.025
(III) oxide	Fe_2O_3	159.69	–824	–742	0.087	0.104
(II,III) oxide	Fe_3O_4	231.54	–1118	–1015	0.146	0.143
Lead	Pb	207.19	0	0	0.065	0.026
(II) oxide	PbO (yellow)	223.189	-215	-188	0.069	0.046
(IV) oxide	PbO_2	239.19	–277	–217	0.069	0.065
(II,IV) oxide	Pb_3O_4	685.57	–718	–601	0.211	0.147
Magnesium	Mg	24.31	0	0	0.033	0.025
carbonate	$MgCO_3$	84.32	–1096	–1012	0.066	0.076
chloride	$MgCl_2$	95.22	–641	–592	0.090	0.071
oxide	MgO	40.31	–602	–569	0.027	0.037
Manganese	Mn	54.94	0	0	0.032	0.026
dioxide	MnO_2	86.94	–520	–465	0.053	0.054
Nitrogen	$N_2(g)$	28.01	0	0	0.192	0.029
(nitrous oxide)	$N_2O(g)$	44.01	82	104	0.220	0.038
(ammonia)	$NH_3(g)$	17.03	–46	–16	0.192	0.035
Oxygen	$O_2(g)$	32.00	0	0	0.205	0.029
atomic oxygen	O(g)	16.00	249	232	0.161	0.022
Phosphorus	P (red)	30.97	–18	–12	0.023	0.021
(V) oxide	P_4O_{10}	283.89	–2984	–2698	0.227	0.212
Potassium	K	39.10	0	0	0.064	0.030
chlorate	$KClO_3$	122.55	–398	–296	0.143	0.100
chloride	KCl	74.55	–437	–410	0.083	0.051
dichromate	$K_2Cr_2O_7$	294.19	–2061	–1882	0.289	0.219
nitrate	KNO_3	101.10	–495	–395	0.133	0.096
oxide	K_2O	94.20	–361	—	—	—
perchlorate	$KClO_4$	138.55	–433	–303	0.151	0.112
permanganate	$KMnO_4$	158.04	–837	–738	0.172	0.118
sulfide	K_2S	110.26	–381	—	—	—
Silicon	Si	28.09	0	0	0.019	0.020
dioxide	SiO_2 (quartz)	60.08	–911	–857	0.042	0.044
Sodium	Na	22.99	0	0	0.051	0.028
bicarbonate	$NaHCO_3$	84.01	–951	–851	0.102	0.088
carbonate	Na_2CO_3	105.99	–1131	–1044	0.135	0.112
chlorate	$NaClO_3$	106.44	–366	–262	0.123	—
chloride	NaCl	58.44	–411	–384	0.072	0.051
nitrate	$NaNO_3$	84.99	–468	–367	0.117	0.093
oxalate	$Na_2C_2O_4$	134.00	–1318	0	0.000	0.142
oxide	Na_2O	61.98	–418	–375	0.075	0.069
perchlorate	$NaClO_4$	122.40	–383	–255	0.142	—
Strontium	Sr	87.62	0	0	0.052	0.026
carbonate	$SrCO_3$	147.63	–1220	–1140	0.097	0.081
chloride	$SrCl_2$	158.53	–829	–781	0.115	0.076
nitrate	$Sr(NO_3)_2$	211.63	–978	–780	0.195	0.150
oxalate	SrC_2O_4	175.64	–1371	—	—	—
oxide	SrO	103.62	–592	–562	0.054	0.045

Table 1. Formula Weights and Thermodynamic Properties for Some Substances Relevant to Pyrotechnics (continued).

Chemical Name	Chemical Formula [a]	Formula Weight	$\Delta H_f°$ [b]	$\Delta G_f°$ [b]	$S°$ [b]	$C_p°$ [b]
Sulfur	S (rhombic)	32.06	0	0	0.032	0.023
dioxide	$SO_2(g)$	64.06	–297	–299	0.248	0.040
trioxide	$SO_3(g)$	80.06	–396	–371	0.257	0.051
Titanium	Ti	47.4	0	0	0.031	0.025
dioxide	TiO_2	239.19	–945	–890	0.050	0.055
Zinc	Zn	65.37	0	0	0.042	0.025
oxide	ZnO	81.36	–348	–318	0.044	0.040
sulfide	ZnS	97.43	–206	–201	0.058	0.046

[a] Unless otherwise indicated, these are crystalline solids. Gases are indicated as (g) and liquids as (l).

[b] Values are for 298.15 K, with units of kJ/mol.

Data are from references 4, 20 and 21. If data were inconsistent in the references, the most recent value is quoted. Data were rounded to the number of significant figures presented in the Table.

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Pyrotechnic Ignition and Propagation: A Review

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ABSTRACT

The ideal pyrotechnic is completely stable in storage and handling, yet performs its mission completely, with absolute reliability, upon demand. Many accidents in pyrotechnics are the result of unintentional ignitions during handling and storage. There can also be serious safety ramifications of ignition and propagation failures of pyrotechnic devices. This review chapter presents a fairly rigorous, but mostly non-mathematical discussion of the ignition and propagation processes.

Keywords: ignition, propagation, heat of reaction, activation energy, spontaneous ignition, thermal run-away, cook-off

Introduction

An understanding of the mechanism of pyrotechnic ignition and propagation will improve one's ability to identify and solve problems with ignition failures (duds) and unintended ignitions (accidents). In addition, many of these same principles play an important role in understanding the control of pyrotechnic burn rate. This chapter will examine these important topics thoroughly, however, not at a mathematically rigorous level. For more detailed and rigorous discussions, readers are referred to the writings of Merzhanov and Abramov.[1,2]

Pyrotechnic Reaction Energy Considerations

Pyrotechnic compositions are mixtures of fuel(s) and oxidizer(s) and often other materials. They are used to produce energy on demand in the form of heat, light, sound, etc. Pyrotechnic compositions are said to be in a "meta-stable" state. That is to say that under typical conditions they are stable and do not react to release their internal chemical energy unless externally stimulated in some way. Probably the most common stimulus is the addition of heat, such as provided by a burning match or fuse. Ignition is the process of stimulating a pyrotechnic composition to release its internal energy and can be defined as "the initiation of self-sustained burning or explosion of a pyrotechnic material".[3]

Figure 1 illustrates the process of ignition by graphing the internal energy of a tiny portion of pyrotechnic composition during the progress of its chemical reaction and is typical of non-spontaneous exothermic chemical reactions.[4] At the left of the graph, where the process begins, the pyrotechnic composition has a certain amount of internal energy. To accomplish ignition, external energy is supplied, such as from a burning match. This addition of energy increases the internal energy of the composition and is seen as a rise in the curve of Figure 1. This is indicated as the "Energy In" part of the reaction. As the process continues, eventually the pyrotechnic composition ignites to release its stored chemical energy to the surroundings. This loss of internal energy is seen as a drop in the curve of Figure 1 and is indicated as the "Energy Out" part of the reaction. The energy that was required to stimulate this release is commonly referred to as the "Activation Energy" (E_a). The net amount of energy produced by the pyrotechnic reaction is referred to as the "Heat of Reaction" (ΔH_r).[a]

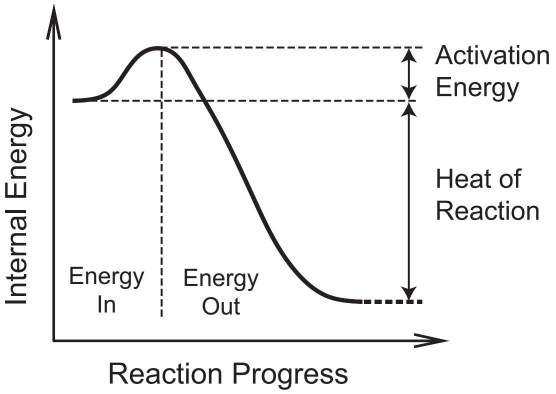

Figure 1. A graph illustrating the flow of energy into and out of a tiny portion of pyrotechnic composition.

Even the smallest particles of fuel and oxidizer in the pyrotechnic composition are clusters of many billions of atoms bound together to form the particle. It is possible to think of the two-step process—energy in and energy out—as first when old chemical bonds are being broken in the fuel and oxidizer, and second, when new chemical bonds are being formed to make the reaction products. This also helps to make it clear why the activation energy[b] requirement acts as a barrier that must be surmounted to initiate the chemical reaction. Until the necessary energy is supplied to break the original chemical bonds, thus freeing individual fuel and oxidizer atoms, they are not available to react with each other to form new chemical bonds.

In a pyrotechnic chemical reaction, a net amount of energy will be produced, providing the new chemical bonds being formed in the reaction products are stronger than the old bonds that must first be broken in the fuel and oxidizer. Table 1 lists the heat of reaction for some two-component (binary) pyrotechnic reactions. The reason that varying amounts of energy are produced is that in each case different numbers and strengths of chemical bonds are broken and formed.

Collections of atoms, such as those bound together in a particle of fuel or oxidizer, are not held in absolutely rigid positions. The individual atoms jostle about (vibrate), back and forth, and up and down. Because of these internal motions, the individual atoms possess energy, often referred to as thermal energy. In the process of jostling with one another, the atoms transfer some of their thermal energy from one to another. The net result of this jostling and energy sharing is that at any instant some atoms have much energy while others have little, and an atom that has much energy now, may have only a little energy later.

Figure 2 is a graph illustrating the distribution of the thermal energy[4] of individual atoms in fuel and oxidizer particles in a pyrotechnic composition at some temperature T_1. The curve goes through the origin of the graph, meaning that zero atoms have zero energy. Thereafter an increasing number of atoms have increasing energy, until a peak is reached, followed by a continuously decreasing number of atoms possessing higher and higher energies. Also shown in Figure 2 is the activation energy E_a that is required to initiate the pyrotechnic reaction. Note that the composition contains some atoms with energies exceeding the activation energy barrier. (In Figure 2 the number of atoms with energies greater than E_a has been exaggerated for clarity.)

Table 1. Heat of Reaction of Binary Pyrotechnic Compositions.[5a]

Fuel	(%)	Oxidizer	(%)	ΔH_r (kcal/g)
Magnesium	(37)	Potassium chlorate	(63)	2.29
Magnesium	(40)	Potassium perchlorate	(60)	2.24
Magnesium	(32)	Barium nitrate	(68)	1.65
Aluminum	(34)	Potassium perchlorate	(66)	2.45
Aluminum	(40)	Sodium nitrate	(60)	2.00
Aluminum	(25)	Iron(II) oxide	(75)	0.96

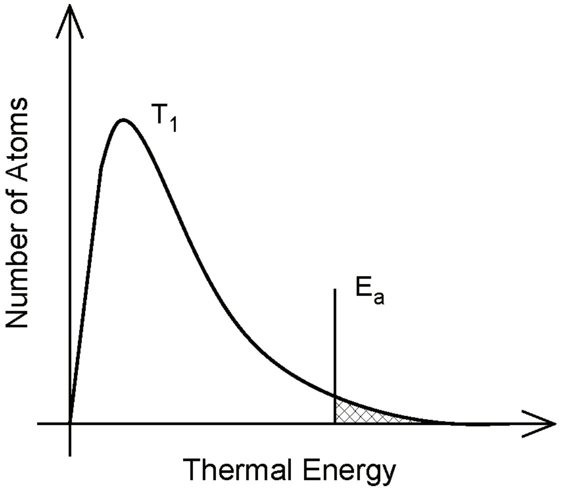

Figure 2. A graph illustrating the thermal energy distribution of atoms in a pyrotechnic composition.

Since some atoms in the pyrotechnic composition already have sufficient energy to react, the question should be "Why isn't the pyrotechnic composition reacting?" The answer is, "It is reacting, but only very, very slowly." To see why this is the case, consider the following: At room temperature, only one atom in roughly every million billion (10^{15}) has the needed activation energy to react.[6] Additionally, only the fuel atoms that are in direct contact with oxidizer atoms can react. The fraction of atoms in a tiny particle that are on its surface, combined with the fraction of those surface atoms that are in direct contact with the right atoms on the surface of other particles is roughly one atom in a million (10^6), thus only one atom in roughly every thousand billion billion (10^{21}) is capable of reacting at any given time. Accordingly, while reactions are taking place, the relative number of those reacting atoms is very, very small.

Thermal Run-Away

If the temperature of the pyrotechnic composition is raised, from T_1 (of Figure 2) to a higher temperature T_2, as illustrated in Figure 3, on average the atoms jostle around with more energy. More significantly, however, the number of atoms with energies exceeding the activation energy barrier increases greatly.[4] As a consequence, there are now many more atoms capable of reacting, and there is a corresponding increase in the rate at which the reactions occur. Recall, however, that these chemical reactions produce thermal energy; thus an increase in the reaction rate causes an increase in the rate of production of heat; which would seem to produce a further increase in temperature; which causes still more atoms to have energies exceeding the activation energy barrier; which causes a still greater increase in reaction rate and the rate of heat production; which causes a further increase in temperature; etc. This accelerating cyclic process is outlined in Figure 4 and leads to what can be called "thermal run-away" and ignition.

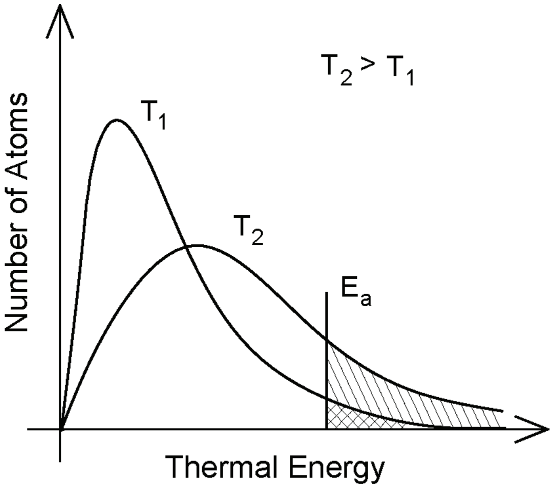

Figure 3. An illustration of the effect of increasing temperature on the distribution of the thermal energy of atoms.

Taken literally, the process outlined in Figure 4, suggests that the slightest temperature rise of a pyrotechnic composition will eventually lead to thermal run-away and ignition. Obviously, as common experience illustrates, this is not correct. The problem with the discussion thus far is that only the rate of thermal energy *production* has been considered, which is only half of the total picture. The rate of thermal energy *loss* from the pyrotechnic composition to the surroundings must also be considered. This more complete energy picture is presented in Fig-

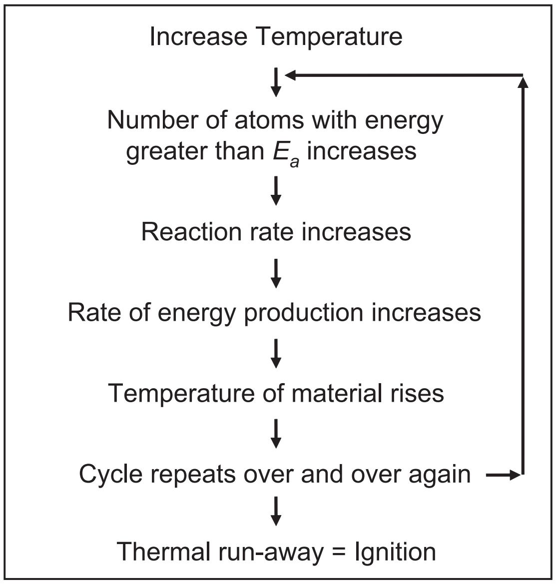

Figure 4. Outline of the accelerating cyclic process leading to thermal run-away and ignition.

ure 5, with both the heat-gain and heat-loss rate plotted as a function of temperature.

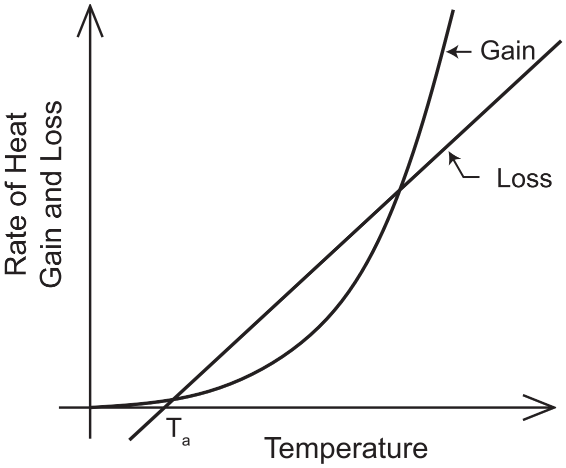

Figure 5. Graph illustrating the rate of heat gain and loss for a pyrotechnic composition as a function of temperature.

The rate (k) of a simple pyrotechnic chemical reaction follows an exponential relationship,[4] sometimes referred to as the Arrhenius equation:

$$k = Ae^{-E_a/RT} \tag{1}$$

where A and R are constants, and T is absolute temperature. The rate of heat gain Q_g is just the reaction rate multiplied by the heat of reaction:

$$Q_G = k \cdot \Delta H_r \tag{2}$$

Thus, in Figure 5, the rate of heat gain curve passes through the origin and rises exponentially (ever more steeply) with increasing temperature.

For a mass of pyrotechnic composition, heat loss from the surface will primarily be from convection through contact with the air. However, any heat generated internally, will first need to be conducted to the surface. Accordingly, for spontaneous heat generation, temperatures at the center of the mass would normally be highest.[c] The rate of heat loss Q_L from the center of the pyrotechnic composition depends on the thermal conductivity of the composition and any packaging, the convective heat loss coefficient, the geometry of the sample (or item), and the difference in temperature between the center of the composition T and ambient temperature T_a. This may be expressed as approximately:[7]

$$Q_L = C\,(T - T_a) \tag{3}$$

where C is a constant derived from the geometry and thermal properties of the pyrotechnic sample (or item). Accordingly, in Figure 5, the rate of heat loss curve is a straight line crossing the temperature axis at ambient temperature and with a slope equal to C.

To illustrate why, under typical storage conditions, pyrotechnic compositions are metastable and do not spontaneously ignite, as suggested by the process outlined in Figure 4, consider Figures 6 and 7. Figure 6 is an enlarged view of the low temperature region from Figure 5. If a pyrotechnic composition is formulated from materials at ambient temperature, the composition will be at the same temperature, at least initially. In Figure 6, note that at ambient temperature, the rate of heat loss is zero, while the rate of heat gain is greater than zero. Accordingly, the temperature of the sample will begin to increase. The temperature of the sample will continue to rise until the rate of gain and loss are equal. This occurs at the crossing point of the "gain" and "loss" curves, where the temperature of the sample T_s has risen to slightly above ambient temperature. (Note that in Figure 6, the temperature difference between T_a and T_s has been exaggerated for clarity.)[d]

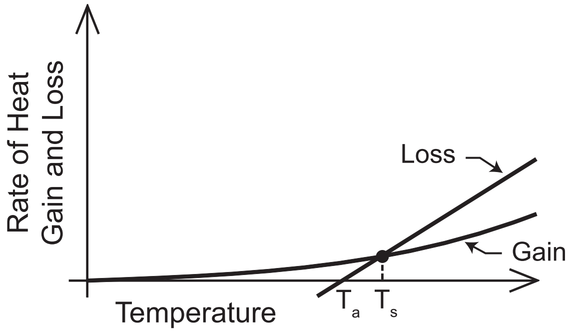

Figure 6. Enlarged view of the low temperature region of Figure 5.

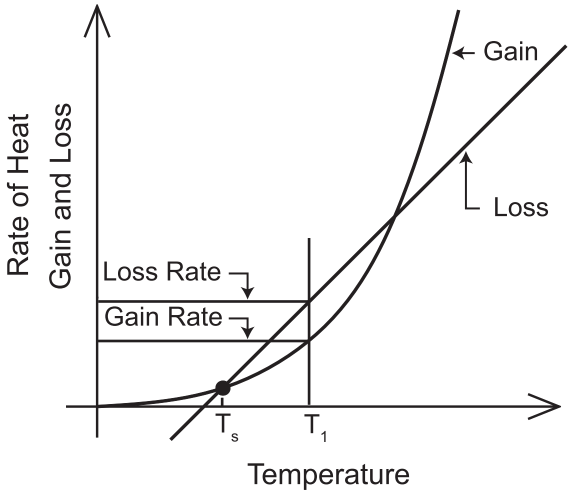

Figure 7. Illustration of the effect of a modest rise in temperature (T_1) of a pyrotechnic composition.

Now imagine that for some reason the pyrotechnic composition was momentarily raised from temperature T_s to T_1, somewhat further above ambient, see Figure 7. In this case, both the rate of heat gain in the pyrotechnic composition and the rate of heat loss from the composition increase. However, the rate of loss is greater than the rate of gain. Accordingly, the net effect will be a loss of thermal energy with time. The temperature of the composition will decrease and must continue to fall to the temperature where the rates of loss and gain are equal (at temperature T_s). From the this discussion, it can be seen that pyrotechnic compositions are at least meta-stable, in that any small addition of energy will not ultimately cause thermal run-away and ignition.

Figure 8 shows that if the temperature of the pyrotechnic composition were raised momentarily to a still higher temperature T_2, that the result would be quite different. In this case, again both the rate of heat gain and the rate of heat loss increase. However, this time the rate of gain has overtaken the rate of loss. Thus at this temperature, there is a net accumulation of heat, producing a further increase in temperature. In fact, this is an ever-accelerating process, because as the temperature increases, the rate of gain increases much faster than the rate of loss. In this case, the process outlined in Figure 4 does apply and leads to thermal run-away and ignition.

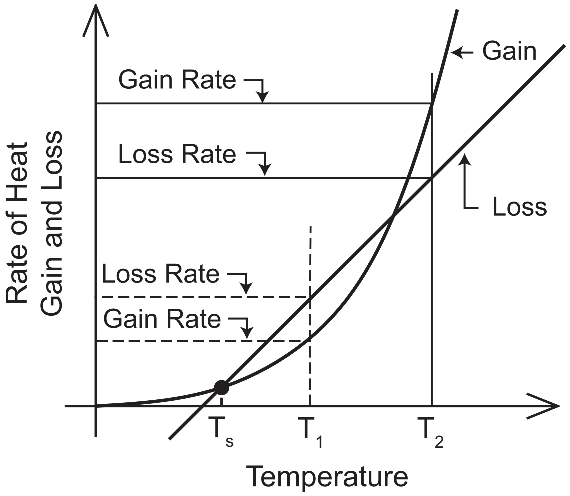

Figure 8. Illustration of the effect of a substantial rise in the temperature (T_2) of a pyrotechnic composition.

Thermal Run-Away Temperature[e]

Obviously, the temperature at which thermal run-away can occur for each pyrotechnic composition is of great importance from a safety standpoint. Whenever a pyrotechnic composition is raised above this temperature, it will begin to undergo thermal run-away and will eventually ignite spontaneously. In Figure 9, the run-away temperature is designated as T_r and is the temperature corresponding to where the gain and loss curves cross for the second time. For any composition, this temperature could be established experimentally (with some effort) or mathematically (providing the gain and loss relationships are known).

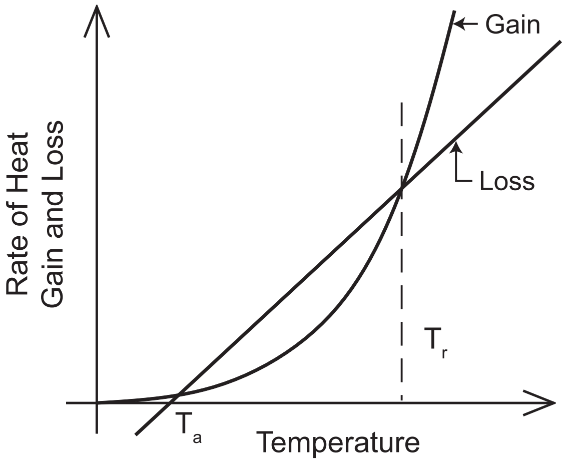

Figure 9. Illustration of the thermal run-away temperature of a pyrotechnic composition, under one set of conditions.

From equations 1 and 2 it can be seen that the rate of heat gain depends on the activation energy and the heat of reaction, which are determined by the formulation of the pyrotechnic composition. The heat of reaction is easy to calculate, providing one knows the equation for the chemical reaction,[5b] or it can be determined experimentally.[5c] Determination of activation energy must be established through experimentation.[9,10] From equation 3, as expressed by the constant *C*, it can be seen that the rate of heat loss depends on the thermal conductivity, the convection coefficient and geometry of the composition, and on ambient temperature. All of these parameters can be determined with only modest effort. However, the rate of heat loss depends on many things other than the pyrotechnic formulation. For example, the degree of compaction of the composition, the size (mass) of the item or sample, and the packaging of the composition all affect the thermal conductivity of the composition or item. Also, the rate of heat loss is a function of ambient temperature. Thus, for each pyrotechnic formulation there is not just one thermal run-away temperature, rather there is one for each of an infinite number of different sets of conditions. This illustrates the problem in trying to use thermal run-away temperature to characterize a pyrotechnic formulation.

Spontaneous Ignition Due to Thermal Run-Away

Even though the use of thermal run-away temperature as a way of characterizing pyrotechnic compositions is of limited value, the concept is important because it helps to identify some potentially dangerous conditions where there will be delayed spontaneous ignitions. For example, Figure 10 illustrates the effect of varying sample size. Note that the rate of heat gain (per gram of composition) is unaffected by sample size, but the rate of heat loss is sample-size dependent. Small samples generally lose heat easily and have a rate of heat-loss curve that is steep, with two crossing points, the higher of which is the thermal run-away temperature. As the sample size increases (medium sample size in Figure 10), the slope of the heat loss curve decreases, lowering the run-away temperature more and more with increasing sample size. At some point, for a large sample, there will only be a single point of contact between the curves. This represents the largest sample, under a specific set of conditions, that theoretically will not spontaneously run-away thermally and ignite. For samples larger than this, the rate of heat gain is always more than the rate of loss, and the sample will always run-away thermally. It may take a very long time, but for large enough samples, eventually, there must always be a spontaneous ignition.

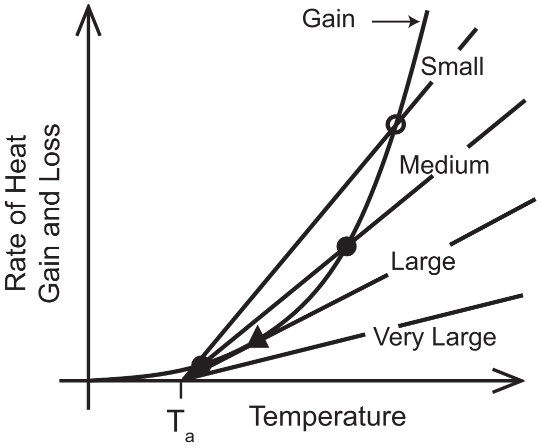

Figure 10. An illustration of the effect of increasing sample size on the rate of heat loss and therefore on thermal run-away temperature.

The rate of heat loss is sample-size dependent because sample size is one factor that affects the constant *C* in equation 3. Another factor is the thermal conductivity of the pyrotechnic composition and its packaging. In Figure 10, poorly conducting compositions and insulating packaging produce effects equivalent to a large sample size.

A somewhat similar situation arises for increasing ambient temperature, see Figure 11. When the ambient temperature is low (T_{a1}), samples lose heat to the surroundings fairly easily. This places the heat-loss rate curve fairly high on the heat-gain curve, producing two crossing points, the higher of which is the thermal run-away temperature. As the ambient temperature increases, it becomes more difficult for the sample to lose heat. The slope of the heat-loss curve is unchanged, but its position relative to the heat-gain curve is lower. This lowers the run-away temperature more and more with increasing ambient temperature. At some point, for high enough ambient temperature, there will only be a single point of contact between the curves. This represents the highest ambient temperature, for this type and size of sample, that will not spontaneously run-away thermally (ignite). For ambient temperatures greater than this, the rate of heat gain is always more than the rate of heat loss, and the sample will always run-away thermally. It may take a long time, but, for such hot ambient conditions, there will eventually be a spontaneous ignition.

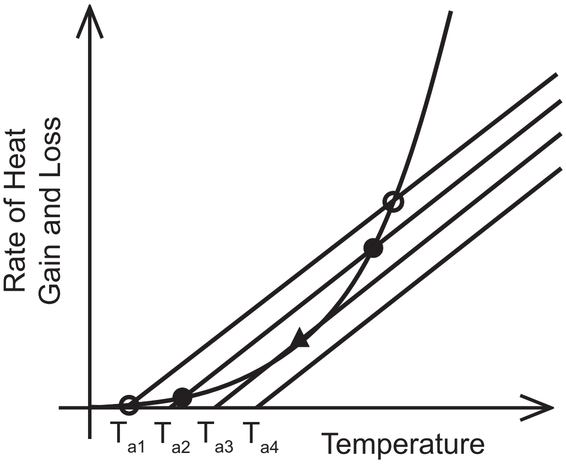

Figure 11. An illustration of the effect of increasing ambient temperature on the rate of heat loss and therefore on thermal run-away temperature.

Just how large a sample and just how high an ambient temperature are required for thermal run-away and spontaneous ignition depends on the chemical formulation and the conditions of its packaging and storage. For some compositions under favorable conditions, it may require a tremendous quantity of material, and it may take an exceptionally long time to run-away and spontaneously ignite. However, under more extreme conditions, or for other compositions, small samples of composition may ignite quickly.

Time to Ignition, "Cook-Off" Tests

The time for any given pyrotechnic composition or device to ignite is a function of the temperature to which it is exposed, as illustrated in Figure 12. If a sample is placed in an oven, its temperature will begin to rise, eventually reaching the temperature of the oven. If the temperature of the oven T_1 is less than the run-away temperature for the pyrotechnic composition, the sample will never ignite (i.e., the time to ignition is infinite).

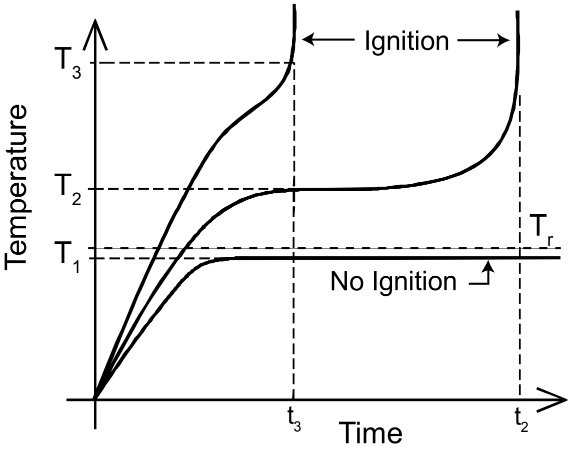

Figure 12. An illustration of the dependence of time to ignition on the temperature to which a pyrotechnic composition is heated.

Suppose the temperature of the oven is increased to T_2, slightly higher than the run-away temperature. Upon placement in the oven, the sample will start to heat up and will eventually rise to the temperature of the oven. For a while, it may appear that nothing is happening with the sample. However, inside the sample, heat is slowly accumulating, raising the temperature, at first perhaps imperceptibly. As the internal temperature rises, the rate of reaction increases, increasing the rate of heat gain, and further increasing the temperature (i.e., thermal run-away has begun). As a result of this ever accelerating process, the internal temperature rises ever more rapidly, until eventually there is an ignition, at time t_2 in Figure 12.

Now suppose the temperature of the oven is increased to T_3, significantly higher than the run-away temperature. Upon placement in the oven, the sample again will heat up, approaching the oven temperature. However, under these conditions, the sample's temperature rise may not slow very much as it reaches the oven temperature, before thermal run-away is at an advanced state with ignition occurring more quickly at time t_3.

Determining the time to ignition, as a function of temperature, has important ramifications for the storage of pyrotechnics (and explosives). If one were to guess wrong, the consequences of an accidental spontaneous ignition could be disastrous. Tests performed to discover the time-to-ignition and temperature relationship are sometimes called "cook-off" tests.[11] In these tests, samples or items are typically placed in a heated bath, after having thermocouples installed internally. Bath and sample temperatures are monitored as a function of time from the start of the test, and the time to ignition or explosion (if either occurs) is recorded.

Ignition and Ignition Temperature

Ignition is one of the more difficult terms to define in pyrotechnics. Obviously it cannot be defined as when chemical reactions start. As was discussed earlier, some pyrotechnic reactions are occurring all the time, although at a very, very low rate. Even after the thermal run-away temperature has been reached, there may be no obvious sign anything is happening. For most observers, the appearance of a flame (high temperature radiant gases) or at least obvious incandescence of the solid phase is taken as the indication that ignition has occurred. As suggested in Figure 12, at the time of ignition very rapidly accelerating reaction rates produce a near instantaneous rise in temperature, typically from several hundred to two thousand degrees Celsius or higher. Thus, the physical manifestations of ignition develop very rapidly as ignition is occurring.

Ignition temperature can be defined as "the minimum temperature required for the initiation of a self-propagating reaction".[12a] However, from the above discussion, that temperature can vary widely depending on sample conditions and on how long one is willing to wait for the ignition to occur. These problems are mostly eliminated for ignition temperature measurements, because the conditions and delay time are usually specified in the procedure to be used. Unfortunately, there are many different procedures that are used; the *Encyclopedia of Explosives*[13] alone lists 14 different methods. This means there can be many more than one ignition temperature reported for the same pyrotechnic composition, depending on which method was used. Fortunately, the various ignition temperatures of the most commonly used methods all tend to be in the same general range, primarily because the measurement conditions of the various methods tend to be somewhat similar.

Obviously, however, the most consistent results will be achieved if all measurements are made using the same method. When evaluating reported ignition temperature data, it is useful to know which method has been used. Three hot bath methods and one differential thermal analysis method are described in the following paragraphs.

Hot Bath Method One: Ignition temperature is the lowest temperature of a bath of Wood's metal,[f] to within 5 °C, that results in ignition within 5 minutes for a 0.1 g sample in a preheated small glass test tube inserted 1/3 its length into the bath.[5a]

Hot Bath Method Two: Ignition temperature is the temperature of a bath of Wood's metal that results in ignition in 5 seconds (determined graphically using time to ignition data) for a 1.0 g sample in a thin-walled brass or copper tube (typically a No. 6 detonator shell).[10]

Hot Bath Method Three: Ignition temperature is the temperature of a bath of Wood's metal, heated at a rate of 5 °C per minute, at which ignition occurs for a 0.5 g sample in a tightly corked glass test tube (125 mm long by 15 mm inside diameter with a 0.5 mm wall thickness).[13]

Differential Thermal Analysis Method: Ignition temperature is the temperature of onset of the ignition exotherm for a 10 to 100 mg sample heated at a rate of 50 °C per minute.[14]

A collection of ignition temperatures for a series of two-component, stoichiometric pyrotechnic compositions are presented in Table 2. Shidlovskiy reports the method as one using an electric furnace instead of a bath of Wood's metal. Unfortunately, he provides no other information on the method, other than an estimate of the accuracy of the results to be within 10 °C. (This data was chosen for inclusion because it was the most systematically complete set of data readily available to the authors.)

It might be of interest to note that a typical pyrotechnic composition raised to its ignition temperature will have about 30 million times more atoms with energies exceeding E_a than at room temperature.[6]

The Effect of Melting and Tammann Temperature

For a pyrotechnic reaction to occur, the atoms (or molecules) must have the required activation energy, and they must be in direct contact with another atom of the correct type. Even for well-mixed solid particles, there are relatively few points of contact between individual particles; see the top illustration of Figure 13. Thus, the number of fuel and oxidizer atoms that are in contact with one another is normally quite small. However, if one of the components melts to flow around the surfaces of the other particles, there is a great increase in the number of atoms now in contact; see the bottom illustration of Figure 13.

Accordingly, melting can have a significant effect on the likelihood of ignition. The potential effect on ignition is outlined in Figure 14. If the percentage of atoms in physical contact increases upon the melting of one component, then more atoms with energies exceeding the activation-energy barrier will then be in contact with one another. That means the reaction rate will then be greater, and with it the rate of production of thermal energy, which means that thermal run-away and ignition can occur at a lower temperature than if melting had not occurred. Thus, it is suggested that if a composition is nearing its ignition temperature, and one component of the composition melts, that could result in ignition occurring at that lower tem-

Table 2. Ignition Temperatures for Binary Pyrotechnic Compositions.[5c]

	Ignition Temperature (°C)				
Oxidizer	Sulfur	Lactose	Charcoal	Mg powder	Al dust
Potassium chlorate	220	195	335	540	785
Potassium perchlorate	560	315	460	460	765
Potassium nitrate	440	390	415	565	890

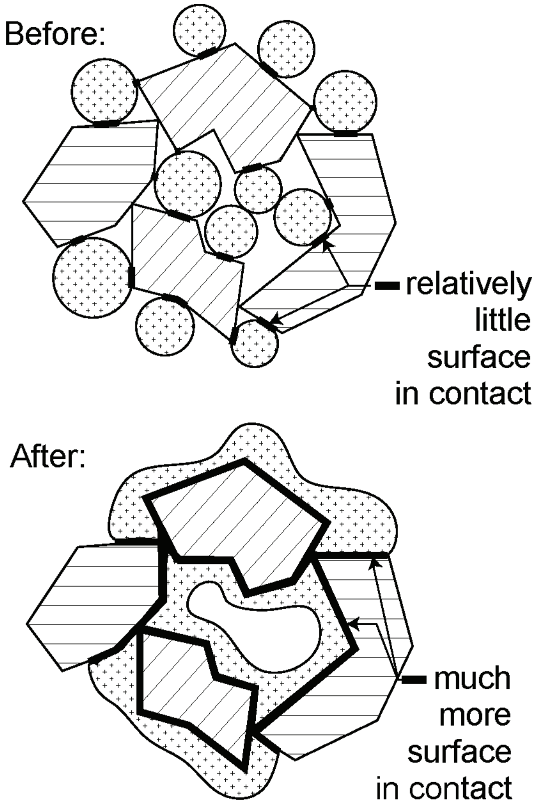

Figure 13. An illustration of the great increase in contact between fuel and oxidizer after one component melts.

Melting of one component
↓
The percentage of atoms in physical contact increases
↓
More atoms with energies exceeding E_a are in contact and will react
↓
Rate of reaction increases
↓
Rate of energy production increases
↓
Thermal run-away (ignition) occurs at a lower temperature

Figure 14. Outline of the effect of one component melting on the process of ignition.

perature. For example, the melting point of potassium nitrate and the ignition temperature of Black Powder are effectively the same.[12b]

Melting can be thought of as occurring when the thermal vibrations of a solid are so strong that many of the bonds, which had been holding the solid together, are broken. While for most pure chemicals melting has a sudden onset at a specific temperature, the vibrations of the atoms in the solid become increasingly strong as the temperature is increased toward the melting point. This can be thought of as the loosening of the bonds holding the solid together. It has been suggested that at an absolute temperature halfway to the melting point, the bonds become so loose that there can be a significant commingling of the atoms of different particles that are in direct contact.[8b] This temperature is called the Tammann temperature after the researcher making this observation.

Tammann temperatures are of interest because samples at or above these temperatures demonstrate significantly increased sensitivity to accidental ignition. Table 3 lists the Tammann temperature for some common pyrotechnic oxidizers.

Table 3. Tammann Temperature for Common Pyrotechnic Oxidizers.[12c]

Oxidizer	Tammann Temperature (°C)
Sodium nitrate	17
Potassium nitrate	31
Potassium chlorate	42
Strontium nitrate	149
Barium nitrate	160
Potassium perchlorate	168
Lead chromate	286
Iron(III) oxide	646

Propagation and the Propagation Inequality

Having successfully ignited a pyrotechnic composition is no guarantee that the reaction will propagate throughout it. This is because the application of an external stimulus, such as a flame, typically provides thermal energy to only a small portion of the composition, and the ignition stimulus is usually of relatively short duration. After its application, the pyrotechnic combustion reaction will continue to propagate through the composition only so long as the pyrotechnic reaction itself provides sufficient energy to the unreacted composition. What is needed is sufficient energy to raise the unreacted composition above its ignition temperature. This process is illustrated in Figure 15. The portion of the rod of pyrotechnic composition to the extreme right has already been consumed by burning. Just to the left of that is a thin disk of composition that has ignited and is still reacting (burning). Just left of that is another thin disk of composition, labeled "pre-reacting material", which has not yet ignited. This disk of pre-reacting material will only ignite if it is raised above its ignition temperature, which means that a significant number of its atoms and molecules will have received at least the required activation energy E_a.

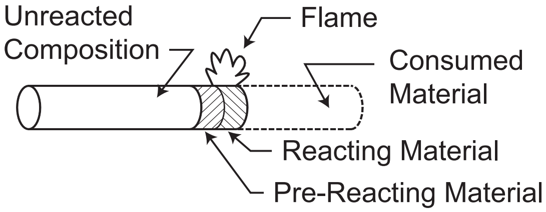

Figure 15. Illustration of a propagating rod of pyrotechnic composition.

Most of the energy being produced by the reacting material (the heat of reaction ΔH_r) is lost to the surroundings. However, some fraction of the energy (F_{fb}) will be fed back from the reacting layer to the pre-reacting layer. The actual amount of energy fed back is just the product of the heat of reaction and fraction that is fed back (i.e., $\Delta H_r \cdot F_{fb}$). Propagation will occur providing more energy is fed back than is required for ignition of the pre-reacting disk of composition. This statement, then, gives rise to something that could be called the "propagation inequality"

$$\Delta H_r \cdot F_{fb} > E_a \tag{4}$$

As long as this relationship holds true, propagation will continue.

Obviously, the probability of successful pyrotechnic propagation is increased by anything that results in more energy being produced by the burning composition, a greater percentage of that energy being fed back, or a reduction of the activation energy requirement. The heat of reaction and the activation energy are determined by the chemical nature of the composition; unfortunately, a thorough discussion is beyond the scope of this chapter.[g] Energy is fed back to the pre-reacting layer through any combination of conduction, convection, or radiation. These are more fully considered in Figure 16, where some of the factors increasing the efficiency of these mechanisms are also presented.

Figure 17 is similar to Figure 15 but provides a more compete description of the propagation process, including information on the relative temperatures expected. Zone (**a**) is unreacted pyrotechnic composition, which has thus far been unaffected and remains at ambient temperature. Zone (**b**) is described as the warm-up zone, where the temperature has started to rise above ambient, primarily as a result of thermal conduction. It is in this zone where reaction rates are first beginning to increase. These reactions are sometimes referred to as "pre-ignition reactions",[8c][h] and contribute some thermal energy. In Zone (**c**), the temperature has risen significantly, at least one component of the composition has melted, and some gaseous material may be bubbling to the surface. Because of the rise in temperature and the greatly increased contact between fuel and oxidizer, the reaction rate in Zone (**c**) and the production of heat is greatly increased. By any definition, Zone (**c**) is considered to have ignited. In Zone (**d**), much of the reaction is occurring in the gas phase; however, some droplets of reacting composition ejected from the surface may still be present. Again the reaction rate and the thermal energy being produced have increased substantially from the previous zone, and the temperature has peaked. Zone (**d**) is the inner portion of the flame envelope. In the final region, Zone (**e**), the energy producing reactions have ceased, and

Conduction:

- **Thermal energy (molecular vibration) is conducted along solids from hotter to cooler.**
- **Factors maximizing conductive feedback:**
  - **Compacted composition**
  - **Metal fuels**
  - **Metal casing or core wire**

Convection:

- **Hot gases penetrate the solid composition along spaces between grains (fire paths).**
- **Factors maximizing convective feedback:**
  - **Uncompacted composition**
  - **Granulated composition**
  - **Cracks in composition**

Radiation:

- **Thermal (infrared) radiation, emitted from flame and glowing particles, is absorbed by incompletely reacted composition.**
- **Factors favoring radiative feedback:**
  - **Solid or liquid particles in flame**
  - **Dark or black composition**

Figure 16. Outline describing the mechanisms of pyrotechnic energy feedback and some of the factors that enhance their effectiveness.

because of heat loss to the surroundings, the temperature begins to fall significantly.

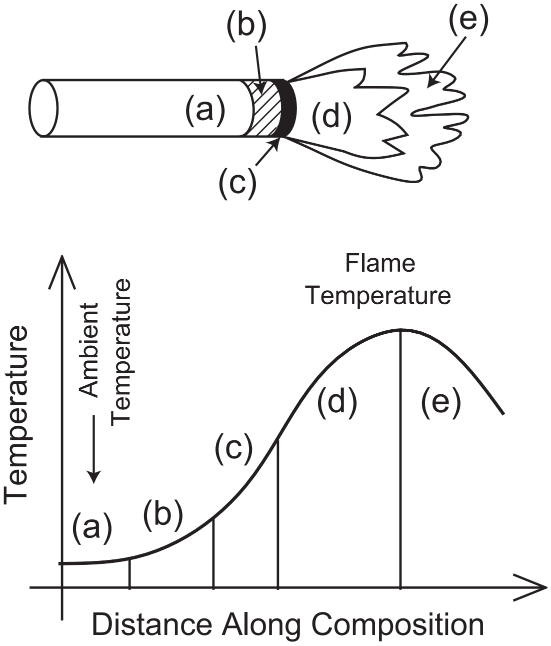

Figure 17. A more complete description of the processes of pyrotechnic propagation:
*(**a**) unreacted composition; (**b**) warm-up zone; (**c**) condensed phase reactions; (**d**) gas phase reactions; and (**e**) reactions complete.*
(Based on reference 5d.)

Conclusion

The subjects of ignition and propagation could have been dealt with much more expeditiously. Specifically, it could simply have been stated that ignition requires raising at least a portion of a pyrotechnic composition to its ignition temperature, and that propagation requires the feed back of sufficient energy for continuing self-ignition of the composition. However, while this would have saved much time, it would have provided little understanding of the important principles involved. Accidents caused by unintentional ignitions continue to plague the pyrotechnics industry. In addition, ignition failures with pyrotechnic devices, whether leaving an unfired-aerial shell in a mortar that needs to be cleared or resulting in a dud device on a battle field, have serious potential for accidents as well. Ignition or propagation failures with signaling smokes or flares may cause someone to not be rescued. It is through a more thorough understanding of the basis for ignition and propagation, that pyrotechnists will be better able to solve potential problems before accidents occur.

Acknowledgments

The authors gratefully acknowledge the technical and editorial assistance of J. Domanico and L. Weinman in the preparation of this chapter.

Notes

[a] More recent usage of this term is "Enthalpy of Reaction".

[b] The use of the term "activation energy" in the context of solid-phase pyrotechnic compositions has a slightly different meaning than in aqueous or gas-phase chemistry. In aqueous and gas-phase chemistry, molecules can be thought of as reacting individually or at least in small groups. In that case, activation energy can be thought of as the amount of energy needed for a collision between two individual molecules to cause them to react. However, a typical pyrotechnic composition is composed of solid particles of fuel and oxidizer, with each particle comprised of many billions of atoms or molecules. In this case, activation energy takes on much more of a macroscopic and less precise meaning. For the purpose of this chapter, activation energy of solid-phase pyrotechnic compositions is generally taken to mean that amount of thermal energy needed to induce a sustained exothermic reaction within a tiny portion of the composition.

[c] Pyrotechnic compositions, especially those of dark color that are exposed to bright sunlight may be an exception to the generalization about the highest temperature expected to be in the middle of the composition.

[d] Note that it is assumed the composition is physically at rest (i.e., it is not being mixed, which adds energy to the system).

[e] In some texts thermal run-away temperature is called the critical temperature[1] or the reaction temperature.[8a]

[f] Wood's metal is a eutectic alloy of bismuth, lead, tin and cadmium. It melts at 70 ºC.

[g] Some oxidizers are known for producing compositions with low activation energies (e.g., chlorates), while other oxidizers tend to produce compositions with especially high activation energies (e.g., oxides and sulfates). Fuels with low melting points or low decomposition temperatures (e.g., sulfur, lactose and acaroid resin) tend to form compositions with low activation energies. Metal fuels tend to produce compositions with high heats of reaction.

[h] Pre-ignition reactions are typically reactions taking place in the solid state. While such reactions can be a source of energy, they generally only contribute in a minor way to promoting ignition. In part, this is because solid-state reaction rates are constrained by the difficulty of fuel and oxidizer commingling while both remain solid.

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Control of Pyrotechnic Burn Rate

B. J. and K. L. Kosanke

ABSTRACT

There may be many times when a fireworks manufacturer will want to adjust the burn rate of pyrotechnic compositions. Sometimes this may be for matters of aesthetics and other times for safety. For example, all of the following are unacceptable:

Strobe stars that flash with so low a frequency that they fall to the ground still burning.

- *Color stars that burn so rapidly that they occasionally explode when a shell flowerpots.*
- *Rockets that fail to lift-off because their thrust is too low.*
- *Rockets that explode upon firing because internal pressures exceed the casing strength.*
- *Salutes that burn like fountains instead of exploding with violence.*
- *Flash powder that explodes when unconfined, even in small quantity.*

In each case, taking action to adjust burn rate should solve the problem.

Depending somewhat on how they are counted, there are at least 15 factors that control pyrotechnic burn rate. A manufacturer that understands how these factors act to affect burn rate may better anticipate when product performance difficulties will occur. Also, such a manufacturer will be better prepared to modify product formulations to correct any problems that do occur.

Each burn rate control factor acts by affecting one or more of the following: activation energy, heat of reaction, and efficiency of energy feedback. In this paper, the 15 factors are presented, explained and examples given.

Introduction

In the burning of most pyrotechnic compositions it is necessary to balance competing processes to achieve the maximum desired effect. For example, when the burst charge of an aerial shell burns too slowly, the result can be a weak and asymmetric shell burst that fails to properly disperse the stars. However, conversely when the burst charge of an aerial shell burns too quickly, the result can be a shell burst that is so powerful as to cause many of the stars to fail to ignite. In addition to aesthetic ramifications, safe performance can also require a balance between too little and too much output. For example, when the thrust produced by a fireworks rocket is too low, the result can be an explosion of the rocket at ground level because the rocket failed to fly into the air. Conversely, when the thrust is too high, the result can again be an explosion at ground level because the internal pressure exceeded the strength of the motor casing.

One mechanism, useful in adjusting pyrotechnic output, is the control of burn rate. Burn rate determines the rate of gas production from a burst charge or a propellant, and thus the rate of pressure rise and peak pressure within a star shell, and the thrust from and internal pressure within a rocket motor. Accordingly, an understanding of the ways in which burn rate can be adjusted can be useful in modifying pyrotechnic formulations to maximize their performance and safety. In this chapter, after a brief theoretical discussion, which forms the basis for understanding how each factor acts to modify burn rate, 15 factors that affect burn rate are presented, discussed and examples given.

Pyrotechnic Ignition

Pyrotechnic materials are said to exist in a "meta-stable" state. That is to say, under normal circumstances they are stable (they do not spontaneously ignite); however, once ignited, the combustion reaction is self-sustaining, producing an excess of thermal energy. The reason pyrotechnic materials do not spontaneously ignite under normal conditions is that ignition requires the input of energy into the composition. Once ignited, however, the pyrotechnic material burns thus producing energy. This two step energy relationship is illustrated in Figure 1, which is an attempt to graph the internal energy of a tiny portion of pyrotechnic composition during its ignition and burning. The first step, when energy is added to the composition to cause its ignition, is seen as an increase in the internal energy of the material. Within the formalism adopted for this chapter, the minimum energy required for ignition is called the "activation energy" for the pyrotechnic composition and is abbreviated as E_a. The requirement for the input of energy, to ignite a pyrotechnic material, is what allows pyrotechnic compositions to be safely made and stored prior to use. If it were not for this activation energy barrier, fuels and oxidizers would ignite on contact. In the simplest of terms, it is possible to think of the required addition of energy as what is needed to raise the material to its ignition temperature. The second step, when the burning composition produces energy, is seen as a decrease in internal energy. The net amount of energy produced during burning is the "heat of reaction" for the composition and is abbreviated as ΔH_r.

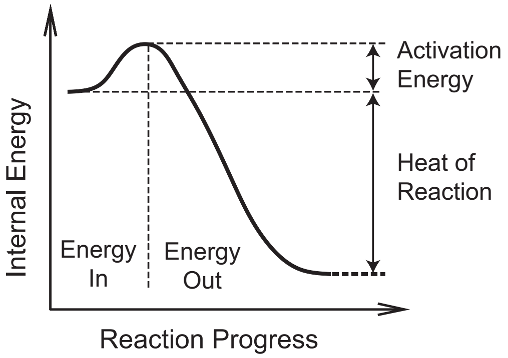

Figure 1. Changes in internal energy as a pyrotechnic composition ignites and burns.

In terms of chemistry, the process of ignition and burning can also be considered a two step process. The first step can be thought of as when chemical bonds are being broken between the individual atoms in particles of fuel and oxidizer. This requires the input of energy, the activation energy. In the second step, new chemical bonds are formed between fuel and oxidizer atoms. This produces energy that flows from the chemical system, the heat of reaction. If the new chemical bonds (fuel to oxidizer) are stronger than the original bonds, there will be a net production of energy. Note that for pyrotechnic materials, the bonds within fuel and oxidizer particles tend to be weaker than those new bonds formed during burning. This is the reason these materials are effective energy producers.

In the simplest of terms, pyrotechnic propagation can be thought of as continuing self-ignition. Consider Figure 2, which is a sketch of a stick of pyrotechnic composition, it can be thought of as a series of thin disks of material. The end disk, designated as reacting material, has received the needed activation energy and ignited. As this layer of material burns, it produces energy, most of which is lost to the surroundings. However, some of the energy is transferred to the next disk, designated as pre-reacting material. If the amount of energy delivered to the pre-reacting layer exceeds its activation energy requirement, then it too will ignite and burn. If this process is repeated for each succeeding disk of composition, then the burning will propagate through the entire stick of pyrotechnic material.

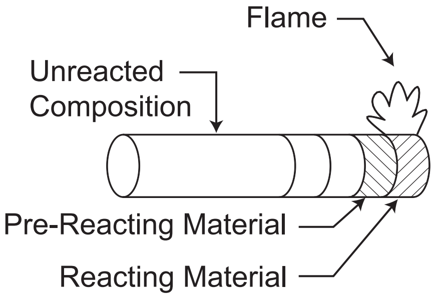

Figure 2. Burning "propagating" along a stick of pyrotechnic composition.

It is possible to quantify the requirement for propagation in what could be called the "propagation inequality". Propagation within a pyrotechnic composition will continue only so long as the amount of energy fed back to the next layer (E_{fb}) exceeds its activation energy requirement, i.e.,

$$E_{fb} > E_a \quad (1)$$

The amount of energy fed back equals the heat of reaction times the fraction of energy fed back (F_{fb}), i.e.,

$$E_{fb} = \Delta H_r \cdot F_{fb} \quad (2)$$

Thus the propagation inequality becomes,

$$\Delta H_r \cdot F_{fb} > E_a \quad (3)$$

So long as the inequality is met, a pyrotechnic composition will propagate. However, if anytime during its burning the inequality fails to be met, burning will cease at that point.

There are three mechanisms by which energy can be transferred from the reacting layer to the pre-reacting layer: conduction, convection and radiation. In conduction, thermal energy, as atomic and molecular vibrations, is passed along from hotter to cooler regions. The factors maximizing conductive heat transfer include compacted composition, metallic fuels, and metal casings or core wires. In convection, hot gases penetrate the composition along the spaces between grains (called "fire paths"). The factors maximizing convective heat transfer include uncompacted composition and granulated or cracked composition. In radiation, thermal (infrared) radiation is emitted from the flame (mostly from incandescent particles in the flame) and is absorbed by the reacting composition. The factors maximizing radiative heat transfer include abundant solid and liquid particles in the flame and dark or black pyrotechnic composition.

Given the relationship in equation 3, it is clear that the factors favoring propagation are: high heat of reaction (much heat produced), a relatively large fraction of energy fed back (efficient energy feedback), and low activation energy (low ignition temperature). When the propagation inequality is just barely met, burning proceeds feebly and is easy to extinguish. When the inequality is abundantly met, the burning proceeds fiercely and is difficult to extinguish.

Factors Controlling Burn Rate

Burn rates are reported as either mass burn rate or linear burn rate, with units of either the mass consumed per unit time (e.g., grams per second) or the distance the flame front progressed per unit time (e.g., centimeter per second). In this chapter, unless stated to the contrary, the term burn rate will mean linear burn rate.

There are at least 15 factors known to affect the burn rate of pyrotechnic compositions. These are listed in Table 1. For each factor listed, the change in burn rate is produced by chemical effects, physical effects, or both. More specifically, the most important of these effects are the three terms in the propagation inequality: activation energy (E_a), heat of reaction (ΔH_r), and the fraction of energy fed back, (F_{fb}). High burn rates are generally favored by any combination of low activation energy, high heat of reaction and efficient energy feedback. Low burn rates tend to be the result of the opposite in each case. Table 1 also suggests which of the three mechanisms typically predominate for each burn rate controlling factor. This is indicated with an "X" in the appropriate column(s).

The remainder of this chapter is a discussion of how each of the 15 factors acts to affect burn rate. Included in Table 1 is a designation of the subsection of this chapter where that discussion can be found. It must be acknowledged, however, that some explanations have been greatly simplified, and less common situations may not have been addressed. Also, in these discussions, at times the concept of activation energy may be more of a construct used to help explain, rather than being treated rigorously on a scientific level. For additional information about ignition and pyrotechnic burning, the reader is referred to previous articles of the authors[1–3] and one or more of the standard reference texts on pyrotechnics.[4–7]

A) Choice of Fuel and Oxidizer

The choice of fuel(s) and oxidizer(s) can significantly affect activation energy, heat of reaction and the efficiency of energy feedback. Accordingly, the selection of fuel and oxidizer has the potential for having a major influence on pyrotechnic burn rate.

Table 1. Factors Controlling Burn Rates of Pyrotechnic Compositions.

Controlling Factor	E_a	ΔH_r	F_{fb}	Section
Choice of fuel and oxidizer	X	X	X	A
Fuel to oxidizer ratio		X		B
Degree of mixing		X		C
Particle size	X			D
Particle shape	X			E
Presence of additives	X	X	X	F
Presence of catalysts	X			G
Ambient temperature	X			H
Local pressure			X	I
Degree of confinement			X	J
Physical form			X	K
Degree of consolidation			X	L
Geometry			X	M
Crystal effects	X		X	N
Environmental effects	X	X	X	O

Regarding activation energy, a significant consideration is the amount of energy required for an oxidizer to make its oxygen available to react with the fuel. Some oxidizers require input of a large amount of energy, while others actually produce energy in the process of releasing their oxygen. This can be seen in Table 2 where the decomposition energy for a few common oxidizers is listed. (Note: A negative number indicates that an input of energy is necessary, while a positive number means that energy is produced during decomposition.)

Table 2. Decomposition Energy for a Few Common Pyrotechnic Oxidizers.

Oxidizer	Product	Enthalpy of Decomposition (kJ/g)	Ref.
KNO_3	K_2O	6.3	4
Fe_3O_4	Fe	4.8	4
$Ba(NO_3)_2$	BaO	1.7	4
$KClO_4$	KCl	-0.036	4
$KClO_3$	KCl	-0.36	8

Regarding heat of reaction, when fuels combine with oxygen, different numbers and strengths of chemical bonds are formed. This can significantly affect the amount of energy produced by the combustion reaction. Table 3 lists heat of reaction for some common fuels combining with oxygen.

Table 3. Heat of Reaction for Some Common Fuels Reacting with Oxygen.

Fuel	Product	Heat of Combustion (cal/g)	Ref.
Al	Al_2O_3	7400	9
Mg	MgO	5900	9
Dextrin	H_2O, CO_2	4200	9
PVC	(a)	3350	10
S	SO_2	2200	9

(a) Products are CO_2, HCl, and H_2O.

Regarding the efficiency of energy feedback, recall that energy can be fed back from reacting to unreacted material by conduction, convection and radiation. The choice of chemicals can affect the efficiency of all three feedback mechanisms. For example: metal fuels have high thermal conductivity thus aiding in conductive feedback; organic fuels produce much gas, which can increase convective energy transfer; and dark colored fuels, such as charcoal, can increase the absorption of radiant thermal energy.

B) Fuel to Oxidizer Ratio

There is always an optimum fuel to oxidizer ratio, one which produces the fastest burn rate. This often corresponds to the situation where the reaction will be essentially complete with little fuel or oxidizer remaining after the reaction. When the fuel to oxidizer ratio deviates from this optimum value, burn rate is reduced. The burn rate continues to fall as the deviation from optimum increases. This can be thought of as mostly a result of a lowering of the heat of reaction for the pyrotechnic composition, although activation energy and efficiency of energy feedback can also change. The heat of reaction falls because, as the fuel to oxidizer ratio deviates from optimum, there will be an increasing amount of fuel or oxidizer left over at the end of the reaction. Less energy is produced, simply because this unreacted material will not have been utilized. The activation energy may change because of changes in the heat capacity and ignition temperature of the composition. The efficiency of the energy feedback can change as a result of changes in the physical properties of the composition as the fuel to oxidizer ratio changes.

As an illustration of the effect of fuel to oxidizer ratio, consider the burn rate derived from data reported for mixtures of boron and barium chromate,[11] presented in Figure 3.

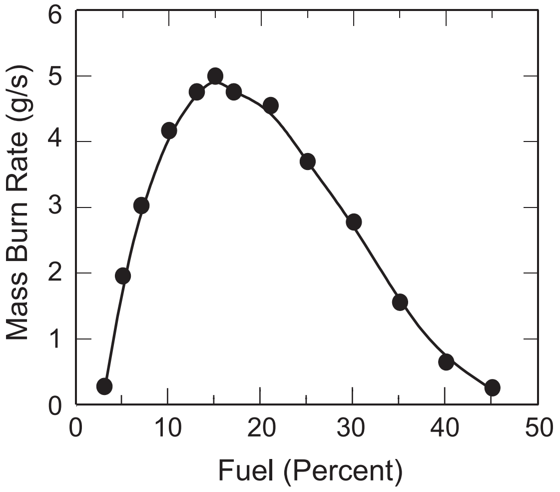

Figure 3. Burn rate for various mixtures of boron and barium chromate.

C) Degree of Mixing

When a pyrotechnic composition is poorly mixed, it will generally have a lower burn rate than the same composition that is well mixed. In essence, this is because, while the entire volume of the poorly mixed pyrotechnic composition may have the optimum fuel to oxidizer ratio, there will be many small regions where the fuel to oxidizer ratio is far from optimum. Within each of these regions, what was said above for burn rate dependence on fuel to oxidizer ratio applies to each of these small regions. In the final analysis, however, the heat of reaction for the total amount of composition may not be significantly reduced. This is because essentially all of the material will eventually react, as fuel or oxidizer physically migrates from region to region, but this takes time (i.e., the burn rate is reduced).

A series of samples of rough Black Powder were prepared and burned to measure their burn rate. Each sample was a loose conical pile of 1 gram of –100 mesh material. This was ignited about half way up on one side of the pile using a hot wire igniter. Burn times were determined by a (field by field) review of a video recording of the burning. Sample A was dry mixed by passing several times through a 60-mesh screen. Sample B was dry mixed for several minutes using a mortar and pestle. Sample C was wet ball milled for 4 hours, dried and crushed to –100 mesh with a mortar and pestle. The charcoal and sulfur for sample D was dry ball milled for 4 hours; then with the potassium nitrate added, and wet ball milled for 8 hours; then dried and crushed to –100 mesh with a mortar and pestle. The average mass burn rate for three measurements of each sample of rough Black Powder is shown in Figure 4.

D) Particle Size

As the size of individual fuel and oxidizer particles is made smaller, the burn rate increases. It is difficult to overstate the degree to which particle size, especially that of the fuel, can affect burn rate. The particle size effect can be considered to be the result of reducing the effective activation energy, because smaller particles require less energy to be heated to the ignition temperature. Also, since only those atoms on the surface of particles are available

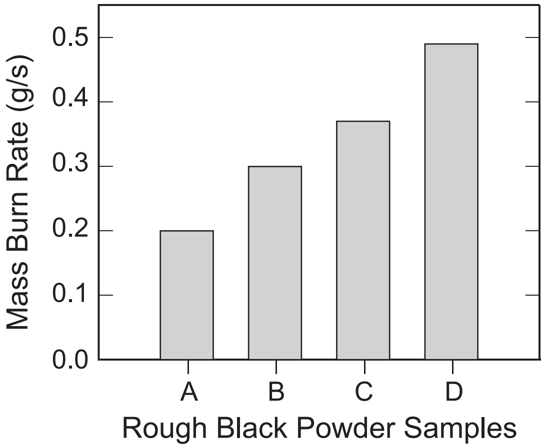

Figure 4. Mass burn rate of samples of rough Black Powder with varying degrees of mixing.

to react, then, as particle size is reduced, the fraction of atoms on the surface increases. Further, presumably as a result of an increasing fraction of atoms on the surface of particles, some researchers have reported slight increases in heat of reaction for compositions with smaller particle sizes.

For a demonstration of the effect of magnesium particle size on the burn time of flares,[10] see Figure 5. (Note: The author did not specify the formulation for the flare composition.)

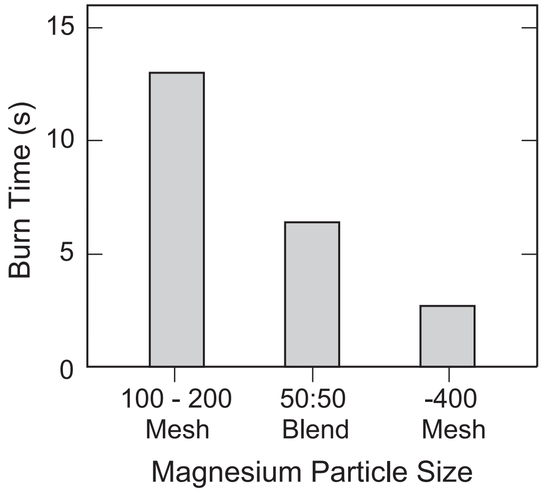

Figure 5. Burn times for flares made with varying magnesium particle size.

For most pyrotechnic compositions, the particle size of the fuel, with its typically high melting point, has the greatest effect on burn rate. The reason that the size of oxidizer particles is of less importance is that most oxidizers melt or have decomposition temperatures at or below the ignition temperature of the pyrotechnic composition. For a comparison of the relative magnitude of the effect of fuel versus oxidizer particle size,[10] see Figure 6, which shows the burn rate for a loose pyrotechnic composition with strontium nitrate (60%), magnesium (25%), and PVC (15%). The greatest burn rate is for the composition with fuel and oxidizer both as fine particles. However, note the relatively small effect of using coarse oxidizer as compared with using coarse fuel. (The mesh range for the fine magnesium was 200–325 and the coarse magnesium was 30–50 mesh; however, the author did not report the mesh range for the coarse and fine strontium nitrate.)

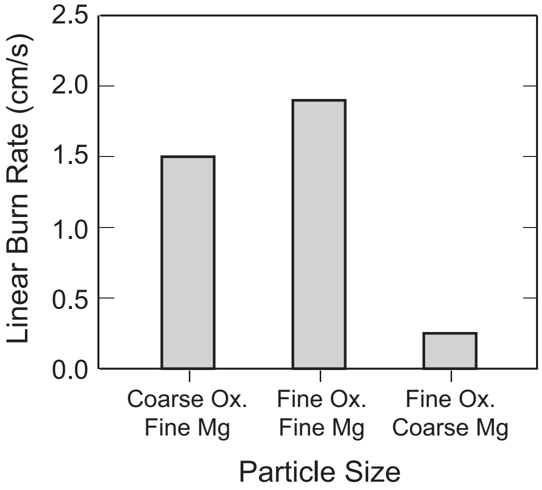

Figure 6. Burn rate for a red flare composition with varying fuel and oxidizer particle sizes.

E) Particle Shape

Particle shape affects burn rate in much the same way as particle size does; with a variation of effective activation energy as the controlling mechanism. Some shapes (e.g., thin flakes) are easier to raise to the ignition temperature than are other shapes. Thin flakes also tend to have a greater percentage of atoms on their surface. All else being equal, the order of particle shape, from lowest to highest burn rate is: spherical, spheroidal, granular and flake. As with particle size, the particle shape of the fuel has the greatest effect on burn rate. Again the reason is that fuels tend to have melting points higher than the ignition temperature of the pyrotechnic composition, whereas, oxidizers tend to melt or decompose at temperatures at or below the ignition temperature.

A series of samples were prepared that contained 64% potassium perchlorate, 27% aluminum, and 9% red gum. In each case the average particle size for the aluminum was 20 microns; however, three different particle shapes were used: spherical atomized, spheroidal atomized, and flake. The pyrotechnic composition was pressed into 10 mm diameter paper tubes using a constant loading force. The burn time for 3.5 gram samples was measured using a stopwatch, and the mass burn rate was calculated. Average results from three measurements of each particle shape are presented in Figure 7.

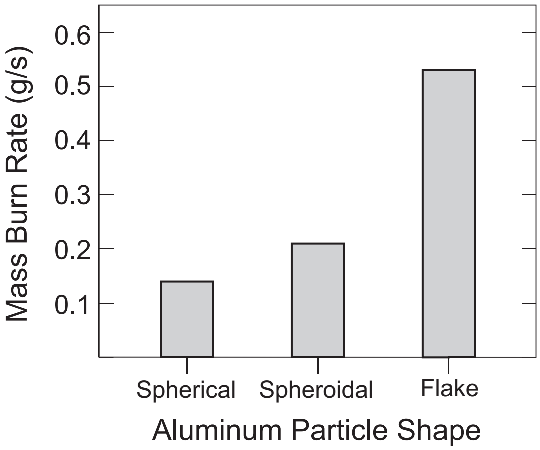

Figure 7. Mass burn rate for a composition using different fuel particle shapes.

F) Presence of Additives

It is possible to think of most pyrotechnic compositions as a pyrogen plus additives; where the pyrogen is the fuel and oxidizer, and the additives are those things that produce the intended pyrotechnic effect. Some common examples of additives are: large granular fuels that produce sparks; agents that produce or enhance colored flame or smoke; a binder to hold a composition together, including the residual solvent used to activate a binder; and a stabilizer or neutralizer to retard undesirable chemical reactions. Usually the presence of additives lowers the burn rate and the amount of lowering increases with increasing percentage of additives. This can be the result of raising the effective activation energy, lowering the heat of reaction, or both.

To see how an additive can act to raise the activation energy of a pyrotechnic composition, consider the case where sodium bicarbonate is added to a glitter composition as a delay agent. The sodium bicarbonate decomposes, consuming energy and releasing carbon dioxide, at its decomposition temperature (T_d = 270 ºC[9]). This is below the ignition temperature (T_i) of the composition, which is probably approximately 350 ºC. As a tiny portion of the glitter composition is heated, (see Figure 8) initially the temperature of the composition rises. However, when the temperature reaches 270 ºC, the sodium bicarbonate begins to decompose, consuming energy, thus keeping the temperature from rising further. After all of the sodium bicarbonate has decomposed, the temperature will again rise. At the ignition temperature, the temperature rises very quickly as burning begins. Since more energy is required for the composition to reach its ignition temperature, the activation energy is higher. As a consequence, more time is required for each tiny portion of composition to reach its ignition temperature (i.e., the burn rate is lower). (Note that the driving off of residual water in a pyrotechnic composition acts in much the same way as the above example.)

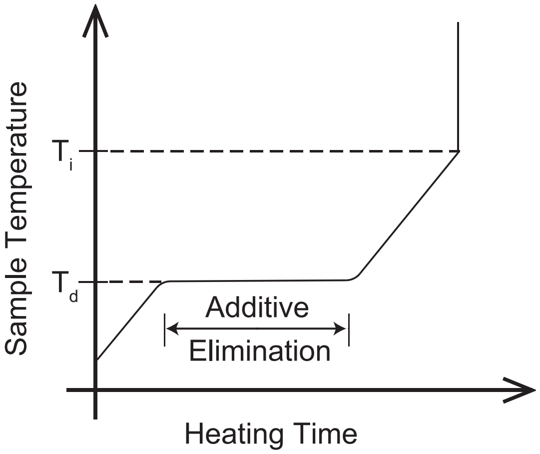

Figure 8. How an additive can act to raise the activation energy of a composition.

A quantity of rough Black Powder was prepared by wet mixing, drying, and grinding to –100 mesh. A series of samples were made that contained various amounts of sodium bicarbonate. Each sample was burned by igniting a loose 1 gram pile with a hot wire on the side of the pile about half way to the top. The time for complete burning was recorded. The result of the addition of sodium bicarbonate on mass burn rate is shown in Figure 9. The value for the mass burn rate for the samples with 20% sodium bicarbonate is uncertain because the samples generally would not burn completely.

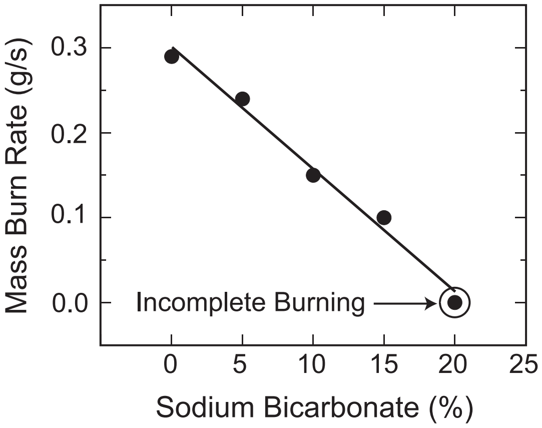

Figure 9. Mass burn rate for rough Black Powder with sodium bicarbonate added.

As an example of how an additive can act to lower the heat of reaction of a pyrotechnic composition, consider the addition of barium carbonate to neutralize trace amounts of acid present in a pyrotechnic composition, or strontium carbonate to act as a color agent. The carbonate is neither oxidizer nor fuel, and thus does not produce energy upon burning of the pyrotechnic composition. Accordingly, on a weight for weight basis, the composition produces less energy. In addition, as the composition burns, if the decomposition temperature of the carbonate is higher than the ignition temperature, it will consume energy reducing the heat of reaction still further. (The decomposition temperatures for strontium carbonate and barium carbonate are 1340 and 1450 °C, respectively.[9])

While most additives to pyrotechnic compositions lower the burn rate, it is sometimes possible for an additive to increase the burn rate of a pyrotechnic composition. When this is the case, it is generally the result of increasing the heat of reaction and/or improving the efficiency of energy feedback. The use of a small amount of a metal fuel is a common way this is accomplished. For example when zirconium is added to a red tracer mix, a significant increase in burn rate results,[11] see Figure 10. This, presumably, is the result of both increasing the heat of reaction (high energy metal fuel) and increasing the efficiency of energy feedback (high thermal conductivity).

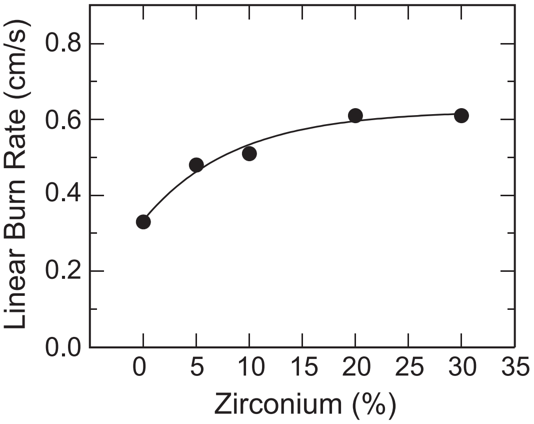

Figure 10. Burn rate for red tracer mix with zirconium added.

G) Catalysts

Catalysts are a special class of additives. They are chemical agents that increase the rate of chemical reactions, normally without being consumed in the process. (In pyrotechnic compositions, the temperatures reached are typically so great that the burn catalysts are consumed.) Pyrotechnically, burn catalysts act to lower activation energy, typically by reducing the decomposition temperature of the oxidizer (i.e., the temperature at which oxygen is made available). Red iron oxide, potassium dichromate, and manganese dioxide are some burn catalysts used in pyrotechnics. For example, the addition of manganese dioxide to potassium chlorate will lower its decomposition temperature by 70 to 100 ºC.[12] A reduction in the oxidizer's decomposition temperature, in turn, acts to lower the ignition temperature of the composition thus increasing its burn rate. How this occurs is illustrated in Figure 11. If the addition of a burn catalyst acts to lower ignition temperature (e.g., from T_{i1} to T_{i2}), less time will be required for each tiny portion of composition to be heated to its ignition temperature (i.e., $t_2 < t_1$). Accordingly, as a stick of pyrotechnic composition burns (Figure 2), less time is needed for the ignition of each successive thin disk of composition (i.e., the burn rate increases).

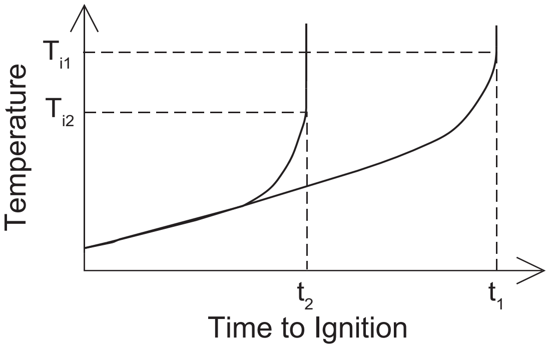

Figure 11. How a burn catalyst produces an increase in burn rate.

A series of samples were made with potassium perchlorate containing small amounts of potassium dichromate (70% total) and shellac (30%). The amount of potassium dichromate varied from 0 to 4%. A four gram sample of each mixture was pressed into a 10 mm diameter paper tube, using a constant loading pressure. Pairs of tubes with the same mixture were burned to determine their average burn rate. The results are shown in Figure 12.

H) Ambient Temperature

The pyrotechnic burn rate increases as the ambient temperature rises, because of a reduction in activation energy. In essence, this is a consequence of the unreacted composition starting out closer to its ignition temperature. Accordingly, less energy is required to bring it to its ignition temperature. This is illustrated in Figure 13, where two tiny samples of the same pyrotechnic composition are heated to cause their ignition. The sample with the higher initial temperature (T_1) requires less time (t_1) to reach the ignition temperature (T_i) than the sample initially at temperature T_2. Accordingly, its burn rate will be greater.

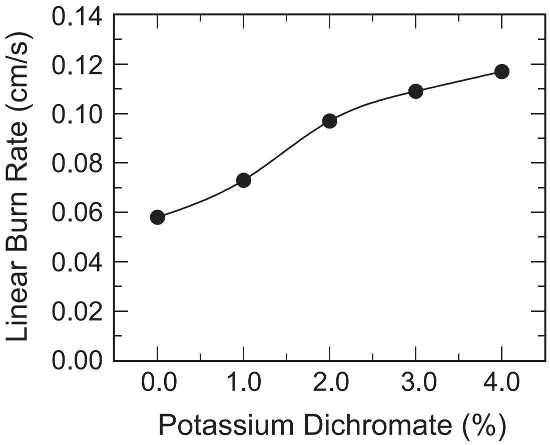

Figure 12. Burn rate of a pyrotechnic composition with varying amounts of potassium dichromate.

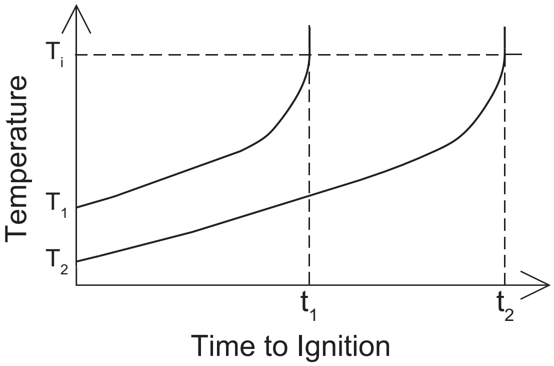

Figure 13. The effect of ambient temperature on burn rate.

As part of a study to determine the characteristics of visco fuse,[13] a measurement was made of the effect of temperature on its burn rate. In this study, groups of 10 pieces of 125-mm long fuse were cooled or heated to various temperatures and then burned to determine the effect of temperature on their burn rate. The results of the study are shown in Figure 14.

I) Local Pressure

Gas generating pyrotechnic compositions generally produce a flame upon burning. For these compositions, the nature and relative position of the flame produced varies as a function of local pressure. As the pressure is increased, the flame envelope becomes smaller, the flame

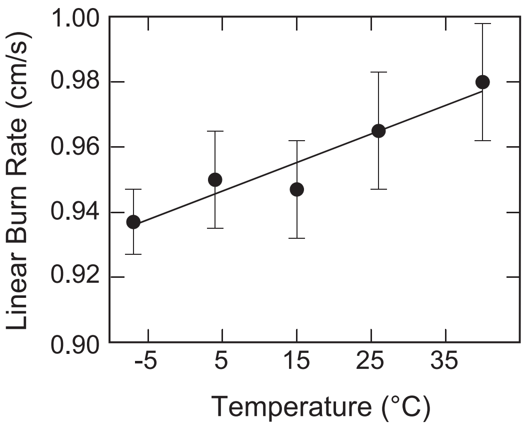

Figure 14. Burn rate of visco fuse as a function of ambient temperature.

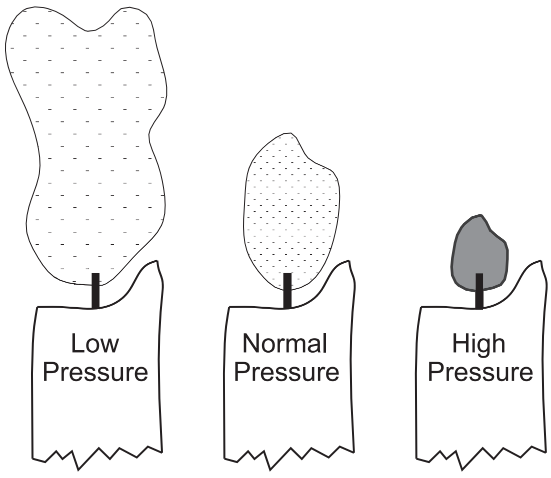

Figure 15. An illustration of the effect of local pressure on a candle flame.

burns hotter, and it is held in closer proximity to the burning surface. This is illustrated in Figure 15, which is a representation of a candle burning under varying local pressure. As the pressure rises, so does the burn rate, because the hotter flame, held closer to the burning surface, increases the efficiency of energy feedback. Although generally not considered to burn with a flame, the burn rate for a smoke composition (oil red, 50%; potassium chlorate, 30%; and lactose 20%) illustrates the effect of pressure, see Figure 16.[6]

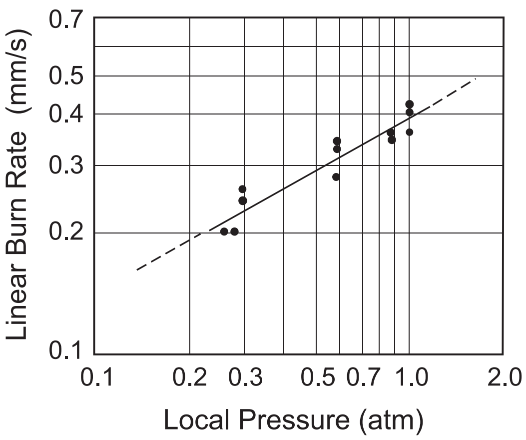

Figure 16. Burn rate of a smoke composition as a function of local pressure.

The relationship between burn rate (R) and local pressure (P) can be expressed mathematically as:

$$R = a \cdot P^b \tag{4}$$

where a and b are constants that depend on the pyrotechnic composition being used. Some values for a and b are given in Table 4 for burn rate in cm/s and pressure in atm.

Table 4. Pressure Dependent Burn Rate Constants for Pyrotechnic Compositions.

Composition	*a*	*b*	Ref.
Smoke Composition (above)	0.038	0.44	6
$KClO_4$ (80%) + Mg (20%)	0.14	0.39	6
KNO_3 (80%) + Mg (20%)	0.25	0.30	6
$KClO_4$ (60%) + Mg (40%)	0.33	0.33	6
$KClO_4$ (60%) + Al (40%)	0.43	0.37	6
Black Powder	1.21	0.24	7

J) Degree of Confinement

The effect of burning pyrotechnic compositions under confinement is complicated. However, the activation energy is not changed, and neither is the heat of reaction, unless significantly different chemical products are formed as a result of confinement. Burning of gas-producing pyrotechnic compositions under confinement, can be thought of as burning under conditions where, until the confining vessel bursts, the efficiency of energy feedback is extremely high. During unconfined burning most of the energy produced is lost to the surroundings as escaping combustion products and radiation. However, when the composition is confined, essentially all of the energy being produced is retained and is available to ignite unreacted pyrotechnic material. Also, because the gaseous products are retained, there will be the effect of pressure accelerated burning, as discussed above. Accordingly, confinement can act to greatly increase the burn rate of gas-producing pyrotechnic compositions, and it would be difficult to overstate the effect that confinement can have on burn rate. For gas-less pyrotechnic compositions, there is considerably less effect from confinement.

K) Physical Form

The physical form of the pyrotechnic composition can make a great difference in its burn rate. Mostly this effects the efficiency of energy feedback and was discussed in more detail in an earlier article on burn types.[3] Generally, for gas producing pyrotechnic compositions, granulated compositions (with so-called fire paths) have high burn rates; large solid masses of composition (with no fire paths) have low burn rates; and fine powders, which can experience burn type transitions, can have highly unpredictable burn rates. Of the three feedback mechanisms, convective energy feedback is the most important. For granulated materials, where fire paths exist, the hot burning gases produced by the reaction can rapidly penetrate between the grains into the unreacted composition, igniting more material in the process, producing more burning gas, penetrating further, in an accelerating process. In this way all of the pyrotechnic composition can come to be ignited very quickly.

In an experiment to demonstrate the tremendous effect physical form can have on burn rate, two transparent plastic tubes, 10 mm in diameter, were filled with Black Powder. In one case, loose 2Fg Black Powder was poured into the tube; in the other case, meal powder was loaded into the tube in small increments and compacted under high pressure to form a dense solid mass. The compacted material burned at a rate of about 10 mm/s; whereas, the granular material burned at a rate more than 1000 times greater, explosively shattering the open tube.

Shimizu points out that burn rate is dependent on the cross sectional dimension of fire paths.[6] Both small and large cross sectional areas result in relatively low burn rates; however, in between, the burn rate can be very much greater. He discusses this using the burn rate of quick match as an example. For quick match, the fire path is the space between the black match core and the loose paper sheath. Figure 17, adapted from Shimizu,[6] illustrates the effect of varying the gap between the match core and the paper wrap. When there is no fire path gap, the burn rate is relatively low; then as the gap between match and paper increases, the burn rate rapidly increases to a maximum value; there after, further gap increases result in a lowering of burn rate, back to the value for burning in open air.

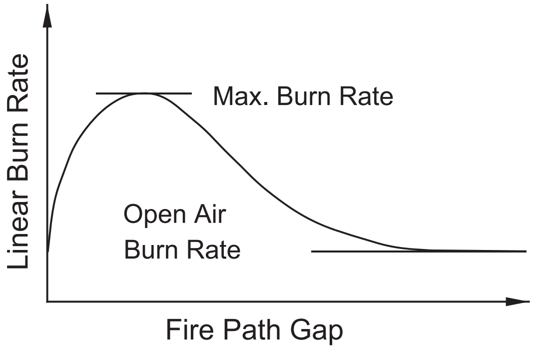

Figure 17. Quick match burn rate as a function of fire path gap.

L) Degree of Consolidation

Degree of consolidation is sometimes referred to as loading pressure and is related to the degree of compaction of pyrotechnic composition as it is made into grains or packed into a device. The effect of varying loading pressure is to change the efficiency of energy feedback. However, whether higher loading pressure increases or decreases the burn rate depends on the nature of the pyrotechnic composition.

If the pyrotechnic composition is gas-producing and convective heat transfer is the most important mode of energy feedback, then high loading pressure generally decreases the burn rate by decreasing gas permeability. That is to say, even in quite tightly compacted compositions, some fire paths remain. These will tend to have small diameters, and will be blocked after short distances, but they do aid in the convective feedback of thermal energy. As the loading pressure is increased, these residual fire paths become thinner and shorter, reducing their effectiveness in aiding energy feedback, and thus decreasing the burn rate.

As an example, consider the effect of increasing loading pressure on the burn rate of granular Pyrodex® (HF-4) when pressed into 12 mm tubes.[14] (Pyrodex® is a Black Powder substitute, based on potassium perchlorate, often used in muzzle loading weapons.) Figure 18 is a graph of the result of increasing loading pressure on the average linear burn rate. Measurements were made using groups of three samples at each pressure. Note the significant decrease in burn rate.

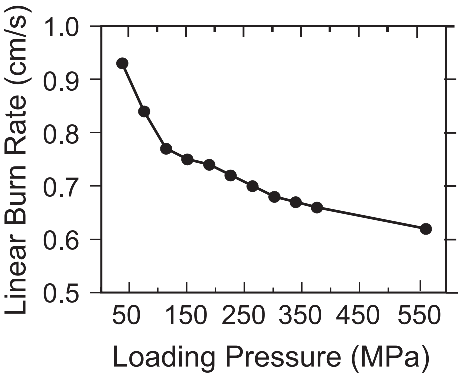

Figure 18. Linear burn rate of Pyrodex® as a function of loading pressure.

Conversely to the above example, if a pyrotechnic composition produces little or no gas upon burning and conductive heat transfer prevails, higher loading pressure generally increases the burn rate. This is because, for such a pyrotechnic material, added compaction increases thermal conductivity, increasing the efficiency of energy feedback, and thus increasing the burn rate.

M) Geometry

Geometric effects are changes in burn rate brought about by changes in the size and shape of the pyrotechnic composition. For the most part, this is the result of small changes in the efficiency of energy feedback. For example, as the size of a grain of composition increases, a slightly greater percentage of the radiant thermal energy produced during burning is radiated back to heat the burning surface. This is illustrated in Figure 19. In the case shown on the left (thin stick of composition), almost all of the radiated thermal energy is lost to the surroundings. The case illustrated on the right is an attempt to consider the effect when a much larger block of composition is burned. However, for simplicity, only the burning of the same small portion (seen to the left) is considered. In this case, almost all of the thermal energy radiated in a downward angle will strike the surface of the composition, thus contributing to the feedback of energy. The effect is to increase the burn rate for larger blocks of pyrotechnic composition. In an experiment to demonstrate this effect, meal powder was compacted into tubes using a constant loading pressure per surface area. Two different size tubes were used, with diameters of 8 and 16 mm. Four trials of each, resulted in an average burn rate for the larger sample that was about 10% greater; a small but real difference.

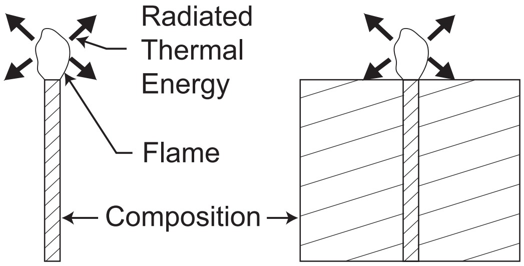

Figure 19. Radiant energy feedback for blocks of pyrotechnic composition.

Another example of geometric effect is the “erosive burning” that occurs along a hole or channel running through a grain of pyrotechnic composition.[3] For erosive burning, energy feedback is very efficient. The flame produced by the burning composition on one side of the hole jets directly across to feed energy to the composition on the other side, and vice versa.

For purposes of this chapter, geometric effect is also taken to include effects such as caused by the thermal conductivity of inert materials in or surrounding the pyrotechnic composition. For example, because of increased thermal energy feedback, a composition pressed into a thin metal tube (or having a metal wire internally along its length) will often have an increased burn rate compared with one pressed into a paper tube (or without the wire).

N) Crystal Effects

Crystal effects include a number of diverse effects all relating to properties of the crystal lattice. One crystal effect may result from the ability to store a small portion of the energy expended during milling or grinding in a crystal lattice.[5] Following the accumulation of this lattice energy, there seems to be a temperature dependent relaxation time during which the stored energy is lost. During the period when significant energy remains stored in the crystal lattice, the effective activation energy for the material is reduced, potentially increasing burn rate. Other crystal effects can be the result of using materials with different methods of manufacture, which produce crystals with different lattice structures, different numbers of defects, and different amounts of trace impurities. Still another possible crystal effect, which may be important in some transitions from burning to explosion, is the piezo-electric effect. It is felt by some that this has the potential for significantly increasing energy feedback by converting compressive pressure forces into an electrical ignition stimulus.[15]

O) Environmental Effects

Most changes in burn rate that occur during storage are the result of the factors discussed above. For example, during repeated temperature cycles, cracks may be produced in a rocket propellant. The resulting (often catastrophic) increase in burn rate is indirectly discussed in Section K. The crack produces a fire path which increases the energy feedback to unreacted composition. Similarly, the deterioration of a star with a metal fuel, which slowly oxidizes during storage, can be thought of in terms of additives (Section F). In this case fuel and oxidizer are being converted to mostly unreactive chemical products. Although these types of environmental effects can act to change burn rates and are important considerations in the storage of pyrotechnic materials, they are generally not seen as mechanisms to control burn rate.

There is at least one environmental effect that actively controls burn rate; that is the speed of air flow past the burning composition. That will affect the fraction of energy being fed back. Consider the case illustrated in Figure 20. In the case of a stationary star (upper diagram), the flame hovers above the star and much of the energy is fed back to the burning surface. In the case of a moving star (lower diagram), the flame will be pushed away from the star by the air movement past it. That this occurs is confirmed by Figure 21, which is a photograph of a group of stars propelled through the air from an exploding shell. It is fairly clear that the stars

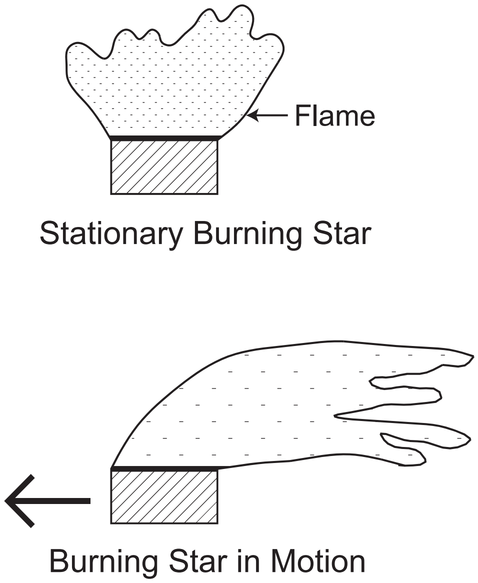

Figure 20. An illustration of the effect of air movement past a star.

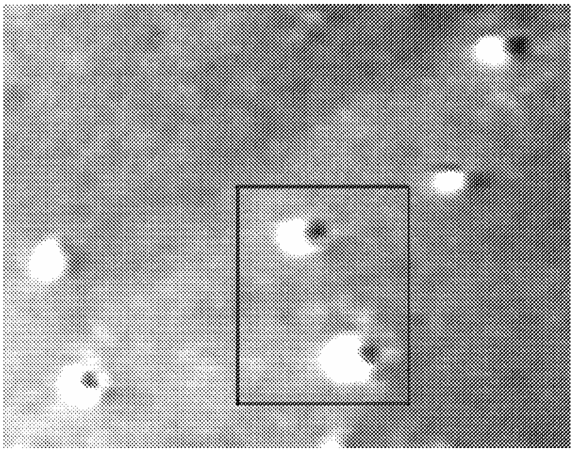

Figure 21. High speed photograph of burning stars.

(dark dots) have their flame envelopes (light areas) trailing behind them. The effect of this is to reduce the fraction of energy fed back, and thereby lowering the burn rate. In other cases the effect of a wind over the burning surface will be to supply extra oxygen for burning, which in some cases can act to increase the burn rate.

Conclusion

There are two important areas in which a better understanding of the factors that control burn rate can be especially important. The first is when it is necessary to alter the burn rate to affect a needed change in the performance of a pyrotechnic device. The second is when some change occurs in the manufacture or condition of a device such that the result is an otherwise unexpected change in burn rate. In either case, the intended or unintended change in burn rate can affect aesthetic performance and more important can seriously affect safety.

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Our Present Knowledge of the Chemistry of Black Powder

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ABSTRACT

Black Powder has been around for centuries and has had a profound influence on the history of the world. Over this time, a considerable amount of knowledge has been gained not only sheds light on the chemistry of Black Powder but also on other pyrotechnic reactions. This knowledge cannot be considered complete, in spite of all the research that has taken place, and this chapter attempts to summarize the present understanding about Black Powder's ignition and propagation chemistry.

Keywords: Black Powder chemistry, ignition, propagation, Black Powder research

Introduction

From early times, when Black Powder came to the attention of the alchemists, researchers have wondered and speculated about its explosive power when ignited. Science has indeed come a long way since the mysticism of the alchemists and the phlogiston theory of combustion. Today our understanding of the chemistry of Black Powder's ignition and propagation is far more accurate and precise.

The speculation of bygone ages has been largely replaced with solid knowledge backed by solid data. However, there remain, to this day, areas of our knowledge about Black Powder that are sparse and even virtually non-existent. Having been around for so long, and studied so extensively, many have concluded that current knowledge about its ignition and propagation characteristics is virtually complete. This, however, is not true.

This paper attempts to summarize present knowledge of the chemistry of Black Powder. Specifically it examines the chemistry of ignition and propagation.

Problems Relating to Black Powder Research

Black Powder research has been hampered by several factors. Perhaps one of the most important of these is the waning interest in its use, with Black Powder having been replaced by other more efficient explosives and propellants. Traditionally Black Powder research (with its necessary funding) has been sponsored by the military. With declining military use came a corresponding decline in research, but not a total decline. Black Powder still has certain superior properties to the more powerful smokeless powers that have largely superseded it. For example: in military use, where Black Powder has been superseded by newer propellants, it still finds uses in fuses and as an initiator of other explosive materials. This utilization is largely due to its superior ability to produce a large percentage of hot solids after ignition. These solids are more efficient in igniting other substances than hot gases.

Some might suppose that Black Powder's use as a fuse or an igniter merits less study than its uses as explosives and propellants. This might be true from a fireworks maker's viewpoint but not from a military standpoint. Recent military research has focused on consistency in performance—a goal critical to Black Powder's role in igniting other propellants.

Another factor influencing the gathering of scientific data about Black Powder is its most important characteristic, its explosive power. To meaningfully study Black Powder's ignition and propagation characteristics, one needs to simulate its actual application as closely as possible. This means that the Black Powder usually needs to burn with explosive force. This force, unfortunately, tends to scatter the combustion components, making their collection and detection difficult. This explosive force is also dependent on its unique application. Thus far, less explosive force is generated in the tube of a fireworks mortar than in a barrel of a gun.

Lack of standardization has also hampered research. Different researchers at different times have used different methods of sampling and testing. This has resulted in “comparing apples with pears” scenarios where data has been misapplied and misinterpreted. The literature frequently refers to research that took place many years ago. And while some of this research may be very well documented, its authors and their associates are no longer available to share their insights through personal correspondence. Thus seeking clarification on many of the finer points in their research is very difficult, if not impossible. Again, this can result in “apples and pears” scenarios when recent experimental data is compared with much older data.

The Importance of Black Powder Chemistry

What is there to be gained from studying the chemistry of Black Powder ignition and propagation? To many the answer is—not much. Where their chief concern is having a powder with reasonably predictable explosive characteristics, many conclude that the study of its chemistry contributes little beyond mere academic interest. However, a lot can be gained from studying Black Powder chemistry. Here are a few reasons why such knowledge can be advantageous:

- Toxic gases may be formed when Black Powder ignites.
- Black Powder still does many unpredictable things.
- Black Powder has certain undesirable characteristics.
- Tighter control of variables is needed for critical applications.
- Knowledge of Black Powder contributes to the general pyrotechnics knowledge pool.

Parameters of this Investigation

There are many variables involved in both the production and utilization of Black Powder. Some of these variables may have a marked effect on the resulting chemical reactions when Black Powder is ignited. For the purposes of this discussion, it is assumed that the Black Powder in question has been made by a process that optimizes the incorporation of its ingredients. These ingredients are also assumed to be: potassium nitrate (KNO_3), sulfur (S) and charcoal (C) in the approximate percentages of 75, 10 and 15, respectively. Thus other Black Powder mixes with different ingredient ratios such as those used in gerbs, drivers and rockets are not examined here.

Here and elsewhere in this paper charcoal is represented merely as carbon (C). This convention is used to both simplify some of the discussions and to accurately represent the works of the various authors quoted. Many of these authors treated charcoal as pure carbon, ignoring its smaller percentages of other elements such as hydrogen and oxygen. So charcoal is represented just as carbon where deemed appropriate and as a complex of carbon and other substances where it is helpful to examine charcoal in greater detail.

Although this paper is mainly confined to the above-mentioned definition of Black Powder, it is useful to explore the properties of sulfurless Black Powder and Black Powder that substitutes sodium nitrate ($NaNO_3$) for potassium nitrate. Black Powder mixes that do not use sulfur give a clearer picture of the importance of sulfur in most Black Powder mixes. Sodium salts are similar enough chemically to potassium salts to merit serious study. In practice, sodium nitrate is used in Black Powder made for blasting applications. Thus, both sulfurless Black Powder and sodium nitrate powder form part of this discussion.

Reactions and Combustion Products

In the early 19th century, Guy-Lussac[1] proposed that the gases formed by exploding Black Powder comprised:

Carbon dioxide (CO_2)	52.6%
Carbon monoxide (CO)	5.0%
Nitrogen (N_2)	42.4%

These results were contested by Piobert[1] but the main disagreement appears to relate to gas volumes rather than content. Later research conducted by numerous other researchers shows that these conclusions concerning the types of gases produced were overly simplistic and that many other gaseous products could be formed. Notable is the extensive research done by Noble and Abel.[2] Nevertheless, these later experiments showed that the principle gases produced from exploding Black Powder are carbon dioxide and nitrogen.

Chevreuil[1] conducted experiments with Black Powder exploded in a gun barrel and also burnt in the open air. These experiments can be considered a milestone in our present understanding of Black Powder chemistry, for they showed that quite different results are obtained when Black Powder is ignited under different conditions. Later experiments by Noble and Abel[2] re-affirmed these results.

Chevreuil concluded that Black Powder exploded in the barrel of a gun reacted according to the following equation:

$$2\,KNO_3 + S + 3\,C \rightarrow K_2S + N_2 + 3\,CO_2 \qquad (1)$$

Part of Chevreuil's reasoning points to the fact that this formula represents almost exactly the proportions found in Black Powder made with the 75:10:15 ratios. Substituting the atomic masses of KNO_3, S and C into the above formula gives:

KNO_3	74.8%
S	11.9%
C	13.3%

This explanation seems to have gained enough credibility in certain quarters that even more than a century later it was still accepted by some. This author has a chemistry textbook[3] dated 1936 that accepts the above theoretical explanation with the above formula modified only as follows:

$$4\,KNO_3 + S_2 + 6\,C \rightarrow 2\,K_2S + 2\,N_2 + 6\,CO_2 \qquad (2)$$

Graham[1] accepted Chevreuil's view, and expanded on it by proposing that potassium sulfide (K_2S) is converted to the sulfate (K_2SO_4) when it is exposed to air.

Slower burning Black Powder, according to Chevreuil, yielded carbon and the following potassium compounds: sulfide, sulfate, carbonate (K_2CO_3), cyanide (KCN), nitrate and nitrite (KNO_2).

In 1857, Bunsen and Schischkoff published a classic paper on Black Powder research.[1,2] This research investigated the nature and proportions of the permanent gases generated when Black Powder explodes and the amount of heat generated by this transformation. From these experimental data, they deduced theoretically the temperature of explosion, the maximum pressure in a closed chamber, and the total theoretical work done on projecting a projectile. It is worth noting that these findings were theoretical in nature, as their experiments did not properly emulate the type of conditions typically found when Black Powder is exploded in a confined space. Their experiments were performed on Black Powder that was deflagrated by being allowed to fall into a heated bulb.[2]

From these observations, they concluded that the permanent gases represented only about 31%, by weight, of the powder and occupied a volume of 193 times that of the original unexploded Black Powder. Table 1 lists their results.[2]

It can be seen from Table 1 that the Black Powder used in this experiment was comprised of a slightly different formula than the commonly used ratio of 75:10:15. Here the approximate ratio is: potassium nitrate 79%, sulfur 10% and charcoal 11%. Also worth noting is their representation of charcoal as a substance comprising not only carbon, but also hydrogen and oxygen.

Berthelot[1] derived the following equation based on Bunsen and Schischkoff's investigations:

$$16\,KNO_3 + 6\,S + 13\,C \rightarrow 5\,K_2SO_4 + 2\,K_2CO_3 + K_2S + 8\,N_2 + 11\,CO_2 \qquad (3)$$

He then developed the first theory about the explosion of Black Powder. Here he drew extensively on the experimental work of Bunsen and Schischkoff. Berthelot's theory assumes two limiting cases for the decomposition of Black Powder.

Table 1. Results of the Bunsen and Schischkoff Experiments.[2]

Sample Size	Components before Ignition (in grams)		Components after Ignition (in grams)		
1 gram of Black Powder			Solids		
	KNO_3	0.7899	0.6806	K_2CO_3	0.1264
				$K_2S_2O_3$	0.0327
	S	0.0984		K_2SO_4	0.4227
				K_2S	0.0213
	Charcoal			KCNS	0.0030
	C	0.0769		KNO_3	0.0372
	H	0.0041		$(NH_4)_2CO_3$	0.0286
	O	0.0307		S	0.0014
				C	0.0073
			Gases		
			0.3138	H_2S	0.0018
				O	0.0014
				CO	0.0094
				CO_2	0.2012
				H	0.0002
				N	0.0998

In Berthelot's first case, K_2CO_3 forms the chief product of decomposition and K_2SO_4 is a by-product.

In his second case, K_2SO_4 forms the chief product of decomposition and K_2CO_3 is a by-product.

In the first case, the decomposition proceeds according to the following three equations:

$$2\,KNO_3 + S + 3\,C \rightarrow K_2S + 3\,CO_2 + N_2 \tag{4}$$

$$2\,KNO_3 + S + 3\,C \rightarrow K_2CO_3 + CO_2 + CO + N_2 + S \tag{5}$$

$$2\,KNO_3 + S + 3\,C \rightarrow K_2CO_3 + 1.5\,CO_2 + 0.5\,C + S + N_2 \tag{6}$$

Berthelot further proposed that the above occurred in the ratios of 1/3 for equation 4, 1/2 for equation 5, and the remaining 1/6 for equation 6.

In the second case, the decomposition proceeds according to equations 4 and 6 above plus the following two equations:

$$2\,KNO_3 + S + 3\,C \rightarrow K_2SO_4 + 2\,CO + C + N_2 \tag{7}$$

$$2\,KNO_3 + S + 3\,C \rightarrow K_2SO_4 + CO_2 + 2\,C + N_2 \tag{8}$$

And the above are supposed to occur in the proposed ratios of 1/3 for equation 4, 1/2 for equation 6, 1/8 for equation 7, and the remaining 1/24 for equation 8.

A different conclusion was reached by Debus[1] who concluded that Black Powder burns in a two-stage process. In the first stage, oxidation occurs according to the following exothermic reaction:

$$10\,KNO_3 + 3\,S + 8\,C \rightarrow 2\,K_2CO_3 + 3\,K_2SO_4 + 6\,CO_2 + 5\,N_2 + 979\text{ kcal }(4096\text{ kJ}) \tag{9}$$

The resulting products are then reduced according to the following endothermic reactions:

$$K_2SO_4 + 2\,C \rightarrow K_2S + 2\,CO_2 + {-58}\text{ kcal }(-242.7\text{ kJ}) \tag{10}$$

$$CO_2 + C \rightarrow 2\,CO + {-38.4}\text{ kcal }(-160.6\text{ kJ}) \tag{11}$$

The resulting potassium sulfide may further undergo the following reactions:

$$K_2S + CO_2 + H_2O \rightarrow K_2CO_3 + H_2S \tag{12}$$

$$K_2S + CO_2 + 0.5\,O_2 \rightarrow K_2CO_3 + S \tag{13}$$

A part of the unburned potassium sulfide and sulfur gives K_2S_2.

Much later Kast[1] derived the following equation:

$$\begin{aligned}
&74\,\mathrm{KNO_3} + 30\,\mathrm{S} + 16\,\mathrm{C_6H_2O}\text{ (charcoal)} \rightarrow \\
&\quad 56\,\mathrm{CO_2} + 14\,\mathrm{CO} + 3\,\mathrm{CH_4} + 2\,\mathrm{H_2S} + \\
&\quad 4\,\mathrm{H_2} + 35\,\mathrm{N_2} + 19\,\mathrm{K_2CO_3} + \\
&\quad 7\,\mathrm{K_2SO_4} + 2\,\mathrm{K_2S} + 8\,\mathrm{K_2S_2O_3} + \\
&\quad 2\,\mathrm{KCNS} + \mathrm{(NH_4)_2CO_3} + \mathrm{C} + \mathrm{S} + \\
&\qquad\qquad 665\text{ kcal/kg (2782 kJ/kg)} \qquad (14)
\end{aligned}$$

From the foregoing, a somewhat confusing picture emerges concerning the chemical reactions (with resulting products) that occur when Black Powder is ignited. While it is tempting to give more credibility to chemical equations derived by more recent research, due caution should be exercised here. The number of resulting variables, after ignition occurs, precludes chemical equations that will be true under all ignition conditions.

Ignition conditions vary widely in practice from high-pressure ignition that occurs in guns (of both large and small caliber) to lower pressures found in fireworks applications such as mortars, Roman candles and mines. Environmental factors such as temperature and relative humidity might also come into play. Noble and Abel[2] found so many variations in their experiments that they concluded that no value could be attached to a general chemical expression relating to the burning of Black Powder. So there is no “one true formula” for the chemical reaction that occurs when Black Powder is ignited. Thus, any formula presented should be treated as an approximation of what happens when igniting Black Powder.

Another consideration is some variation in the formula used in Black Powder manufacture. While the traditional Waltham Abbey ratio of 75:10:15 can be regarded as a standard, some variations do occur in practice. Propellant powders used by the military and in fireworks usually stick quite closely to the 75:10:15 ratio. (This is illustrated in Tables 2 and 3).

Note that in Table 2 the percentage value of potassium nitrate includes tiny percentages of impurities such as potassium sulfate and potassium chloride.

The data in Tables 2 and 3, gathered approximately a century apart, indicate that the 75:10:15 ratio has been fairly closely adhered to, especially with the more modern powders. This is not only true for Black Powder produced in Britain and the USA, but for Black Powder manufactured elsewhere as well. For example, Shimizu[5] gives an analysis of Japanese Black Powder containing 74.20% potassium nitrate, 9.62% sulfur, and 16.18% charcoal.

However, much variation exists in powders used for blasting. Here, not only do the ratios of the three principal ingredients differ, but also it is common to find additional ingredients in such powders. Blasting powders also tend to substitute sodium nitrate for potassium nitrate and some use both oxidizers. Substitutes for charcoal are also found in some blasting powder formulas. Tables 4 and 5 show some of these variations.

Table 2. Analysis of Black Powders (circa 1875).[2]

Description	Potassium Nitrate (%)	Sulfur (%)	Charcoal (%)	Water (%)
Pebble Powder	74.76	10.07	14.22	0.95
Rifle Large-grain	75.1	10.27	13.52	1.11
Rifle Fine-grain	75.18	9.93	14.09	0.80
Fine-grain	73.91	10.02	14.59	1.48
Spanish Spherical Pebble Powder	75.59	12.42	11.34	0.65
Sporting Powder	77.99	9.84	11.17	—
Austrian Cannon Powder	73.78	12.80	13.39	—
Austrian Small Arms Powder	77.15	8.63	14.27	—
Cannon Powder	74.66	12.49	12.85	—
Russian Powder	74.18	9.89	14.83	1.10

Table 3. Analysis of Black Powders (circa 1975).[4]

Description	Potassium Nitrate (%)	Sulfur (%)	Charcoal (%)	Water (%)	Ash (%)
Du Pont 3814	73.88	9.97	15.71	0.30	0.14
Du Pont 7625	73.59	10.61	14.84	0.82	0.14
CIL 1-Keg-A	73.13	10.83	14.61	0.64	0.79
CIL 1-Keg-B	73.13	10.83	14.61	0.64	0.79
GOE 76-3	74.34	10.25	14.66	0.48	0.27
Du Pont 7846	74.01	9.92	15.01	0.79	0.27
GOE 78-1	74.43	9.95	14.54	0.49	0.58
GOE 78-2	74.45	9.88	14.88	0.20	0.59
CIL 8-2-73	72.92	10.83	14.78	0.65	0.82
CIL 4-23	73.93	10.63	14.05	0.63	0.48

Further consideration should be given to other variations in manufacture such as the degree of incorporation and the resulting density of the powder. Also, a major factor that often is not given the consideration it deserves is the type of charcoal used.

Charcoal's Significant Influence

While little variation is found in potassium nitrate of high purity and minimal variation in sulfur, significant differences can be found in the different charcoals used in Black Powder. These differences can be largely attributed to the fact that charcoal is derived from organic matter, this matter being either animal or vegetable in origin. Black Powder appears to have been made exclusively with vegetable charcoal. Any possible experiments with animal charcoal

Table 4. Blasting Powder Compositions (Potassium Nitrate Based).[1]

Description	KNO_3 (%)	Sulfur (%)	Charcoal (%)	Ammonium Sulfate and Copper Sulfate (%)
Strong Blasting (French)	75	10	15	
Slow Blasting (French)	40	30	30	
No. 1 Blasting (German and Polish)	73–77	8–15	10–15	
No. 1 Bobbinite (with 2.5–3.5% paraffin) (British)	62–65	1.5–2.5	17–19.5	13–17
No. 2 Bobbinite (with 7–9% starch) (British)	63–66	1.5–2.5	18.5–20.5	

Table 5. Blasting Powder Compositions (Sodium Nitrate Based).[1]

Description	$NaNO_3$ (%)	KNO_3 instead of $NaNO_3$ (%)	Sulfur (%)	Charcoal or substitutes (%)
No. 1 Black Blasting (German)	70–75	up to 25	9–15	10–16
Blasting (American)	70–74	—	11–13	15–17
No. 3 Black Blasting (Petrolastite or Haloclastite)	71–76	up to 5	9–11	15–19 of coal-tar pitch
No. 2 Black Blasting	70–75	up to 5	9–15	10–16 of lignite

are not on record, at least not in any prominent literature in the English language. And even if it could be proven that certain animal charcoals exhibited superior properties, cost and other practical considerations would preclude their use in Black Powder.

The two most influential variables in charcoal are:

- The type of material from which the charcoal is derived.
- The method used to make the charcoal.

Charcoal Varieties

Given the abundant variety of vegetable matter in existence, the potential exists to create an endless variety of charcoals. In practice, Black Powder manufacturers have focused on materials that were readily available and suitable for Black Powder manufacture. Typically, softer woods such as willow, poplar and alder have been used. Specifically the "white wood" from such sources is preferred.[1]

In willow trees alone, many different species exist throughout the world. Even within the same species of willow, variations in its wood exist due to such factors as weather, soil conditions, the age of the tree, and the part of the tree from which the wood is taken.

Research on maple charcoal has also indicated that differences in charcoal properties can exist even within batches of charcoal obtained from the same supplier.[6]

Charcoal Manufacture

Different methods of charcoal manufacture can impart different properties to the charcoal. Even variations in the same method can yield different results. For example, charcoals produced at lower temperatures retain meaningful percentages of volatiles. Higher temperatures drive these volatiles out of the charcoal. Excessively high temperatures can cause the charcoal to transition into graphite.

For centuries, charcoal used in Black Powder was made using traditional methods such as igniting a large pile of wood and then covering it with earth to exclude oxygen from the air. Typically, a kiln was used, consisting of a pile of wood covered with earth or other material. Modern variations use metal covers and are more efficient.[7] But these are still not optimal for charcoal used in Black Powder. At the end of the 18th century, an Englishman, Richard Watson, invented a new method that revolutionized charcoal manufacture.[8] This method used metal cylinders that were filled with wood and sealed prior to heating. Ballistic tests on Black Powder made with this charcoal showed an increase in range of about 60%.

Temperature Considerations

The temperature at which charcoal is made has a very large influence on the temperature at which it burns. This property of charcoal was explored by Violette in 1848.[1,8] Violette prepared charcoals in a retort, using different types of wood, and subjecting the woods to different temperatures of carbonization. Violette's work was a milestone in research on the properties of charcoal. Some of his findings are reflected in Tables 6 and 7.

Table 6. The Effect of Carbonization Temperature on Charcoal's Chemical Composition.[1]

Carbonization Temperature (ºC)	Charcoal Color	Yield (%)	Composition of Charcoal (%)		
			C	H	O + N
280–300	brown	34	73.2	4.3	21.9
350–400	black	28–31	77–81		
1000	black	18	82.0	2.3	14.1
1250	black	18	88.1	1.4	9.3

Table 7. The Relationship between Carbonization Temperatures and Ignition Temperatures.[1]

Carbonization Temperature (ºC)	Ignition Temperature (ºC)
260–280	340–360
290–350	360–370
432	400 (approx.)
1000–1500	600–800

Thus, Black Powder made with charcoal carbonized at lower temperatures will ignite at lower temperatures, and it burns at lower temperatures. This could be advantageous or disadvantageous, depending on the application. Typically, blasting powders are designed to burn at lower temperatures. Highly carbonized charcoal tends to absorb moisture less readily than less carbonized charcoal. Thus, certain tradeoffs exist in charcoal made for Black Powder manufacture, and thus it is wrong to describe any charcoal as ideal.

Volatiles

Volatiles in charcoal noticeably affect the burn rate of Black Powder. Generally, it is desirable to use such charcoal rather than charcoal where the volatiles have been driven out. Sassé[6] determined that a 25% volatile content was about the optimal amount for Black Powder use. This figure came from his own research, which correlated with research done by others who are referenced in his paper.[6]

Charcoal Variations

The many variations in charcoal have influenced research by the US military. Notable is the research done by Rose[9] at the Naval Ordnance Station at Indian Head, Maryland and by Sassé at the US Army Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland. Both research projects aimed at producing more uniform powders by establishing more exacting standards for charcoal. Rose's research compared charcoal made from different species of trees, while Sassé[6] focused on maple charcoal. Even within the narrower confines of Sassé's research, notable variations in properties were found between charcoal samples. One example is the variation in volatile content of between 21 and 29%. Sassé concluded that the properties could vary even between different samples in the same lot obtained from a single supplier. He suggests that these variations are due to variations in the wood used and differences in temperature in different parts of the kiln. His proposed solution to this problem is to preblend such charcoal to obtain a more predictable Black Powder.

Chemical Analysis

Charcoal should never be regarded as pure carbon, but rather as an organic hydrocarbon complex. Just as there is no one true equation for Black Powder's chemical reaction, there is no one true formula for charcoal. Again, some authors of textbooks and technical papers have erred here. The formula for charcoal depends on which charcoal it is meant to represent. Often this representation is approximate and not exact. Table 8 shows that even charcoal obtained from the same type of wood may have variations in chemical content.

The data in Table 8 is extracted from experiments conducted by Sassé[6] in trying to determine the characteristics of maple charcoal. These data demonstrate that noticeable differences in chemical composition are to be found in charcoal made with the same type of wood.

Table 8. Chemical Characteristics of Roseville Maple Charcoal.[6]

Sample	O_2 (%)	C (%)	H_2 (%)	N_2 (%)	S (%)	Ash (%)
1	12.71	78.40	3.26	0.44	0.68	5.11
2	13.10	78.40	3.24	0.35	0.01	4.90
3	14.20	75.83	3.15	0.35	0.02	6.45
4	14.14	75.41	3.24	0.34	0.02	6.85
5	16.03	76.87	3.49	0.32	0.01	3.30

These values, however, are close to the empirical formula of C_8H_4O. Sassé[10] also refers in a later paper to other empirical formulas for charcoal:

- $C_{14.57}H_{7.17}O_{1.00}$
- $C_{8.68}H_{4.96}O_{2.00}$

Charcoal Substitutes

Charcoal substitutes have been investigated by researchers seeking Black Powder with characteristics that are more predictable. Notable is the research conducted by Wise, Sassé and Holmes,[11] which was followed by research done by Weber.[12] Many different crystalline organic compounds were tested by Wise, et al., who concluded that some of these compounds showed promise as viable alternatives for charcoal. Their research, however, did not exhaustively test the properties of the powders produced, and they concluded that such tests were necessary before claims of a viable charcoal substitute could be considered conclusive.

Weber focused on a process that used phenolphthalein as a charcoal substitute, with promising results. His findings, however, were not subjected to all the test criteria outlined by Wise, et al.[11]

None of these findings has resulted in a large-scale commercially viable production process. Possibly the cost of alternate substances such as phenolphthalein is in itself prohibitive. However, there may be niche applications of these alternate formulations where cost and large-scale manufacture are not major factors.

The foregoing discussion focused on the resulting products produced when Black Powder is ignited and its ignition allowed to go to completion. While some of this discussion has involved intermediate reactions in the combustion process, it has not attempted to explain the ignition process itself (i.e., what happens when heat of sufficient intensity is applied to the powder, causing it to ignite).

The Ignition Process

The following discussion examines the ignition process itself.

Principal in importance in Black Powder ignition is its oxidizer, potassium nitrate. Here, as with other oxidizers, potassium nitrate supplies oxygen to the reaction. This oxygen, if supplied with sufficient heat, causes the two other components to burn. Given the right combination of the ratios of the ingredients and an efficient method of manufacture, the resulting Black Powder will burn very rapidly. This rapid burning makes it useful as an explosive or propellant.

While the potassium nitrate supplies most of the oxygen to the reaction, a small percentage of oxygen is contributed by the charcoal and also possibly by the atmosphere. Charcoal itself contains oxygen atoms in its chemical composition and may contain absorbed oxygen and other atmospheric gases.

Ignition Phases

Although Black Powder ignites very rapidly, its ignition can be separated into several distinct phases. The most important phase is the decomposition of the potassium nitrate, which is preceded by a pre-ignition phase. This decomposition of the potassium nitrate is essential for it to yield its important oxygen component to the process. The decomposition starts with the melting of the potassium nitrate.

Potassium nitrate melts at 334 °C. Its counterpart, sodium nitrate, used in various blasting powders, melts at 307 °C. This suggests that sodium nitrate powders ignite at lower temperatures, which indeed they do. Interestingly, a eutectic mixture of potassium nitrate and sodium nitrate melts at 220 °C.[1]

Experiments performed by Hoffmann[1] have shown, however, that the Black Powder ignition process begins at a much lower temperature. This is due to the influences of the charcoal and sulfur. An important factor here is the melting point of sulfur, which is about 115 °C. Thus at about 150 °C, molten sulfur reacts with hydrogen to form hydrogen sulfide (H_2S). This H_2S then reacts with the KNO_3 to form potassium sulfate

(K_2SO_4). This reaction generates heat, causing the KNO_3 to melt. This process is often referred to as the pre-ignition process.

Sulfur's Importance

The importance of sulfur has been demonstrated in experiments performed by Hoffmann.[1] These experiments showed that sulfur did the following:

- Facilitated an increase in the quantity of gases evolved on explosion
- Reduced initial decomposition temperature and temperature at which explosion occurred
- Intensified the sensitiveness of mixtures to impact
- Counteracted the formation of carbon monoxide

The above conclusions were drawn in part from some of Hoffmann's following experimental data:

- Potassium nitrate ignited with carbon produces only K_2CO_3, but in the presence of sulfur produces CO_2, K_2SO_4 and K_2S. Thus, more gases are created by exploding Black Powder that contains sulfur than Black Powder that does not.
- A mixture of two moles of KNO_3 and three moles of carbon (charcoal with a 71% carbon content) begins to decompose at 320 °C and explodes at 357 °C, while a mixture of two moles of KNO_3 and one mole of sulfur begins to decompose at 310 °C and explodes at 450 °C. A mixture of KNO_3 with both sulfur and charcoal yields both lower decomposition and explosive temperatures as shown in an experiment where a mixture of two moles of KNO_3, one mole of sulfur and three moles of carbon begins to decompose at 290 °C and explodes at 311 °C. This latter experiment is very significant in that it shows that sulfur does not only reduce decomposition and explosion temperatures, but it greatly narrows the gap between initial decomposition and explosion temperatures.
- Sulfur increases the sensitiveness of Black Powder mixes to impact while carbon (charcoal) reduces it. This is shown by the following experimental data. A 2 kg mass dropped from 45–50 cm caused a mixture of KNO_3 and sulfur to explode while a mixture of KNO_3 and charcoal was unaffected. A mixture of KNO_3 with both sulfur and charcoal exploded when a 2 kg mass was dropped on it from a height of 70–85 cm.

Hoffmann[1] also concluded that sulfur counteracts the formation of carbon monoxide when Black Powder explodes and also has an impact on the amount of potassium cyanide (KCN) gas produced. This is because the addition of sulfur causes K_2SO_4 to be formed in addition to K_2CO_3. Thus, the amount of potential K_2CO_3 is reduced. The formation of K_2CO_3 causes both carbon monoxide and potassium cyanide to be formed as follows:

$$K_2CO_3 + 2\,C \rightarrow 2\,K + 3\,CO \qquad (15)$$

$$2\,K + 2\,C + N_2 \rightarrow 2\,KCN \qquad (16)$$

The decomposition of K_2SO_4 does not result in either carbon monoxide or potassium cyanide gases forming, as shown in the following equation:

$$K_2SO_4 + 2\,C \rightarrow K_2S + 2\,CO_2 \qquad (17)$$

The importance of sulfur in Black Powder is further emphasized by experiments in trying to find a substitute for charcoal. Such experiments were conducted by Wise, et al.[11] Their research demonstrated that sulfur has a profound effect on combustion when phenolic materials were used as charcoal substitutes. However, their experiments did reveal opposing trends when different types of phenolic materials were used. For example, quinizarin and anthraflavic acid both produced more rapid burning powders with the absence of sulfur. Other polyphenols exhibited the opposite trend but to a lesser degree. These data challenged the perceived importance of the sulfur being reduced by organic compounds and strengthened the hypothesis that the influence of sulfur is more marked in its role in the flame-spread rate after ignition occurs. Wise, et al. concluded that this hypothesis needs to be explored further using both charcoal and charcoal-substitute mixes.

Sulfurless Black Powder

No discussion about the role of sulfur in Black Powder would be complete without examining useable Black Powder that does not contain any sulfur. Here the term “useable” denotes Black Powder that performs adequately as an explosive, propellant or igniter. Probably the most famous type of sulfurless Black Powder was the so-called “Cocoa” powder, which used incompletely carbonized charcoal.[1] This charcoal, known as “Cocoa” or “Red” charcoal, was typically manufactured at a temperature of 140–175 °C. It had a carbon content of 52–54%, which is much lower than other charcoals used in Black Powder. Its major drawback was its sensitivity to friction, which easily ignited it.

A stoichiometric mixture of sulfurless Black Powder comprises 87.1% potassium nitrate and 12.9% charcoal. The decomposition occurring after ignition can be represented theoretically as follows:

$$4\ KNO_3 + 5\ C \rightarrow 2\ K_2CO_3 + 2\ N_2 + 3\ CO_2 \qquad (18)$$

In practice, sulfurless Black Powder mixtures are generally not used for propellants, but rather as igniters. These have a potassium nitrate content of between 70–80% and a charcoal content of between 20–30%. Some “sulfurless” powders actually do contain a small percentage (about 2%) of sulfur, which is far below the normal percentage.

Binary Mixtures

Blackwood and Bowden[1] made extensive studies on the ignition of Black Powder and also on the following binary mixes:

- potassium nitrate + sulfur
- sulfur + charcoal
- potassium nitrate + charcoal

Amongst their findings, they concluded that ignition could take place as low as 130 ºC, depending upon the pressure to which the Black Powder was subjected. They also confirmed the importance of having charcoal with the right constituents. In their opinion, it was advantageous to remove the constituents that could be dissolved with organic solvents. This, they said, made ignition easier and gave a faster burn rate.

Blackwood and Bowden formulated the mechanism for Black Powder’s ignition and subsequent burning reactions. Accordingly, sulfur reacts first with the organic substances in the charcoal:

$$S + \text{organic compounds} \rightarrow H_2S \qquad (19)$$

Potassium nitrate reacts almost simultaneously with these organic compounds:

$$KNO_3 + \text{organic compounds} \rightarrow NO_2 \qquad (20)$$

The following reactions may also occur:

$$2\ KNO_3 + S \rightarrow K_2SO_4 + 2\ NO \qquad (21)$$

$$KNO_3 + 2\ NO \rightarrow KNO_2 + NO + NO_2 \qquad (22)$$

$$H_2S + NO_2 \rightarrow H_2O + S + NO \qquad (23)$$

This last reaction proceeds until all the H_2S is consumed. The remaining NO_2 then reacts with the unconsumed sulfur according to the following reaction:

$$2\ NO_2 + 2\ S \rightarrow 2\ SO_2 + N_2 \qquad (24)$$

The SO_2 formed in the above reaction may then immediately react with the KNO_3 as follows:

$$2\ KNO_3 + SO_2 \rightarrow K_2SO_4 + 2\ NO_2 \qquad (25)$$

Reactions 23 and 24 are endothermic while reaction 25 is strongly exothermic. Reactions 19 to 25 constitute the ignition process.

Blackwood and Bowden concluded that the chief reaction is the oxidation of charcoal by the potassium nitrate. This is when the Black Powder starts to burn.

Flame Spread Rates

The flame-spread rate of Black Powder is firstly dependent on the solid salts produced after ignition has commenced. These tiny hot pieces of solid matter are driven into the surrounding Black Powder, causing it to ignite and the flame to spread until all the powder is consumed. While the production of solid hot particles produced by different chemical reactions is an important factor in Black Powder’s flame spread characteristics, other physical attributes are also important.

Many processes have been tried over the centuries to improve and control the flame-spread attributes of Black Powder. Essential to these attributes is the process of granulation or corning where the Black Powder is formed into solid grains. Recent research on the influence of physical properties on the burn rate has been done by Sassé[13] and also by White and Horst.[14] Sassé's research showed flame spread to be dependent on density, surface area and free volume. White and Horst found that grain position and the ability of grains to move was important.

Thus, the flame-spread rate of any sample of Black Powder is dependent both on the chemical reactions that take place and on the physical attributes of the powder grains.

The Influence of Moisture

Most Black Powder contains some moisture, and this property does have an effect on the powder's ignition and explosive properties. Nearly every Black Powder manufacturing process uses water, some of which remains in the powder. Black Powder may also absorb moisture from the atmosphere. There remains a certain amount of controversy as to whether a certain small percentage of moisture aids ignition. The author's own observations indicate that it might. Some have made similar claims that have been refuted by other authorities. Shimizu[5] refers to an optimal moisture content of about 1%, but this statement in itself appears based more on hearsay rather than empirical evidence from experimentation.

Where there is agreement, is the fact that moisture does have an effect and that variations in moisture content do produce variations in ignition. So, where uniformity in performance is critical, the challenge is to find a range of moisture content where performance can be regarded as sufficiently uniform and then, to control this moisture range.

One suggested range is 0.3 to 0.5%.[15] Here the challenge is to keep the moisture level above 0.3% while not allowing it to exceed 0.5%. This is far more difficult to achieve than merely aiming at a specified upper moisture limit.

The Effect of Aging

Another area of controversy is the effect of aging on Black Powder. Black Powder has shown itself to be far less susceptible to aging than many other explosives, but the question is: Does it actually (like a good wine) improve with age? And if it does improve with age, under what conditions? And why does it improve with age? One possibility is that the charcoal in the Black Powder absorbs oxygen from the atmosphere over a period of time. Some tests have, however, been done on aging Black Powder. Notable among these are the tests performed by Kosanke and Ryan[16] on US Civil War vintage Black Powder (ca. 1865). These tests showed that such powder performed very well in spite of its age.

The question of aging is a difficult one to answer as the aging process itself, by its very nature, takes a long time. A proper objective test would be to determine the properties of a batch (or batches) of Black Powder and then perform the same tests after an aging period. Practically speaking, this would be difficult to achieve.

Conclusion

Over several centuries, a considerable amount of knowledge has been gained concerning the chemistry of Black Powder. Some of this knowledge comes from extensive research done under tightly controlled laboratory conditions and supplemented with field research in practical applications. But there is still a lot that is not known. And there is still a lot to be gained from further research and experimentation.

A big challenge still is in achieving consistency in performance. Even with modernized, tightly controlled manufacturing techniques, there is still one major variable in the equation—charcoal. Perhaps one day a viable alternative to charcoal will be found, or a method to produce charcoal with very tightly controlled specifications.

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Notes

Pyrotechnic Primes and Priming

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ABSTRACT

If a pyrotechnic item does not ignite when intended, it is a failure. It makes no difference that had it ignited; it would have produced a spectacular display or a life-saving distress signal. Primes and priming techniques are important in producing high quality pyrotechnic effects, because through their use reliable ignition can be achieved.

In this review chapter, after presenting some basic information, propagation energy diagrams are explained and used to discuss the role and manner of functioning of pyrotechnic primes. In the course of the discussion, a number of ignition and propagation problems will be investigated and solutions demonstrated. The chapter concludes with a discussion of some basic prime formulations and methods for their application.

Introduction

A pyrotechnic prime is a composition applied to the igniting surface of the main pyrotechnic composition, to enhance the probability of successful ignition. Figure 1 illustrates the basic manner of use of a prime layer to aid in the ignition of an aerial signal flare and a fireworks gerb. In the simplest terms, the characteristics of a good prime are that:

- It is easily ignited (but not so easy that accidental ignition is likely).
- It generates abundant thermal energy upon burning.
- It has an efficient mechanism for energy feedback to the unignited composition.

Before the discussion of primes and priming techniques, a review of pyrotechnic ignition and propagation is appropriate (for a more complete discussion, see reference 1). Following this is a discussion of propagation energy diagrams of the type introduced by Shimizu.[2]

Pyrotechnic Ignition and Propagation

Pyrotechnic materials are said to exist in a “meta-stable” state. That is to say, under normal circumstances they are stable (they do not spontaneously ignite). However, once ignited, the combustion reaction is self-sustaining, producing an excess of thermal energy. Pyrotechnic materials do not spontaneously ignite under normal conditions because the ignition process first requires the input of energy into the com-

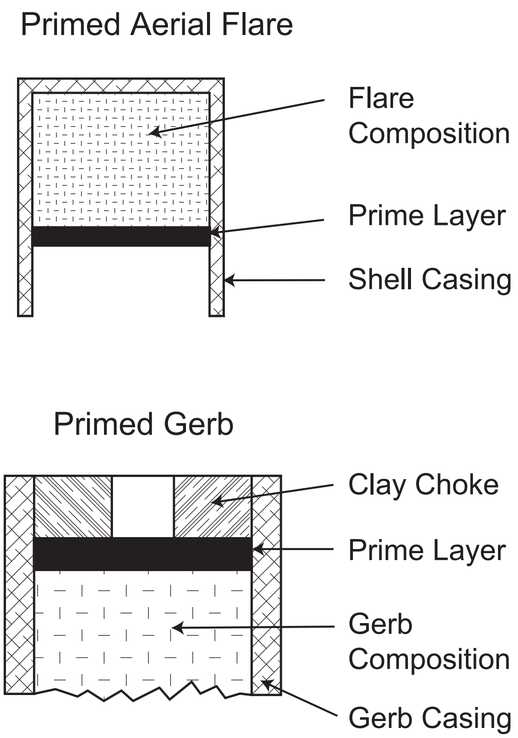

Figure 1. Illustration of a prime layer on an aerial signal flare and a fireworks gerb.

position to raise its local temperature. Once ignited, pyrotechnic combustion reactions can be self-sustaining, because there is a net production of energy as the composition burns. This two-step energy relationship is illustrated in Figure 2, which tracks the internal energy of a tiny portion of pyrotechnic composition during its ignition and burning. The first step, when energy is added to the composition, is seen as an increase in the internal energy of the material. Within the formalism adopted for this chapter, the minimum energy required for ignition is called the "activation energy" for the pyrotechnic composition and is abbreviated as E_a. The requirement of an input of energy to cause the ignition of a pyrotechnic material, allows pyrotechnic compositions to be safely made and stored prior to use. If it were not for this activation energy barrier, fuels and oxidizers would ignite on contact. In the simplest of terms, it is possible to think of activation energy as the energy needed to raise a tiny portion of the material to its ignition temperature. The second step in Figure 2, when the burning composition produces energy, is seen as a decrease in internal energy. The net amount of energy produced during burning is the "heat of reaction" for the composition, abbreviated as ΔH_r (In modern parlance, heat of reaction is more properly termed enthalpy of reaction).

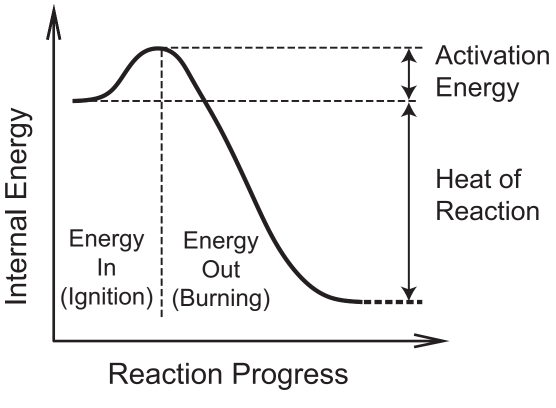

Figure 2. Changes in internal energy as a pyrotechnic composition ignites and burns.

In terms of chemistry, the process of ignition and burning can also be considered as two steps. The first step can be thought of as when chemical bonds are being broken between individual atoms in the tiny particles of fuel and oxidizer. This requires the input of energy (the activation energy). In the second step, new chemical bonds are formed between individual fuel and oxidizer atoms forming the products of the reaction. This bond forming produces energy which flows from the chemical system (the heat of reaction). If the new chemical bonds (fuel to oxidizer) are stronger than the original bonds, more energy is produced than is consumed, and there will be a net production of energy. Note that for pyrotechnic materials, the bonds within fuel and oxidizer particles tend to be weaker than the new bonds formed during burning, and this is the reason these materials produce energy upon burning.

In the simplest of terms, pyrotechnic propagation can be thought of as continuing self-ignition. To illustrate this, consider Figure 3, which is a sketch of a stick of burning pyrotechnic composition, and which can be thought of as a series of thin disks of material. The composition to the far left in Figure 3 has already been consumed by burning. The disk designated as "reacting" layer has ignited as a result of having received its needed activation energy. As this layer of material burns it produces energy, most of which is lost to the surroundings. However, some of the thermal energy produced is transferred to the next thin disk, designated as "pre-reacting" material. If the amount of energy delivered to the pre-reacting layer exceeds its activation energy requirement (i.e., it receives more energy than is required for its ignition) then it too will burn. If this process is repeated for each successive disk of composition, the burning will propagate through the entire stick of pyrotechnic material.

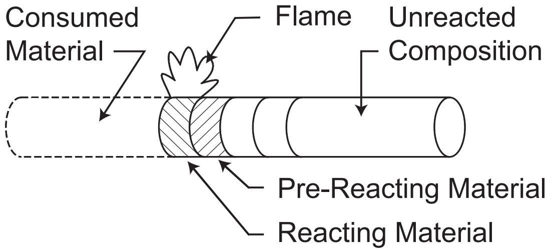

Figure 3. Burning "propagating" along a stick of pyrotechnic composition.

It is possible to quantify the requirement for propagation in what might be called the "Propagation Inequality". Propagation within a pyrotechnic composition will continue only so long as the amount of energy fed back to the next layer (E_f) exceeds its activation energy requirement

$$E_f > E_a \tag{1}$$

The amount of energy fed back equals the heat produced (heat of reaction) times the fraction of that energy being fed back (F_{fb})

$$E_f = \Delta H_r \times F_{fb} \tag{2}$$

Thus the propagation inequality becomes

$$\Delta H_r \times F_{fb} > E_a \tag{3}$$

So long as the inequality is met, a pyrotechnic composition will propagate. However, if anytime during its burning, the inequality fails to be met, burning will cease at that point.

There are three mechanisms by which energy can be transferred from reacting to pre-reacting layers: conduction, convection and radiation. In conduction, thermal energy, as atomic and molecular vibrations, is passed along from hotter to cooler regions. The factors maximizing conductive heat transfer are those things that increase thermal conductivity, for example having compacted composition, the use of metallic fuels, and the presence of metal casings or core wires around or within the composition. In convection, hot gases penetrate the composition along the spaces between grains (generally called "fire paths"). The factors maximizing convective heat transfer are those things that allow for gas penetration, for example having uncompacted composition and granulated or cracked masses of composition. In radiation, thermal energy is passed from hotter to cooler regions as long wavelength light (infrared). The factors maximizing radiative heat transfer are those things that facilitate the emission and absorption of thermal energy, for example having abundant incandescent particles (solid and liquid) in the flame and using a dark colored or black pyrotechnic composition.

Given the relationship in equation 3, it is clear that the factors favoring propagation are: high heat of reaction (much thermal energy produced), a relatively large fraction of energy fed back (efficient energy feedback), and low activation energy (low ignition temperature and low specific heat for the composition). When the propagation inequality is just barely met, burning proceeds feebly and is easy to extinguish. When the inequality is abundantly met, the burning proceeds fiercely and is difficult to extinguish.

Propagation Energy (Shimizu) Diagrams

The nature of ignition and propagation problems and how priming can overcome these problems can be difficult to comprehend. However, a qualitative understanding can be facilitated through the use of propagation energy diagrams, such as used by Shimizu.[2] These diagrams are a clever combination of a sketch and a graph. See Figure 4. The lower portion of the diagram is simply a sketch of a stick of pyrotechnic composition as in Figure 3. The composition is shown as initially having a burning surface *a-b*, which has burned to the current burning surface *a'-b'*. Above the sketch is a graph of energy as a function of distance along the composition. Here the two terms from the propagation inequality, equation 1, are charted. The energy being fedback, E_f, is shown as a dashed line. Activation energy, E_a, is shown as a solid line.

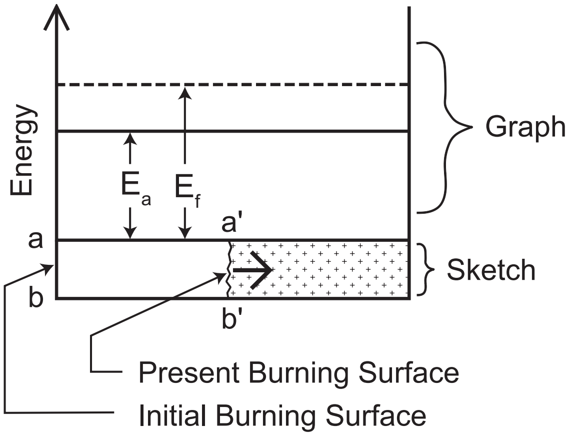

Figure 4. Illustration of Shimizu's Ignition and Propagation Energy Diagram.

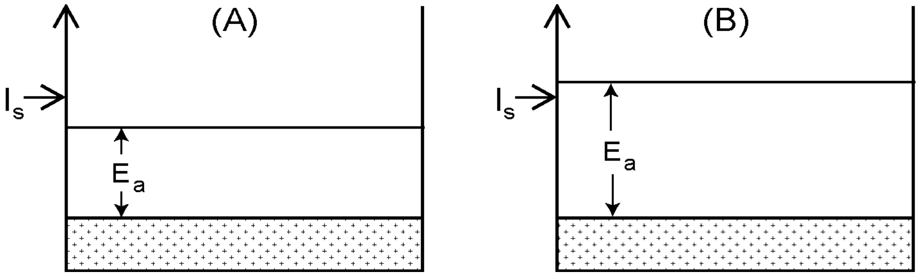

Figure 5. Illustration of varying activation energy requirement for ignition.

When the process of ignition is discussed, the amount of energy (ignition stimulus) being delivered to the exposed surface of the composition is shown as an arrow from the side, labeled I_s in Figure 5. The source of the ignition stimulus can take any of several forms. It could be direct thermal energy, such as provided by a burning fuse. However, it could also be mechanical energy such as from impact or friction, or electrical energy such as from an electrostatic discharge.

Consider the two cases illustrated in Figure 5. In case **A**, the activation energy required for ignition is relatively low, well below the amount of energy being supplied by the ignition stimulus. In this case, ignition of the composition is assured. (For simplicity, the amount of energy fed back during burning has not been shown.) However, in this case, since the activation energy requirement is quite low, it is possible that accidental ignition could result from unintentionally supplying sufficient energy during the preparation or loading of this composition. In case **B**, the activation energy requirement is quite high and exceeds the level of the ignition stimulus. In this case, the pyrotechnic composition will not be ignited by this level of ignition stimulus.

In Figure 6, propagation is considered for three compositions with varying activation energy needs. In each case, it is assumed that the ignition stimulus exceeds the activation energy requirement and has not been shown. In case **C**, the activation energy needed is greater than the amount of energy being fed back (solid line is higher than dashed line). Accordingly, even though the ignition stimulus is sufficient to cause ignition of a small portion of the composition, it will fail to propagate once the stimulus ends. As soon as the input of ignition energy has ended, burning must cease.

In case **D**, the activation energy requirement is less than in case **C**. Now, slightly more energy is fed back to pre-reacting layers than is needed to cause their ignition. Accordingly, there will be propagation of burning throughout the length of composition. However, because there is only a slight excess of thermal energy being fed back, the burning will be feeble and the flame will be relatively easy to extinguish. In case **E**, there has been a further reduction of the needed activation energy, with a relative

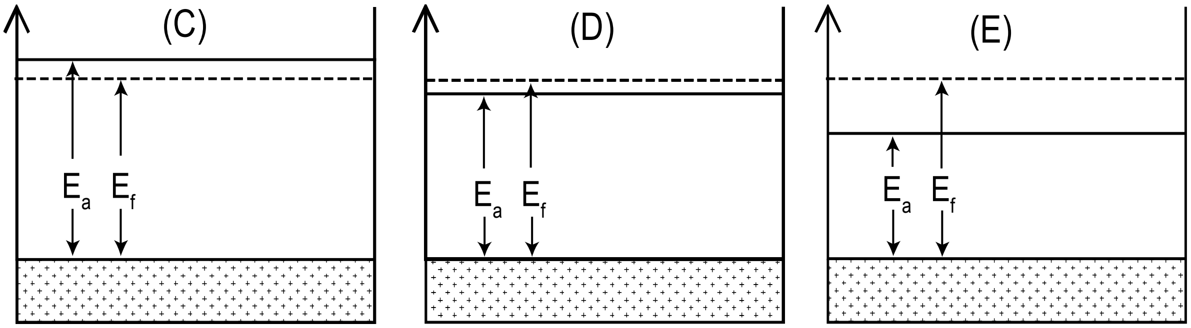

Figure 6. Illustration of the effect of varying activation energy on propagation.

abundance of energy being fed back to prereacting layers. As a result, propagation is assured and burning will proceed vigorously.

Basic Priming Situations

The role of a pyrotechnic prime is to help assure the ignition of the main pyrotechnic composition. Consider the situation illustrated in case **F** of Figure 7. For the purpose of this example, the pyrotechnic composition might be for a signal flare or a fireworks star. Based on what was discussed above, if this composition were successfully ignited, it would propagate successfully and burning would be fairly vigorous. (Ample energy would be fed back, E_f, compared with that needed for propagation, E_a.) However, the level of ignition stimulus, I_s, is not sufficient to accomplish ignition, it is less than E_a. In this case it is irrelevant how well the item was capable of functioning had it ignited, since it does not ignite.

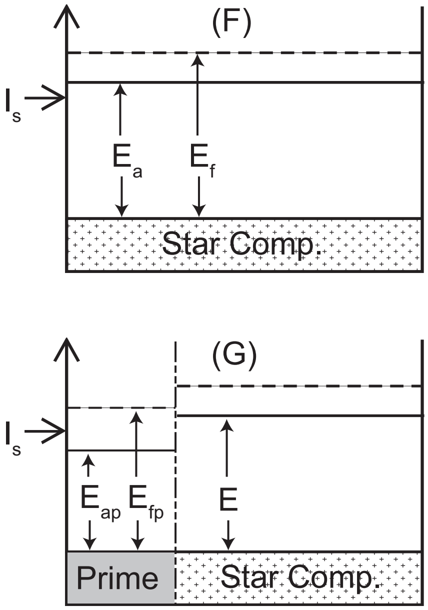

Figure 7. Illustration of how priming aids ignition.

Now consider case **G**, this has the same main composition and ignition stimulus as in case **F**. However, a prime layer has been included (thickness exaggerated). Note that the activation energy requirement for the prime is less than that of the main composition. Accordingly, the ignition stimulus is now sufficient to achieve ignition of the prime. Further, the prime will successfully burn to the interface with the main composition, E_{fp} is greater than E_{ap} (the subscript "*p*" denotes the prime composition). At the interface between the compositions, burning continues because the energy supplied by the prime, E_{fp}, also exceeds that needed for ignition of the star composition, E_a. In this case, the use of a layer of prime was successful in causing the ignition of the main (star) composition.

There are many times when different pyrotechnic compositions are in contact and when successful performance depends on the burning of one composition to successfully ignite the next. One example would be in a thermite grenade, where the delay column must eventually ignite the thermite composition. Another example would be in a color changing fireworks star, where a burning outer layer of composition must ignite the inner star composition. (See Figure 8.)

Some propagation scenarios are illustrated in the diagrams in Figure 9. In case **H**, burning will successfully pass the interface between the two compositions because E_{f1} is greater than E_{a2}. (The subscripts *1* and *2* denote compositions type 1 and 2.) If the order of the two compositions is reversed, which would be the case for a color change from something like willow to silver flitter, a situation like the diagram shown as case **I** results. This time the burning will not pass through the interface between the compositions because E_{f2} does not exceed E_{a1}. The solution to this problem can be to include a prime layer between the two star compositions, as illustrated in case **J**. This time the burning composition 2 will ignite the prime layer, $E_{f2} > E_{ap}$, and the burning prime will ignite composition 1, $E_{fp} > E_{a1}$.

Typically for military applications a prime will be specially formulated for each use. However, in some fireworks applications, it is common to create the prime by simply mixing compositions 1 and 2 in roughly equal proportions. When the two compositions are chemically compatible, the resulting mixtures tend to have an activation energy requirement and energy feedback that is approximately midway between

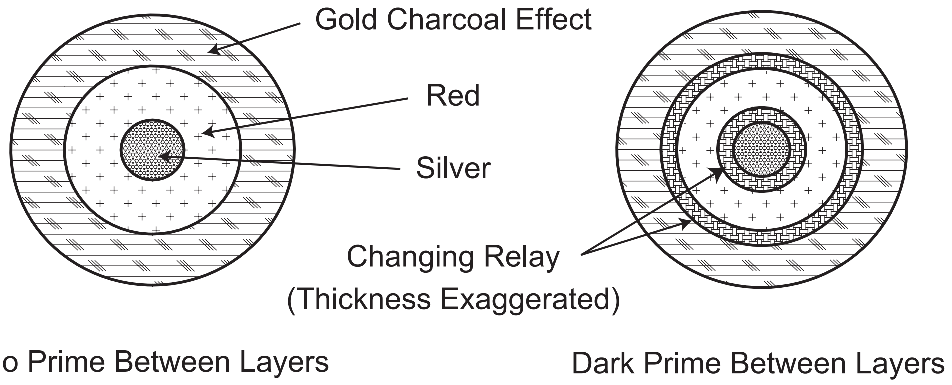

Figure 8. Illustration of the cross section of color changing fireworks stars.

the two. (See reference 3 for some information regarding pyrotechnic chemical compatibility.)

Probably the most common use of such "composition mixture" primes is in the rolling of color changing stars. However, in some instances the gap between the energy fed back by the first composition and the needed activation energy of a second composition is too large to be reliably spanned through the use of a single intervening prime layer. Such a difficulty can be overcome simply by using more than one prime layer, each formulated to bridge part of the gap. In fireworks this can be accomplished by varying the ratio of the two compositions in the mixture. For example, instead of using 50% of each composition, one prime composition could use a mixture of 67% of the first composition and 33% of the second. This could be followed by a mixture of 33% of the first composition and 67% of the second composition; such a 2-layer prime is illustrated as case **K** in Figure 9. In principle, the use of successive layers of variously formulated primes can be used to successfully span any gap between E_f and E_a.

In fireworks there can also be aesthetic reasons for using a special prime between compositions of color change stars. (See Figure 8 again.)These special prime compositions burn with the emission of very little visible light and may be called "dark prime" or "color change

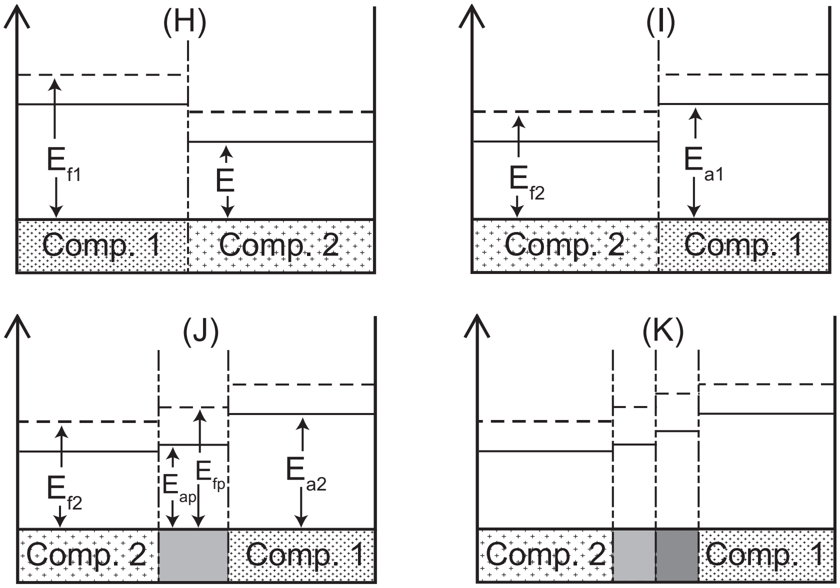

Figure 9. Potential successful and unsuccessful burning of pairs of pyrotechnic compositions.

relay”. The first aesthetic problem is that when the star burns through the interface, for a brief time, both compositions will be burning. At best this will produce an output that is some mixture of the two intended effects, which may not appear as a crisp and clean change of effects. Further, sometimes neither effect will be successfully produced by the mixed burning compositions.

A second aesthetic reason is that as a practical matter, it is not possible to make color change stars so perfectly and ignite them so consistently that all stars burn through the color change at the very same instant. Human perception is such that a momentary random dimming of a collection of burning stars as they are changing color is less noticeable than having a mixture of stars burning to produce two different colors at the same time. As a result, the effect of using a dark prime layer, even when there is no need in terms of successful propagation, is to create the illusion of a perfectly synchronized and precise color change. Figure 10 is an example of a competition grade aerial shell burst, in which the stars used a layer of dark prime. In this time exposure photograph, note the brief periods of no light emission between the production of the color and comet spark effect.

Figure 10. Demonstration of the use of a “dark prime” in a color changing fireworks star.

Other Propagation Problems

There are a series of other propagation problems that can be visualized through the use of propagation energy diagrams. Although not all of these are problems that can be solved through the use of primes, for completeness, they are nonetheless included in this chapter.

Many pyrotechnic devices are made by adding solvents to the pyrotechnic composition. This may be done to activate a binder, to temporarily suppress sensitivity to accidental ignition, to minimize dust production while loading, or to facilitate compaction of the composition. If use of the pyrotechnic device is attempted while it still contains a significant amount of this solvent, there can be a failure of the item. The basic reason for this is shown in Figure 11, which illustrates the process of raising such a composition to its ignition temperature (T_i). As thermal energy is added, at first its temperature rises with a slope dependent on the rate that energy is supplied and the heat capacity of the composition. However, when the boiling point of the solvent is reached, for a period of time the temperature remains nearly constant because the added thermal energy is being consumed in the process of evaporating the solvent. Once the solvent has been eliminated, the temperature of the composition again rises toward the ignition temperature (T_i). Obviously, in this case considerably more thermal energy was required to reach the ignition temperature of a composition containing a solvent. In effect, such a composition has a significantly higher activation energy requirement, which is dependent on the amount of solvent it contains.

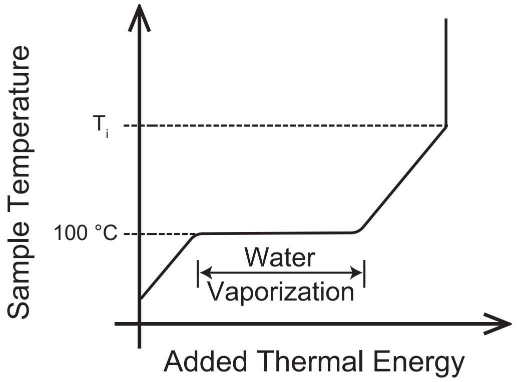

Figure 11. Illustration of the energy consumed by vaporizing water from a moist composition.

When a pyrotechnic item that still contains some residual solvent is ignited, it can fail to burn completely. This can be illustrated using Figure 12, which is a simplified propagation energy diagram for a pyrotechnic device still containing some residual water from the time of its fabrication. The outside of the item (toward the left), where it is exposed to the air, is shown as having dried completely. The inside of the item (toward the right) is shown as being moist as a result of the water added when it was made. In between is a band of composition shown as having increasing moisture content. When this item is ignited, at first, where the composition is dry, it will burn successfully because the energy being fedback exceeds its activation energy requirement. Burning will continue into the zone of increasing moisture content, even though the burning becomes more feeble as the activation energy requirement increases. However, when the point is reached where E_a has risen to equal E_f, burning must cease. Here, the obvious solution is to use no more solvent than necessary and to allow sufficient time for its substantially complete evaporation before its use.

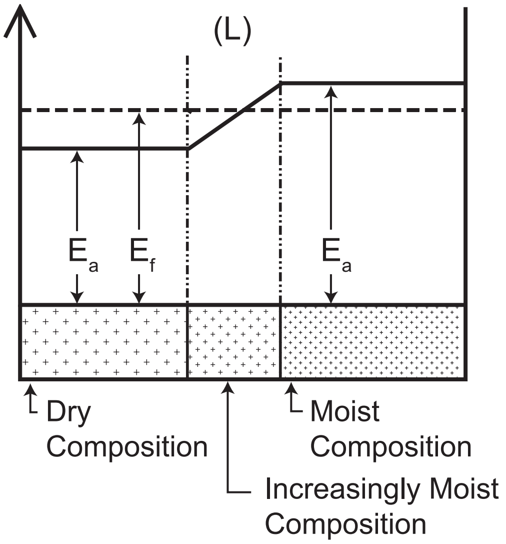

Figure 12. Propagation energy diagram for a progressively moist composition.

The feedback mechanism for some pyrotechnic compositions is primarily thermal conduction. These tend to be compositions that produce essentially no gaseous combustion products, most notably delay compositions used in military devices such as hand grenades. For such items, a crack through or separation of the delay column can result in a failure to propagate past that point. Figure 13 is a propagation energy diagram illustrating the cause of such a failure. When the delay column is initiated, at first it propagates successfully because E_f ex-

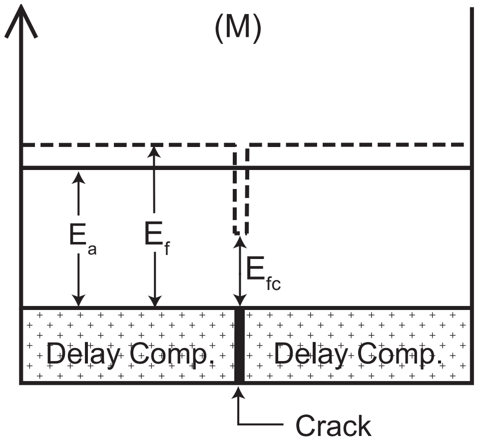

Figure 13. Propagation energy diagram for a delay column with a crack in the composition.

ceeds E_a. However, at the point of the crack or separation, there will be a substantial decrease in the amount of thermal energy being fed back. This is because the air gap, even if quite narrow, has significantly reduced the thermal conductivity. At this point, when E_{fc} falls below E_a, propagation must cease.

In fireworks, a somewhat similar propagation failure can occur as stars are expelled from a Roman candle or hard bursting aerial shell. In these cases, propagation can sometimes fail because E_f momentarily drops below E_a. Figure 14 is an illustration of two burning stars. In the case where the star is stationary, the flame hovers relatively close above the burning surface of the star. This allows ample opportunity for thermal energy to be fedback from the flame to the burning surface via radiation. However, in the case where the star is moving rapidly through the air, the flame will be cooled because of greater mixing with air and the flame will be deflected away from the burning surface. In effect, the amount of thermal energy being fedback to the burning surface will be reduced. Figure 15 is a photograph taken while measuring the explosive force of a bursting fireworks aerial shell. However, it also documents the way the flame trails behind moving stars.

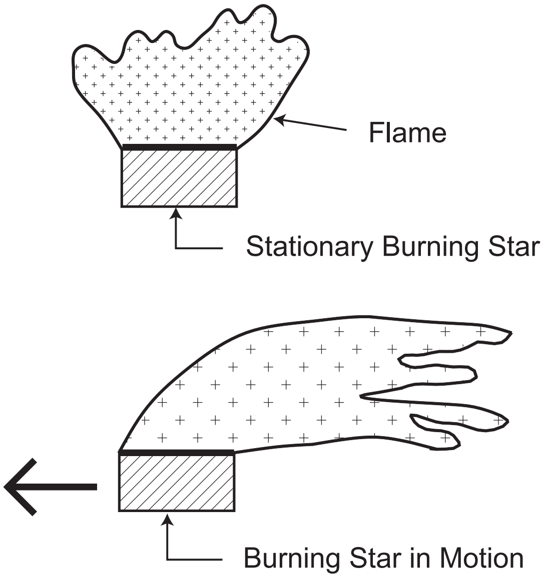

Figure 14. Illustration of a burning fireworks star, when stationary and when moving through the air.

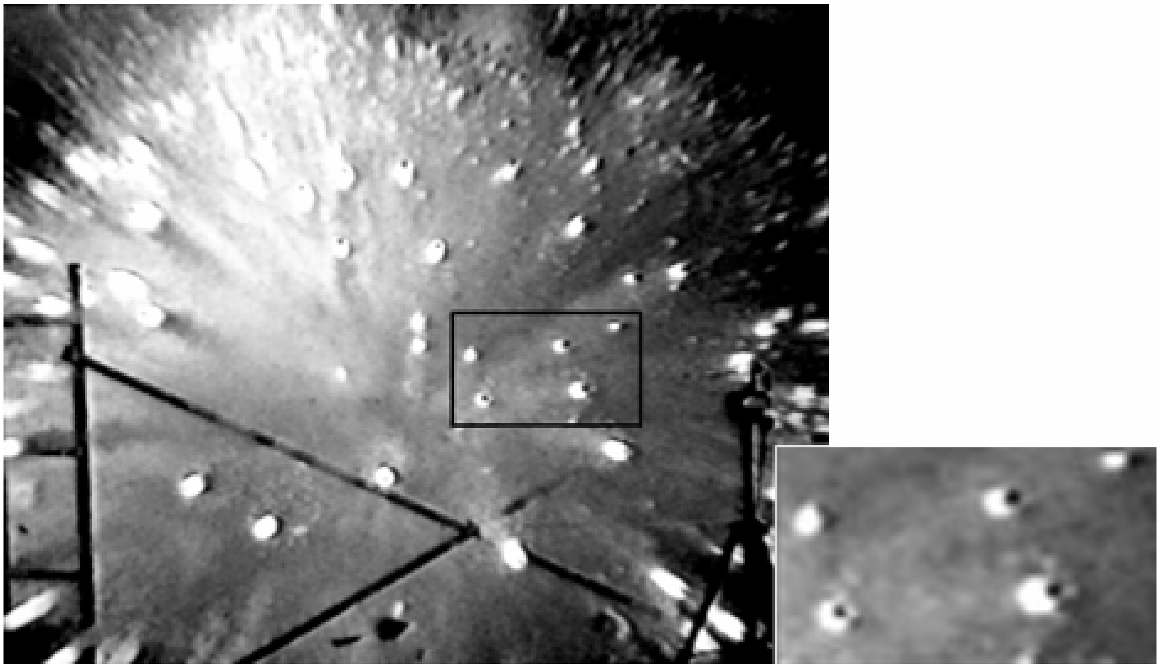

Figure 15. Photo and enlargement taken of a bursting fireworks aerial shell demonstrating the way the flame trails behind the moving stars.

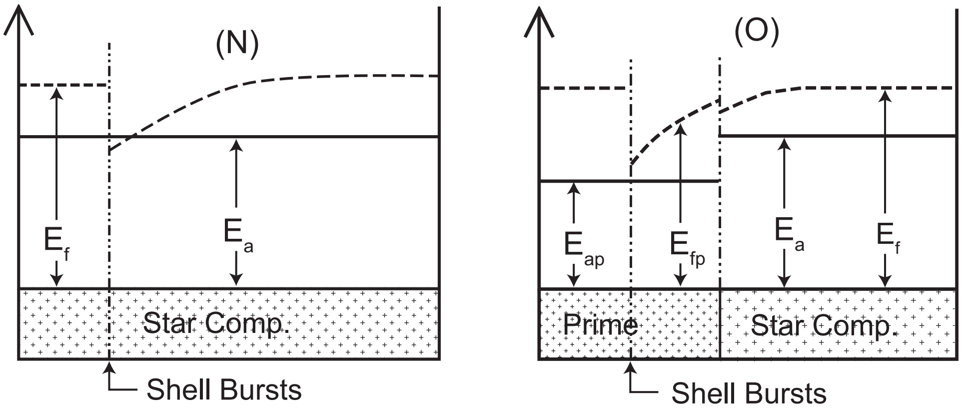

Figure 16. Ignition and propagation energy diagram of unprimed and primed stars as they are expelled from a bursting fireworks aerial shell.

Case **N** in Figure 16 is a propagation energy diagram for an unprimed fireworks star as it is expelled from an exploding aerial shell. (Note that the amount of star burning before the shell burst has been exaggerated.) Initially the star ignites and burns because E_f exceeds E_a. However, as the aerial shell bursts, and the star is then expelled at high velocity, E_f drops because the flame now trails significantly behind the star. In this case, because E_f falls below E_a, the star is extinguished. (This effect is sometimes referred to as a star being "blown blind".) After the shell bursts, aerodynamic drag acts to quickly reduce the speed of the star, and as a result, if the star had stayed lit, the flame would have moved back closer to its surface. Accordingly, E_f would increase, soon exceeding E_a and approach its initial value. That is to say, if it could be arranged to keep the stars lit just after the shell burst, the stars would stay lit and burn completely.

Unlike the previous two examples of propagation failure, this is a case where priming can help. In case **O** of Figure 16, a layer of prime (thickness exaggerated) has been applied to the star's surface. In this example, when the aerial shell bursts, again there is a drop in the energy fed back (E_{fp}). However, because it is a characteristic of the prime that there is a larger differential between E_{fp} and E_{ap}, this time E_{fp} does not fall below the activation energy requirement of the prime, and the prime layer continues to burn. If the prime layer is thick enough, such that the star slows sufficiently by the time the prime layer is depleted, E_{fp} will have risen sufficiently that burning will continue and the star will be consumed in its intended display.

Prime Formulations

The most widely used pyrotechnic primes are based on Black Powder. Some typical applications help assure the ignition of signal flares, fireworks stars and fountains, special effect gerbs, and fusing systems. When cost is not a major consideration, the Black Powder would be commercially manufactured. Where the prime is to be pressed into place, any of the granulated powders in the range of 20 to 60 mesh may be used. Where a slurry is to be prepared, a fine grained powder such as meal D or fine meal will be combined with a suitable binder before use. In fireworks, typically a less expensive "rough powder" will be used. Rough powder is a handmade powder with the same basic formulation as Black Powder (see Table 1) but without the extensive mechanical processing of Black Powder. As a consequence, rough powder has burning characteristics that are somewhat inferior to Black Powder, but fully adequate for its use as a fireworks prime.

Table 1. Prime Formulations (without listing the binder used).

Ingredient	Rough Powder	Enhanced Rough Powder	Potassium Perchlorate Based	Enhanced Perchlorate Based	Dark Prime	Alternate Dark Prime
Potassium nitrate	75	75	—	—	75	78
Potassium perchlorate	—	—	70	70	7	—
Potassium dichromate	—	—	—	+5(c)	—	—
Charcoal (very fine)	15	15	10	10	8	12
Sulfur	10	10	—	—	—	—
Antimony sulfide	—	—	—	—	3	—
Red gum (accroides)	—	—	20	20	2	—
Shellac	—	—	—	—	—	10
Silicon (–200 mesh)	—	+5(b)	—	—	—	—
Reference	Common	Kosanke(a)	Kosanke(a)	Kosanke(a)	Shimizu[4]	Jennings-White[5]

(a) These particular formulations were developed in about 1980; however, it is not intended to imply that similar or identical formulations had not been previously developed and used by others.

(b) The amount of silicon powder used can be varied according to the need. Typically 3 to 10% was found to be effective.

(c) Smaller amounts of potassium dichromate (as little as 1 or 2%) are effective in improving the vigor of the propagation of this prime. Because of the various serious health hazards associated with potassium dichromate,[6] it is advisable to use no more of this chemical than is necessary to accomplish the need.

There are occasions when the thermal output of Black Powder or rough powder may not be adequate to reliably ignite the main pyrotechnic composition. One such example from fireworks is in the priming of some strobe star compositions. A common method for increasing thermal output is the addition of a high energy fuel, such as fine mesh aluminum, to the basic rough powder prime. The choice of aluminum will be effective in increasing the heat of reaction of the prime, and there are instances where this is sufficient. (The use of fine aluminum also tends to increase the light produced, which can be aesthetically undesirable.) Fine mesh silicon is another fuel that can provide the same increase in thermal output and also improve the efficiency of energy feedback. Upon burning silicon forms molten silicon dioxide (glass). This combustion slag can aid in the conduction of thermal energy to the yet unignited composition.

One place that such a high temperature slag is particularly effective is where the prime is employed to cause the ignition of material that is not in direct contact with the prime. An example is the prime applied to a Bickford type fuse on the inside of a pyrotechnic device, in which a spray of combustion products from the end of the fuse is intended to provide the ignition stimulus for the device. When silicon is used as an additive in the prime, not only will additional energy be produced, but also molten droplets of glass will be included in the combustion products.

The "enhanced" rough powder formulation in Table 1 is an example of an energetic slag-producing prime. Note that the amount of silicon used in the prime formulation can be adjusted to meet the need. Note further that the silicon powder has been added to rough powder without reformulating the prime for the maximum production of energy. At the time this formulation was used, this was mostly done for convenience, as a supply of rough powder was already available for other applications, and various amounts of silicon powder could be added to fit the particular need at the moment. The lack of necessity to reformulate the prime tends to demonstrate the efficacy of the prime. However, to some extent, this thermally enhanced prime may rely on atmospheric oxygen for complete combustion.

There are times when a nitrate-based prime such as Black Powder is inappropriate; for example when priming a composition including ammonium perchlorate. In this case, when either composition is moistened with water (or more slowly by withdrawing moisture from the air) a double decomposition (metathesis) reaction can occur to form the hygroscopic oxidizer, ammonium nitrate. When this occurs, the application of the prime may prevent the ignition of the device. There are also times when the presence of sulfur in a prime can be problematic; for example when priming a composition containing a chlorate. In this case, the chlorate and sulfur combination gives rise to concern regarding the sensitiveness to accidental ignition. A prime formulation avoiding the use of both a nitrate and sulfur is the potassium perchlorate-based prime in Table 1. This prime is useful in many applications, but it does not offer the same level of burning persistence as Black Powder primes. This can result in problems maintaining the burning of items moving rapidly through the air. When necessary to overcome this problem, a fiercer burning prime will result when a small amount of the burn catalyst potassium dichromate is added to the composition. However, because of the health risks associated with potassium dichromate,[6] appropriate precautions must be employed, and no greater concentration of potassium dichromate than necessary should be used.

Finally in Table 1 are two dark prime (color change relay) formulations. The first formulation is fairly traditional. Whereas the second is simpler and avoids the use of antimony sulfide, which may produce sensitiveness problems when priming compositions containing a chlorate. Another group of prime formulations is presented in Table 2 without comment except for the table notes.

Prime Binding

In most instances, it is necessary to attach the prime composition to something, such as a pyrotechnic device or a fuse. To hold the mass of prime together and in place on the item, some form of binding system must be used. Probably the most common method, especially for fireworks, is to add a small amount (typically about 5%) of an aqueous binder to the prime composition. The binder is activated with the addition of water; the prime is applied to the component being primed and allowed to dry. Dextrin (made from corn or potatoes) is the most common aqueous binder used in Western countries, and soluble glutenous rice starch is the most common in the Orient. In the past, gum Arabic was also commonly used, especially in the manufacture of black match and for priming fuses. Recently, several new families of aqueous binders with variable thixotropic properties are being employed, including polyvinyl alcohol (PVA), sodium carboxymethylcellulose (CMC), and hydroxyethylcellulose (HEC). For these binders, the length of the polymer chain (whether manmade or natural) is selected to control their viscosity and thus their thixotropic properties. Such binders can be useful when it is desired to hold the components of a prime in suspension in a slurry and retard their settling out during use.

Water activated primes require fairly long periods to dry, typically at least several hours and potentially even days. The drying period must be especially long in some applications, such as when there is a chance that water has migrated from the prime into the powder core of a fuse. To some extent drying time can be reduced when a water plus alcohol mixture (typically in a 50:50 ratio) is employed. Another advantage of a water-alcohol mixture is that surface tension is reduced, making it somewhat easier to mix the solvent into the prime composition and to coat surfaces with the prime. However, it is thought that the use of alcohol may inhibit the effectiveness of some aqueous binders.

Table 2. Additional Prime Formulations.

Ingredient	Starter Mixture[(a)]	Thermite Igniter[(b)]	First Fire[(c)]	Tracer Igniter[(d)]	Magnalium Thermite[(e)]	Hot Perchlorate Prime[(f)]
Potassium nitrate	70	—	—	—	—	—
Potassium perchlorate	—	—	—	—	—	60
Barium peroxide	—	31	—	78	—	—
Iron(II-III) oxide (black)	—	29	—	—	—	—
Iron(III) oxide (red)	—	—	25	—	75	—
Red lead oxide	—	—	25	—	—	—
Charcoal (very fine)	30	—	—	—	—	15
Calcium resinate	—	—	—	2	—	—
Red gum (accroides)	—	—	—	—	—	5
Aluminum (fine)	—	40	—	—	—	—
Magnesium (fine)	—	—	—	20	—	—
Magnalium 80:20 (200 mesh)	—	—	—	—	25	—
Silicon (fine)	—	—	25	—	—	10
Titanium	—	—	25	—	—	—
Zirconium (60–200 mesh)	—	—	—	—	—	10
Reference	Ellern[7]	Ellern[7]	Ellern[7]	Ellern[7]	Jennings-White[5]	Jennings-White[5]

(a) "Sulfurless Black Powder" is typically bound using nitrocellulose lacquer.

(b) A high thermal output, relatively easily igniting, modified thermite used as an ignition mixture for normal thermite.

(c) An easily igniting, high thermal output prime based on Goldschmidt (thermite) reactions.

(d) Good resistance to high speeds through the air, used to prime tracers.

(e) The use of 80:20 magnalium overcomes much of the ignition difficulties of normal thermite, allowing its use as a prime.

(f) Essentially a modification of the potassium perchlorate prime from Table 1 that produces significantly greater thermal output.

With the wider range of chemicals in use today, and especially with metal fuels, there may be concern about the water reactivity of pyrotechnic compositions. (For more information on potentially hazardous chemical combinations, see reference 3.) One effective solution to this problem is simply to avoid the use of aqueous binding systems. When prime formulations already contain red gum or shellac, typically as fuels, those ingredients can also be employed as the binders for these primes. These binders are activated with a suitable solvent, most commonly an inexpensive alcohol. Both methanol (wood alcohol) and isopropanol (rubbing alcohol) are frequently used. However, methanol vapors are hazardous to breathe, potentially producing optic nerve damage,[8] and isopropanol typically contains up to approximately 30% water. Thus the best choice for an alcohol is probably denatured ethanol (grain alcohol). When compositions do not already contain an alcohol activated binder, a small amount of such binder can be added to the formulation. Probably the most commonly employed nonaqueous binding system is nitrocellulose lacquer, usually 5 to 10% nitrocellulose in an acetone solution. Typically, the drying time for nonaqueous binding is shorter than for water activated binding systems, and the nitrocellulose lacquer system is especially fast drying. However, some systems, such as red gum activated with alcohol, form a gummy mass and can be especially slow to dry.

All materials, even crystals, are capable of plastic flow under the influence of a sufficiently high pressure. This plastic flow of material can be effective to bind a prime together and to other materials. When a pyrotechnic formulation contains relatively soft materials like shellac, red gum, asphaltum, or sulfur, the pressures required for plastic flow binding are sufficiently low as to be readily accomplished by pressing, even into paper casings. Obviously, because no solvent is involved, no drying time is required for plastic flow binding.

Prime Application Techniques

Often, especially in fireworks, the main pyrotechnic composition is prepared wet, using a solvent to activate its binder. If the same solvent will dissolve the binder in the prime composition, the simplest method of application is to apply loose dry prime composition to the exposed damp surfaces of the main composition. In so doing, some of the solvent will migrate from the main composition into the prime composition thus activating the binder in the prime composition. Accordingly, when the item dries, some of the prime will then be bound to the surface of the main composition. This "dusting" process can be more thoroughly described using the example of "cut stars" in fireworks. Cut stars are prepared by first forming amply moistened star composition into a "loaf", which is a solid block of hand-compacted composition. This loaf is then cut using the equivalent of a dull knife, first into slices, and then each slice is diced into cubes. To apply the prime to such stars, first the work surface is dusted with a thin layer of prime composition. When a slice of the star composition is cut from the loaf, it is allowed to fall onto the loose prime composition, some of which will stick to its moist surface. Then additional prime composition is dusted onto the top surface of the slice, to which some will adhere. After dicing the slice of star composition into cubes, to the extent practical, prime composition is dusted onto the freshly exposed surfaces of the cubes. Using dusting to prime pyrotechnic compositions is fairly simple and, providing an excess amount of prime has been used, has the advantage of producing a prime surface that tends to readily take fire. This is because the outer most surface of prime is relatively loose, rough-textured and free from any significant buildup of binder (discussed further below). However, dusting suffers from the disadvantage that generally only a small amount of prime can be made to stick to the surfaces; for most items, this is probably only a few percent by weight. Another problem is that the dusted prime can easily be removed with rough handling.

Some pyrotechnic items, such as color changing fireworks stars, as illustrated in Figure 8, are made as a series of layers, like the structure of an onion. In western countries, the layering process is commonly produced by alternating the application of a spray of water (or other solvent) and dry pyrotechnic composition. The spray of water causes the surface of the item to become sticky, providing a ready surface for the dry composition to adhere. For such items, probably the most effective method of applying the final prime coating is simply to conclude the cumulative layering process with some number of layers of prime. (Similarly, the dark prime between the color compositions of color changing stars can be applied in layers.) The use of a layering process has the advantage of allowing any number of layers of prime to be applied (i.e., any amount of prime to be applied). This can be quite important in some situations; for example, when difficult to ignite and easily extinguished fireworks stars are propelled from hard breaking aerial shells. To maintain their burning, there must be sufficient prime to continue burning until the stars have slowed sufficiently for the star composition itself to be able to remain ignited (as depicted in Figure 16). In these cases, often the outer prime layer may be 10 to 20% by weight of the star. For easy ignition of prime composition applied by layering, it is important that the very last application of dry composition be in excess to what would normally adhere to the surface. This will help produce an outer surface that is rough and mostly free of solvated binder, similar to that described above for prime applied by dusting.

For small completed items and especially fuses, "slurry" priming is often used. In this case, sufficient binder solvent is added to the prime composition to make a thick but flowing slurry. The viscosity of the slurry is controlled by the amount of solvent and the choice of binder (and possibly flow control additives). Viscosity is adjusted to meet the needs of the particular application method, which tends to fall into three categories. In many cases the prime slurry is simply applied by painting using a small brush. Another common method (to apply a more viscous prime slurry) is from a container under pressure, for example using a squeeze bottle such as used for food products like mustard or catsup. This has the advantage of generally allowing the application of a thicker coating of prime than is practical by painting with a brush. The third slurry application method is sometimes used to completely coat the surface of the item or device to be primed. In this case, the item is briefly submerged in the prime slurry, either individually using a forceps (tweezers) to hold the item, or in batches using a course screened basket containing the items. Following the dipping process it is common to dust a layer of dry prime onto the exposed surfaces of the items.

Many pyrotechnic devices have the main pyrotechnic composition compacted using a press. Examples of such items are signal flares, tracers, whistles, fountains, drivers, etc. For these items, it is often convenient to apply the prime layer using compaction (plastic flow binding). In these cases, one or more increments of prime composition are used in the pressing of the item, such as illustrated in Figure 1 for an aerial flare and fireworks gerb. For devices made using compaction, this is probably the most common prime application method.

Regarding prime application methods, there are a few additional subjects that should be considered that can greatly affect ignitablitiy. Figure 17 has photographs of two fireworks aerial shells with their Bickford-style timing fuses primed. The shell in the top photo has had a layer of prime painted over the end of the fuse. The shell in the bottom photo has had a larger amount of prime applied using a squeeze bottle, then the prime was pressed lightly into a bed of loose granular Black Powder, some of which then adhered to the prime surface.

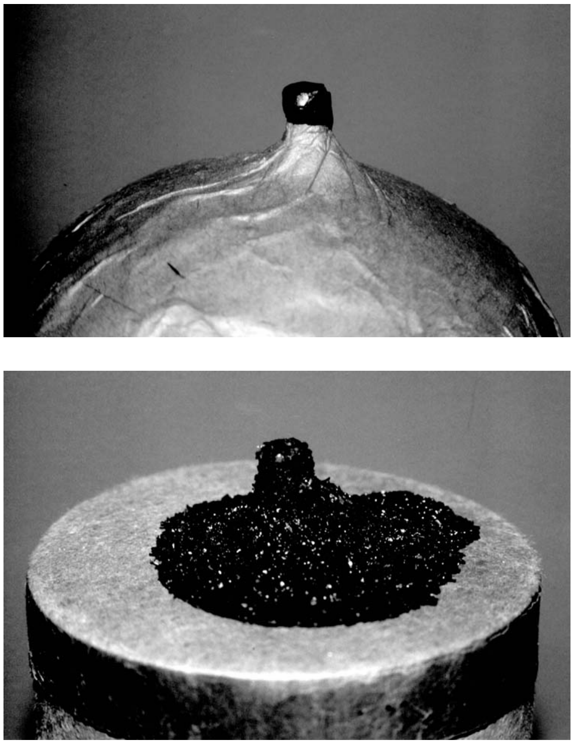

Figure 17. Examples of fuse priming methods with greatly differing probabilities for successful ignition.

All else being equal, the larger the primed surface area, the greater the probability it will successfully be ignited by any given ignition stimulus. The reason is simply one of probability. If all locations on the primed surface have an equal chance of being ignited, the probability of ignition increases as the number of locations (surface area) increases. In the upper photo in Figure 17, the total prime surface area is approximately ¼ square inch (160 mm^2), while that in the bottom photo has approximately 10 times more primed surface.

The surface texture of the prime coating is also important. Generally, if the surface is smooth and hard, such as pictured for the prime layer in the upper photo of Figure 17, ignition will be more difficult than if the surface is rough, such as for the prime layer in the lower photo. With a rough surface, the tiny exposed points will raise more quickly and to higher temperatures than the bulk of the prime coating. Accordingly, these points are more likely to take fire and cause the rest of the prime to ignite, even when the amount of energy supplied would not otherwise have been sufficient.

Another potential surface problem for prime compositions applied wet with solvents, is that during the drying process a thin layer of binder can form on the surface. As illustrated in Figure 18, this can occur because, as the solvent migrates to the surface, it carries dissolved binder with it. Then as the solvent evaporates, the binder (and other soluble components) are left behind on the surface. This collection of binder can produce a surface that is quite resistant to ignition, both because of its chemical composition and because it can be quite smooth. The likelihood of experiencing this problem can be reduced if a minimum amount of solvent is used, and if the surface is dusted with dry prime composition or granular Black Powder.

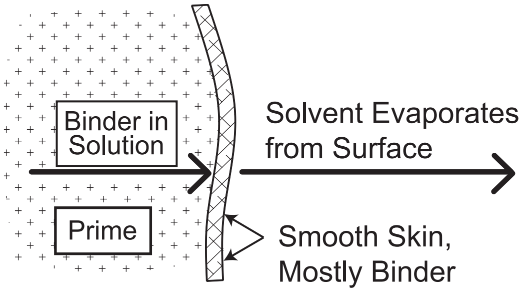

Figure 18. Illustration of the formation of a "skin" of mostly binder on the surface of prime.

Alternatives to Priming

One alternative method applies to Bickford style fuse. It is more common to "cross match" such fuse as shown in Figure 19, than it is to apply a coat of prime composition. In this case a hole has been punched through the fuse such that it intersects the powder core of the fuse. Inserted into the hole is a thin piece of black match (cotton strings impregnated and coated with Black Powder). In this case, if any point on the surface of the black match is ignited, quickly the entire black match is consumed and the powder core of the time fuse is ignited.

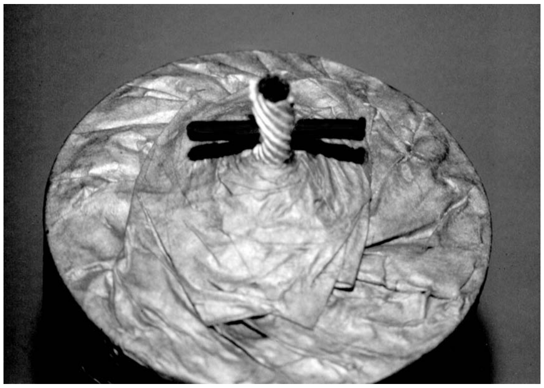

Figure 19. Example of a fireworks aerial shell with a "cross matched" time fuse.

In some cases, the main pyrotechnic composition of an item itself has ignition and burning properties that are similar to prime compositions. If that is the case, there is no need for the application of a prime to its surface to help insure ignition. Examples of some pyrotechnic compositions that will likely have properties that are sufficiently prime-like are: rough powder-based spark-producing compositions, most fireworks glitter compositions, and chlorate-based colored flame compositions. However, as with prime compositions, consideration must be given to the physical condition of its surface. To achieve successful ignition, rough textured surfaces are preferred to those that are hard and smooth.

Conclusion

Many failures of pyrotechnic items and devices are the result of the inability to cause their ignition at the time of their intended use. Properly formulated and applied pyrotechnic prime compositions when present on the ignition surface can significantly improve the probability of successful ignition. Ideal prime compositions are those that: are easily ignited (have a low activation energy requirement), but not so easily ignited that accidental ignitions are likely; upon burning, produce abundant thermal energy (have high heats of reaction); and have efficient means of feeding thermal energy to the main pyrotechnic composition.

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Notes

Pyrotechnic Delays and Thermal Sources

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ABSTRACT

The technology associated with pyrotechnic delays, together with the many factors, both physical and chemical, that affect the performance of delay compositions and influence the design of delay elements have been outlined. The production of heat by thermite and thermate systems is similarly discussed.

Keywords: pyrotechnics, gassy delays, black powder, gasless delays, thermites, thermates, incendiaries, Goldschmidt reaction

Introduction

The combustion process of a pyrotechnic composition can be used to provide a time interval ranging from a few tens of milliseconds to several minutes between successive mechanical, electric or explosive events. Any composition will take a finite time to burn over a given length, but the requirements of safety, time reproducibility and ignition transfer reliability, particularly in modern military applications have resulted in the development of specific formulations known as pyrotechnic delays. Compositions of this type, when consolidated into a tube (usually by pressing the powder mixture under high loads) burn at reproducible linear rates. The assembly consisting of an ignition source, the tube, pressed composition and ignition transfer system is called a *delay element*.

A delay element can be used to provide a safety interval, for example, between the deployment and detonation of a hand grenade, to allow time for a projectile to reach its target or to form part of an electro-mechanical sequencing system for a fuze train. Pyrotechnic delays have found many applications, even in these days of cheap electronic timing systems because of their simplicity, the high degree of inherent safety, their ruggedness and reliability, and also because they do not require a power source such as a battery.

Although pyrotechnic reactions can be designed to produce diverse physical effects, including time delays, the basic combustion process is exothermic (i.e., heat is evolved). The appropriate selection of chemical ingredients can optimise heat production and because very high temperatures are produced, one or more of the reaction products will be in the liquid phase. Such specific formulations are usually known as *thermites* and can be used to cut, burn or weld metals. With controls applied to design parameters, the reaction dynamics of thermite compositions can be closely regulated, resulting in reproducible propagation velocities and very low volumes of gaseous reaction products. As a result, certain thermite type formulations, known as *'gasless' delays,* can be used in hermetically sealed systems to produce very accurate delay intervals in explosive trains. Because the chemistry of gasless delay compositions is often identical to that of thermites, both are considered together in this chapter.

Delay Compositions

Until World War II, Black Powder was the basis of virtually all delay elements used in munitions, whether formed into columns by a wrapping process (*Bickford or safety fuse*), coating as a paste onto hemp yarn (*quick match*) or by the more sophisticated method of pressing the material into metal tubes or channels. Black Powder, if it can be kept dry, can be used to provide quite accurate time intervals. It produces a significant volume of permanent gas during combustion (about 300 mL/g of Black Powder), and so devices containing Black Powder must be vented, otherwise, the combustion rate will

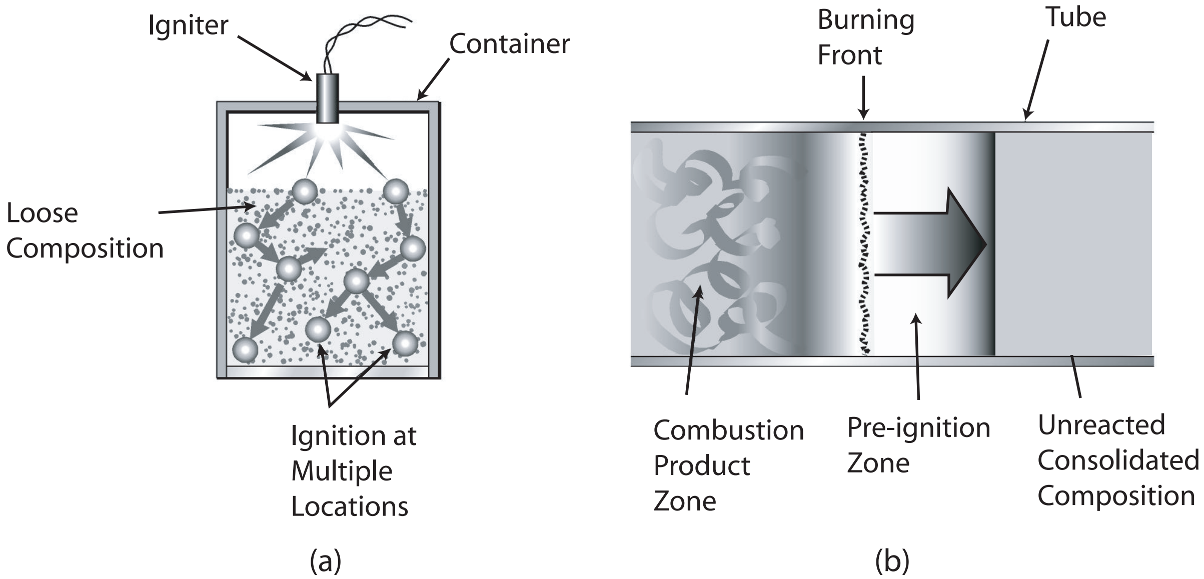

Figure 1. Combustion in the loose and consolidated states.

increase due to pressurisation, and short delay times will result. In high altitude applications where the ambient pressure is low, long delay times and possible extinguishment of the vented column are likely due to heat losses from the system. However, because the charcoal ingredient in Black Powder is somewhat hygroscopic, the delay column must be sealed from the environment during storage. Mechanical solutions to these competing requirements have increased the complexity of gas-producing (gassy) delay systems and are only partly successful.

With the development of weapons systems required to operate with high levels of performance reliability and reproducibility under a wide range of environmental conditions, the gassy delay system has been displaced by a relatively new type of composition—the gasless delay. As its name implies, the gasless delay composition produces comparatively little permanent gas during combustion. For this reason, the combustion rate is less affected by pressurisation of the burning front and as a result, the delay element can be totally sealed from its operational and storage environments. In other words, time intervals of high accuracy can be produced whether the system operates at great depths beneath the sea or in the vacuum of space. Moreover, hermetically sealed delay elements incorporating gasless delays can be stored for long periods without deterioration due to the ingress of moisture.

However, gassy delays have not been entirely superseded. Many new formulations have been developed, resulting in delay systems that exhibit better time accuracy over their service life than the Black Powder type. The burning rate-pressure dependency of gassy delays, particularly at extremely high pressures, is still used in certain fuze systems to produce millisecond duration sequencing intervals between safety and arming events.

Combustion in Consolidated Columns

Before examining delay compositions in some detail, it is necessary to compare the mechanisms of combustion in the loose and consolidated states. Figure 1a shows a container filled with loose Black Powder. Upon initiation of the prime ignition stimulus, the grains of powder immediately beneath the stimulus are ignited. These burn, generating hot combustion products that are free to ignite surrounding grains throughout the void spaces in the filling. The low bulk density of the filling, the turbulence caused by the combustion process and the consequent ignition of Black Powder at many sites remote from the prime stimulus means that the combustion rate is very rapid. The confinement offered by the container causes the process to occur under pressure and an explosion will generally result.

If, rather than fill the loose Black Powder into a container, it is laid out in a trail, made into a paste and coated onto a cord, or lightly stemmed into a tube, a slower burning rate generally results. In early mining operations, such arrangements were used as fuses to introduce a delay interval between ignition of the fuse and explosion of the main charge. However, combustion propagation along the fuse train is not well controlled—burning particles ejected or windborne from the trail, or flashing down the cord or tube are capable of igniting the main charge too soon—a highly dangerous situation. It was William Bickford, with the development of hemp-wrapped Black Powder fuse in the early 1800s,[1] who improved the safety of blasting operations and laid the basis for the future development of highly accurate pyrotechnic delay elements.

The combustion process shown in Figure 1b is much slower and more controlled. This is because the pyrotechnic filling has been compacted by pressing it into a tube to a density approaching its theoretical maximum (TMD), and the void spaces throughout the composition have therefore been reduced to as low a level as possible (typically 2–12% of the total volume). The void space is the total volume of the space between the ingredient particles; this is largely determined by the physical properties of the ingredients and the compaction pressure.

In a pressed composition, the products of combustion (e.g., gases and heat) are unable to travel far into the consolidated column and combustion is confined to a relatively thin propagation zone known as the *burning front*. The tube, into which the composition is pressed, not only has the function of supporting the column in a mechanical system, but also allows combustion to occur only at the burning front. Although delay compositions generally consolidate well into tubes, the risks associated with the possibility of uncontrolled burning must be considered in the design of a delay element. Adhesion failure between the composition and the delay tube wall can have serious consequences (such as a short or nonexistent delay time in a hand grenade).

As shown in Figure 1b, the plane of the burning front proceeds in a ‘cigarette fashion’ from left to right through the column of composition at a notionally constant speed. Immediately to the left of the burning front is the combustion product zone and to the right is the pre-ignition zone where the unreacted composition is heated by the intrusion of combustion products (gases, liquids and thermal radiation) into the consolidated column. Largely, it is the degree of pre-heating of the reactants before the arrival of the burning front that determines the rate at which the column combusts.

Burning Rate

The burning rate of a pyrotechnic composition is the speed at which the burning front proceeds along the length of the consolidated column. The burning rate can be expressed in units of length per second (*linear burning rate*), or mass consumed per second (*mass burning rate*), depending upon the application. However, it is important to understand that the measured linear burning rate is really an average value—the speed at which the burning front progresses through the column may continually increase and decrease under the influence of a wide range of factors. These are related to the properties of the composition itself and to other stimuli both internal and external to the system. For a pyrotechnic delay composition filled into a device, the cumulative effect of these influences results in a measured burning time for a particular column length—the *delay interval*.

Because the time produced by a given system is often of more direct relevance to the pyrotechnist than the length of the column, many designers and researchers have used a reciprocal unit to quantify the burning rate of pyrotechnic compositions. The *reciprocal linear burning rate* (RLBR) is expressed in units of time per (convenient) unit of length (e.g., s/cm) rather than as a speed value (cm/s or mm/s). The reader will encounter the use of both units in the literature, and it is largely a matter of personal preference as to which value is employed.

However, pyrotechnic performance characteristics, including explosives sensitiveness are related to the burning rate of a composition and therefore the two units must never be confused.

The RLBR can be used as a primary quantifier of a pyrotechnic composition. Although the burning rate will likely be altered by the combustion environment (e.g., certain mixtures burn faster under increased pressure and temperature), the RLBR value is normally determined at ambient pressure and temperature. It allows an immediate comparison to be made of the burning rates of different formulations and can also be used to predict the pyrotechnic effect likely to be produced by various formulations and composition types. For example, a flare composition that burns at a faster rate will generally produce higher luminous emission than a similar, but slower burning formulation.

Determination of Burning Rate

Often, the pyrotechnist faced with the problem of making a composition that burns at a specified rate for a particular application can physically blend two similar formulations having different RLBR values to achieve the required burning rate. Usually, the burning rate under ambient conditions can be readily determined by using one of the following techniques:

(a) Incremental Method

This is probably the most common method used to fill delay elements for applications such as hand grenades. A small mass of loose composition is loaded into the delay tube and consolidated using sufficient force to produce a high compaction pressure (typically >150 MPa). Successive increments are loaded and pressed in this way until the required column length is achieved. The mass of each increment is limited so that density variations throughout the consolidated column do not cause excessive variations in the burning rate (the interfaces between the individual increments can cause a momentary slowing of the burning rate). The column length may be increased or reduced, depending on the reaction dynamics of the system, to achieve the specified delay interval. This filling technique is time consuming and the results are somewhat dependant on operator skill levels, and therefore may not be cost effective for long (>5 s) delay intervals or the determination of the RLBR in the laboratory.

(b) Extrusion Method

A faster method for filling delays was developed in the UK in the 1960s—a length of lead tubing, which has been closed at the bottom by crimping, is volumetrically filled with loose composition. This is stemmed by hand using a wooden drift and the tube is crimped at the top. The filled tube is then passed through a set of reduction rollers in a specially designed machine until the required diameter is obtained. The first 5–10% of the extruded length is discarded from each end and the remainder is then cut into equal lengths using a sharp knife. Each length is ignited with a match and the burn time is recorded with a stopwatch or video system. The average burning time for the lengths is then calculated and (in the case of RLBR) expressed as a function of length.

The process compacts the lead-sheathed composition to about 100 MPa so that longer lengths can be loaded and subsequently pressed into delay elements, reducing the number of increments and the likelihood of burning time variations. The technique is especially applicable to the determination of the RLBR under ambient conditions because it is much quicker, cheaper and less skill dependant than the incremental method and delays of longer length can be more readily produced.

Factors Affecting Burning Rate

A wide range of factors can influence the burning rates of pyrotechnic compositions, including those intrinsic to the compositions themselves and other factors introduced by the device into which they are filled or the operational combustion environment:

- thermochemical properties of the reactants
- stoichiometry of the composition
- chemical and physical properties of the reactants; including purity, particle size and behaviour under compression

- thermal conductivity of the composition, particularly the fuel ingredient
- thermal conductivity of the tube housing the column
- thermal radiation from the reaction products and probably the infrared (IR) absorption characteristics of the composition's ingredients
- convective effects at the burning front
- volume of temporary and permanent gases produced by the composition
- pressure at the burning front
- characteristics of the condensed combustion products
- void space in the filling and consolidation pressure
- environmental effects such as the temperature of the surroundings and spin
- design of the device, particularly the end seals
- number and size of composition increments
- diameter and length of the column
- the mechanical strength of the column
- the type of ignition source
- the 'first fire' (priming composition) that might be used

While a delay composition having a fast burning rate is generally more reproducible than a slower burning formulation, the collective influence of all these factors (to a greater or lesser extent) determines the overall time interval produced by the delay element. Considering the above list, it might not seem possible that a pyrotechnic delay element could ever give a consistent time, but pyrotechnic delays are used in explosive trains to produce accurate time intervals, often under very adverse conditions. The pyrotechnist faced with designing a delay element or solving production problems with an existing system must consider all these influences to be successful.

Thermochemistry and Stoichiometry

The intrinsic burning rate of a delay composition is mainly determined by the chemical ingredients, their proportions in the composition, and also their thermochemical properties. For example, an oxidiser that decomposes exothermically (such as potassium perchlorate, $\Delta H_r^\circ = -3.7$ kJ/mol of $KClO_4$) will require less heat from the system for decomposition than an endothermic oxidiser (such as barium nitrate, $\Delta H_r^\circ = 220.0$ kJ/mole of $Ba(NO_3)_2$). This means that, all other factors remaining equal, the combustion temperature and the burning rate of the system containing the exothermic oxidiser will be greater. An oxidiser or fuel that undergoes a phase change or a phase change at higher temperature during the combustion process will remove heat from the system and slow the progression of the burning front accordingly. Chemical impurities in the ingredients, and the mere presence of the mixed ingredients themselves may lower the onset decomposition temperature of the oxidiser or alter the combustion characteristics of the fuel.[2] These factors may cause variations in performance.

To compare the relative thermal output of fuel ingredients, the Q_1 value is often used:

$$Q_1 = \frac{\Delta H_f^\circ}{mA} \tag{1}$$

where ΔH_f° is the heat of formation (enthalpy) of the oxide, A is the atomic (or molecular) weight of the fuel and m is the number of atoms of the fuel in the product molecule. For a given particle size and surface area, a fuel such as boron that produces more heat when it oxidises ($Q_1 = 58.96$ kJ/g) will react faster than a less reactive fuel such as silicon ($Q_1 = 32.40$ kJ/g). Depending on its proportion in the composition, a fuel may also combust to produce higher or lower oxides and alter the thermal output (where Q_2 is the heat of combustion per unit mass of reactants) of the combustion process. McLain[3] gives an example:

$$Mn_{(s)} + 1/2\ O_{2(g)} \rightarrow MnO_{(s)} \qquad Q_2 = 5.43 \text{ kJ/g} \tag{2}$$

$$Mn_{(s)} + O_{2(g)} \rightarrow MnO_{2(s)} \qquad Q_2 = 5.98 \text{ kJ/g} \tag{3}$$

$$2Mn_{(s)} + 3/2\ O_{2(g)} \rightarrow Mn_2O_{3(s)} \qquad Q_2 = 6.07\ \text{kJ/g} \qquad (4)$$

Diluents or modifiers may be added to the formulation to cause deliberate changes to the burning rate. A diluent is a material that may not take part in the combustion reaction, but which will physically separate the fuel and oxidiser and reduce their combined reactivity. It may also serve as a heat sink, removing thermal energy from the burning front and slowing the combustion reaction. Examples of diluents include kaolin, kieselguhr, chromic oxide, and magnesium oxide.

Rate modifiers usually undergo a physical or chemical change that removes heat from the system, for example by melting or decomposing to produce a gas that directly carries heat away from the burning front. Some phase change modifiers include the low melting point oxidisers, potassium nitrate and potassium dichromate and organic fuels such as lactose, which dehydrates on heating.[4] Gas producing modifiers such as sodium bicarbonate, calcium carbonate and calcium oxalate may also be used in gassy delays.

Delay compositions are generally formulated to be slightly fuel rich for two reasons:

- in gasless delays, the excess fuel is required to consume any oxygen gas that might otherwise be evolved by the reaction[5]
- excess fuel increases the combustion temperature, which leads to a higher combustion rate and improved reproducibility[3]

However, the determination of the optimum theoretical ratio of reactants for a delay formulation (particularly gasless mixtures) can be difficult for the designer because of the high combustion temperature of the burning front (approximately 2000–3000 °C). Deciding upon the actual product species existent at these temperatures can be assisted by computer codes such as the NASA-Lewis CEC76 program in which the conditions of temperature and pressure can be ascribed to the burning front to more accurately estimate the products.

Because of this difficulty, experimental techniques are commonly used to examine the effect of ingredient proportions on the burning rate of the composition. For example, in binary systems several delay formulations are prepared in which the fuel/oxidiser ratio is widely varied around the stoichiometric ratio (between fuel deficient and fuel rich). A number of delay columns of set length are then prepared and ignited under ambient conditions of temperature and pressure. The burn times of the columns are then measured and converted to burning speed (or RLBR) values for each formulation. These are then plotted against fuel content to give a relationship similar to that shown in Figure 2.

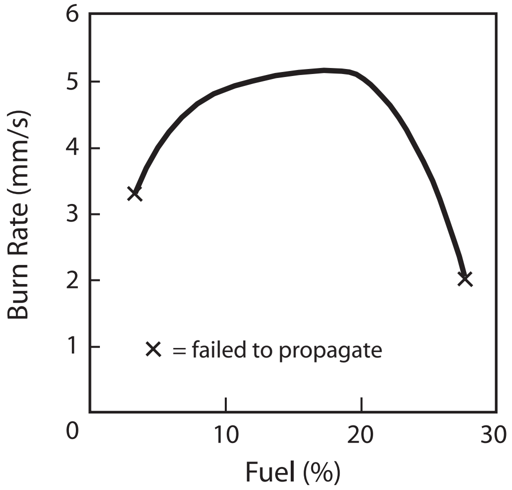

Figure 2. Burning rate vs. fuel content for a binary delay system.

When designing a delay element, it is necessary not only to select a composition having a particular burning rate, but it is equally important to ensure that the chosen formulation exhibits the required burning rate on the flat region of the burning rate vs. fuel content curve. If not, small variations in the fuel content as a result of poor mixing or ingredient segregation can significantly affect the burning rate and ultimately the time produced by the delay element. Therefore, homogeneity provided by proper ingredient preparation and mixing techniques is critically important in most delay compositions.

For formulations containing more than two ingredients, the same experimental technique is used, but the results are plotted as shown in

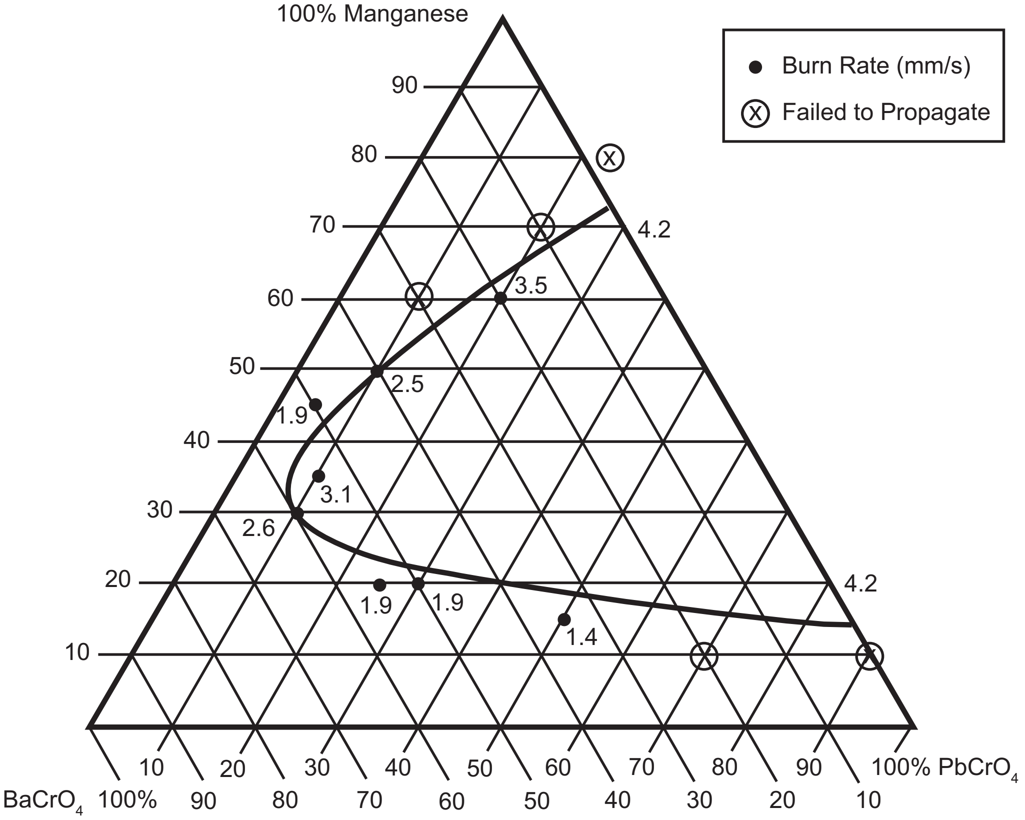

Figure 3. Burning rate vs. ingredients content for a ternary system.

Figure 3. This diagram shows the relative percentages of the oxidisers plotted against the percentage of fuel ingredient for a manganese/barium chromate/lead chromate delay system. The method can also be used with compositions containing two fuels and a single oxidiser.

Physical Properties of the Reactants

The physical properties of the reactant chemicals can have a significant effect on the burning rate and burning rate reproducibility of a pyrotechnic delay composition. Usually, the mean particle diameter of the ingredients (particularly of the fuel component) is reduced as much as possible (often to less than 10 µm) to produce the most reproducible burning rate for a given system. Although a high surface area fuel (e.g., made by a cutting or stamping process) can be expected to burn more rapidly, fuels having a low surface area (e.g., spherical particles manufactured by an atomising process) tend to combust in a more reproducible manner—a factor essential for a delay system. Another important consideration is the particle size distribution of the ingredients—chemicals having large particle size disparities can result in inconsistent burning, particularly if the composition is not well mixed.

Purity and Moisture

Because of the tight performance tolerances often placed upon delay systems, it is particularly important that each chemical ingredient of the composition is as pure (or as consistent) as possible. The chemicals used in pyrotechnic compositions normally contain impurities and these may produce unwanted effects such as the production of gas, catalytic effects, chemical instability or thermochemical changes, all of which can alter the burning rate. The chemical specifications usually set limits for particular impurities so that these effects are minimised.

Moisture must be eliminated from gasless delay compositions because of the numerous chemical and physical changes it is likely to cause within the system during both storage and combustion. For example the gradual oxidation of the fuel due to the presence of moisture will alter the available fuel content of the composition, and to a lesser degree, the change of water to vapour during combustion will cool the reaction, pressurise the burning front or directly remove heat from the system. In both these circumstances the burning rate is likely to change.

Some impurities however, may provide beneficial effects such as reducing the thermal decomposition temperature of the oxidiser or assisting the combustion of the fuel and hence improve the ignition or propagation characteristics of the composition. Boron, for example normally contains about 5–10% impurities yet serves as a versatile and effective pyrotechnic fuel. Very pure boron on the other hand is relatively difficult to ignite.

Thermal Conductivity within the Column

The use of a fuel having high thermal conductivity, such as a metal powder, increases the burning rate due to preheating effects. This effect not only demonstrates that the thermal conductivity of the column is one factor controlling the burning rate[6] but also gives the pyrotechnist another means of altering the burning rate of different formulations to suit specific requirements. The appropriate selection of the fuel ingredient or the addition of a diluent to act as an insulator or heat sink will alter the conductivity of the column and as a consequence, slow the burning rate.

Similarly, the pressing load (and the flow properties of the ingredients under increased pressure) can affect the burning rate by altering the thermal conductivity of the column by bringing the ingredients into more intimate contact with each other.

Direct Heating

The reactants in the pre-ignition zone are directly heated by thermal radiation from the combustion reaction, and it is therefore likely that the infrared absorption characteristics of the ingredients will help determine the burning rate of the system.

The reactants immediately ahead of the burning front are also heated by direct contact (conduction) with the reaction products, particularly if they are in the liquid phase. Gaseous or solid products are often carried quickly away from the burning front by thermal expansion or gas flow and so have less time to transfer energy to the unreacted ingredients.

Reaction Products

The reaction products also influence the burning rate of a consolidated column of pyrotechnic composition, often long after the combustion front has passed. At the time of burning, the specific heat of the products and their physical state at the combustion temperature will influence the heating processes occurring at the front (e.g., gaseous products may pressurise the system causing an increase in the burning rate). However condensed phase products (slag), formed once the burning front has passed, may alter the dynamics of heat loss and gas flow, thereby altering the temperature and pressure at the front and therefore the propagation speed of the burning front. In some burning delay columns, slag continually accumulates until it is suddenly displaced by internal gas pressure; it then reforms with the result that the burning rate tends to be erratic. In order to minimise the problem with compositions of this type, the diameter of the delay column is often increased.

Sometimes a formulation of ingredients is deliberately chosen so that the slag quickly solidifies, rendering the column impermeable to gas flow. This isolates the burning front from external factors that may otherwise adversely affect the burning rate or even extinguish combustion. This is the so-called ‘self-sealing’ type of delay system that can be used underwater or in ignition transfer applications where directional projection of the reaction products is desirable. A composition that has been found to exhibit self-sealing properties is:

Manganese	34%
Barium chromate	30%
Lead chromate	36%

Void Space and Compaction Pressure

The degree of preheating of the reactants for a given system is controlled by the intrusion of the hot combustion products into the pressed column of composition. This in turn is partly determined by the void space present in the compact. Most consolidated compositions exhibit microscopic spaces between the ingredients, even when pressed at very high loads. The reason for this is that once a certain density is achieved, no further movement of particles within the compact is possible. The total volume of the void spaces present in a composition depends on the formulation, the physical characteristics of the ingredients, including their particle size and shape and the presence of substances such as waxes or resins that can deform or flow under pressure. In delay columns, where very small particle size ingredients are normally used, the void space is generally quite low.

In spite of the low void space, delay columns are sufficiently porous for the combustion gases to flow ahead of the burning front, particularly if a pressure differential exists between one end of the column and the other. This can be demonstrated by pressing a slow burning ‘gasless’ delay composition into an open-ended metal tube and igniting it with the opposite end connected to a water-filled manometer. Even with no gas flow restriction at the ignition end, the manometer will soon be seen to rise, long before the burning front reaches the end of the delay column. This flow, if unhindered by a tube end closure, will heat the column, raise the temperature of the reactants and increase the burning rate. If the system is sealed and the igniter generates significant pressure, the burning rate may be further increased.

Conversely in slow burning delay systems, if one or more of the ingredients undergoes a phase change and liquefies during the preheating process, the molten material may be forced into the void space of the unreacted composition by internal pressure. This may act as a seal, reduce gas flow through the column and depress the burning rate. The burning characteristics of the system may become quite complex, particularly under pressure.

Void space clearly influences the regularity of the burning front and for this reason, pyrotechnic delays normally incorporate finely ground ingredients that are pressed at a high compaction pressure to minimise any effects related to variations in void space. The effect on the burning rate of compaction pressure and density variations due to increment interfaces should be considered when designing a delay element.

Environmental Factors

With the composition parameters controlled as much as possible, the pyrotechnist must also consider environmental factors during the combustion period that may influence the burning rate. The ambient temperature, the thermal conductivity of the surroundings, the combustion pressure and operational factors such as acceleration or spin contribute effects that must be considered to achieve the required delay time.

When deciding on the mechanical design aspects of a delay element, the thermal output of the delay composition and its environment must be taken into account. A fast burning, hot system will be less affected by thermal losses than a slower burning, cooler composition. The faster-burning compositions can therefore be filled into small tube diameters and still yield very reproducible results, whereas the column diameter should be increased to produce similar results from a cooler system.

The temperature of the delay column, both prior to and during combustion, influences the burning rate. For military and aerospace applications, delay elements must provide an accurate time interval, which is specified to within certain limits over a set environmental temperature range, often between –40 and +60 °C. Depending on the formulation, most gasless delay compositions burn about 25% slower at the lower temperature and 25% faster at the higher temperature than they would at room temperature. Gassy delays are less affected by temperature variations because of the intrinsic removal of reaction products from the burning front.

For similar reasons, the thermal conductivity of the delay tube itself and its immediate surroundings are factors contributing to the time interval produced by the system. Highly conductive materials such as aluminium, copper or brass will transfer thermal energy along the length of the tube, heat the remaining composition and increase its burning rate. Any surrounding components in thermal contact with the delay tube may slow or even remove sufficient energy from the system to extinguish the burning composition (Refer to Figure 4). It is normal practice to use low thermal conductivity materials such as stainless steel for the manufacture of delay tubes to reduce these effects. Aluminium alloy delay tubes can be used in slow burning systems, but the metal should be anodised to reduce surface conductivity.

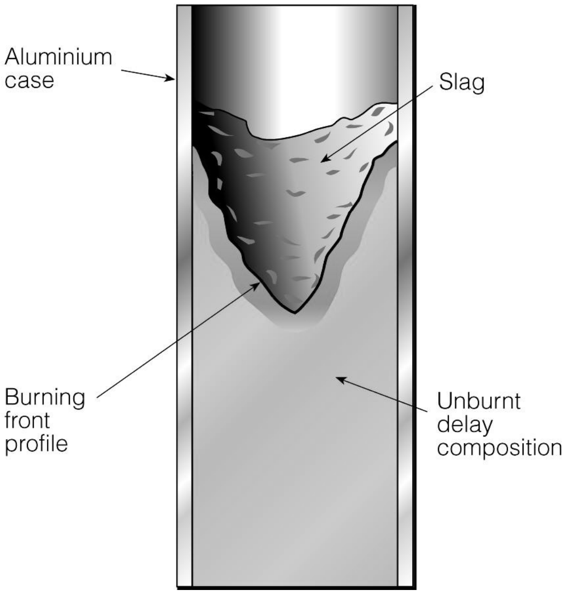

Figure 4. A delay column that has failed due to heat losses.

Pressurization of the burning front often leads to an increase in the burning rate, although the effect is generally more pronounced with gas-producing delays. Increased pressure at the burning front confines the combustion products to the reaction zone and increases the temperature. Combustion products are forced to greater depths into the compact and this also increases the burning rate due to preheating of the delay column. Decreased pressure may have the opposite effect, particularly with gassy systems, by assisting in the removal of reaction products from the system—this causes a drop in temperature and possibly leads to propagation failure. In extreme circumstances, such as a pressure drop caused by the ejection of an igniter or sealing disc (particularly at high altitudes) can cause the entire burning front to dislodge from the column and so extinguish the delay element.

The combustion pressure may be the result of environmental conditions such as deployment altitude, the reaction products of the composition, or a deliberate attempt on the part of the pyrotechnist to improve the reproducibility of the system. Obviously if a system is designed to operate under sealed conditions, the effectiveness of the gas seals will determine the reproducibility of the delay element; one major cause of delay elements failing to produce the specified interval or standard deviation is internal gas venting to atmosphere past the environmental seals.

Longitudinal or angular acceleration might be expected to affect the burning rate, particularly if solid to liquid phase transitions are a result of the combustion process. When designing delay fuzes for gun-launched, spin-stabilised ammunition, the delay composition must be formulated and engineered to withstand the associated forces—this is mainly achieved by the choice of oxidiser, with ionic solids exhibiting better compaction and mechanical strength properties than amorphous or covalently-bonded substances. In general, gasless delays tend to burn at a slower rate under spin; this is because the molten reaction products of gasless systems are displaced from the combustion front. In projected ammunition, high acceleration forces along the line of flight can cause propagation failures for a similar reason.

Design and Manufacturing Factors

A number of design and manufacturing factors can affect the delay interval produced by a delay element:[7]

- length and diameter of the column
- the burning rate of the composition
- density of the column
- type of igniter used
- the use of a priming composition
- design of the delay element, particularly the end seal

- ignition transfer and the mechanical strength of the column

Although a pyrotechnic delay element is an inherently simple system, it often requires more careful design and manufacturing techniques than any other type of pyrotechnic device. To achieve its performance criteria, the delay element requires close control from its inception, materials selection and preparation, mixing, pressing and final assembly as part of a pyrotechnic or explosive train.

(a) Column Length and Diameter

For a given composition with a defined burning rate, it is primarily the length of the consolidated column that determines the overall time interval produced by the system. Unfortunately, the pyrotechnist is often consulted last and is given minimal space in the item of ordnance in which to incorporate the delay element. This can mean that the preferred delay composition cannot be used because of space restrictions and so a less-than-ideal composition may have to be used in a shorter length. This requires that all the factors that affect the burning rate must be highly controlled in order to achieve a reproducible delay interval. In some instances, filled delay columns have needed to be mechanically machined to close length tolerances after pressing in order to produce the time accuracy required by modern missile systems.

The diameter of the delay column is usually chosen as a matter of space efficiency, but care should be taken to ensure that sufficient thermal energy is available to account for heat losses in the system and still maintain the reproducible propagation of the burning front. A composition, burning in a larger diameter column, has more composition per unit length and hence increased thermal energy to maintain smooth and reliable propagation.

(b) Burning Rate and Filling Density

As a general rule, the use of faster burning compositions in longer columns with greater cross-sectional area more readily meet stringent time specifications. This is because faster burning systems are less affected by thermal losses caused by conduction into the surrounding medium. A slower burning composition of the same type produces less heat per unit length and is therefore more susceptible to variations in propagation speed, particularly during the initial burning period when maximum temperature differential is experienced by the system. Gasless compositions that burn much slower than about 3–4 mm/s tend to be unreliable—this limits the practical length for an incrementally-pressed delay element to about 75 mm, or a time interval of about 25 s. For longer intervals, delay elements have sometimes been made by pressing compositions into flat ‘C’ sections (e.g., in early artillery rounds), by utilising the lead tube extrusion technique and pressing into long, straight tubes (for intervals of up to 30 s), or by forming the lead-sheathed composition into unpressed, spirally-wound delay elements; these can provide time delays of several minutes.

A delay column should be manufactured to ensure that the density throughout the consolidated column is as consistent as possible. Normally, a pressed pyrotechnic composition incorporates zones of density variation within the compact. In a delay element, this is highly undesirable because composition density and void space greatly influence the burning rate. The solution normally employed to produce a consistent compact is the incremental filling technique where a series of small increments of composition are pressed into the tube to form a column of the required length. However, even within each consolidated increment there are density disparities, with a zone of increased density opposite the pressing drift and reduced density in the middle of the increment (See Figure 5). As the burning front approaches and crosses each increment interface, the burning rate slows. The more increments in the column (particularly with slow burning compositions), the more significant the time differences between delay elements can become. The lead tube extrusion process can be used to reduce delay time variations due to the effect of increment interfaces, simply because there are less interfaces over a given column length.

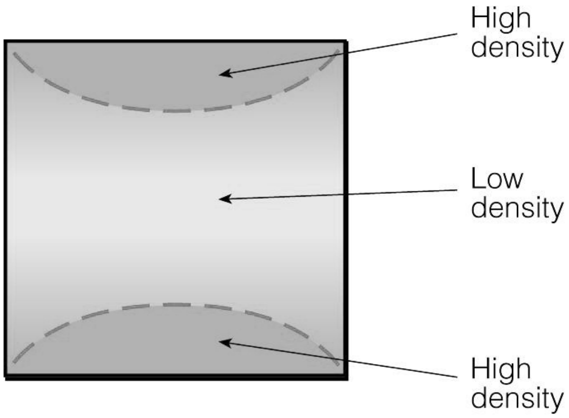

Figure 5. Density variations in a pressed column.

(c) Ignition Source

The type of ignition source can affect the manner in which a delay composition burns. For example, ‘hard’ igniters such as a gas-producing percussion primer or electric fuzehead may produce less reproducible combustion[8] by generating sufficient pressure to significantly increase the burning rate, disrupt the surface of the pressed composition, or even vent the system by ejecting the igniter assembly. A ‘gasless’ fuzehead or low gas-producing primer, although generally preferred as a ‘soft’ ignition source (hot particles rather than hot gases) for pyrotechnics, may not produce a consistent pressure in the *free space* incorporated between the igniter and the pressed column in a typical delay element; this will likely result in delay time variability. Both the delay composition and its igniter must be carefully matched to ensure performance reproducibility.

(d) Priming Compositions

Often when using a slow burning delay composition, the ignition surface must be primed to ensure reliable ignition transfer from the igniter. This means pressing a small increment of a faster and hotter burning formulation onto the delay column. While the actual burning time of the priming composition usually makes negligible contribution to the overall delay interval, the heat generated during its combustion will produce certain effects:

a) The delay composition may be initially ‘overdriven’ leading to a slightly faster burning rate during light up.

b) The heat from the priming may also help to bring the system to thermal equilibrium with its surroundings at a somewhat faster rate.

Both these effects will make a contribution to the delay interval and should be taken into account.

(e) Ignition Transfer and Sealing

While a delay element is usually a sealed unit during storage and its initial operation, it is always required to perform an additional function at the conclusion of the burning process, usually ignition transfer. This either means that a space is provided into which a loose filled ignition transfer or gas-producing composition is loaded or a tube closure seal must be disrupted to allow incandescent delay composition reaction products to exit the end of the tube. The implications of each of these situations on the burning rate of the delay column are quite different.

In the first case, gas can more readily flow through the compact and preheat the column; the burning rate can be expected to be relatively fast. But as the burning front approaches the end of the column, mechanical support for the remaining composition is diminished and it may break away due to internal gas pressure. Unless the design provides support for the end of the column, erratic and short times may result. Delay elements are often required to perform with high reliability and accuracy under extreme conditions of mechanical shock and vibration. Some delay compositions exhibit superior mechanical strength to others, with gassy delays generally exhibiting greater mechanical integrity than gasless compositions. This difference relates to the physical properties of their ingredients and the designer must consider this when choosing a composition for a particular application.

When the tube is fitted with a gas-tight base-seal, the gaseous reaction products are less able to flow through the column and the burning rate will be relatively slow. This has the advantage however that once the seal is expelled (often by melting) the high internal pressure will cause the reaction products to be ejected over large distances, providing an excellent ignition transfer stimulus. The designer must ensure that the end seal is effective throughout the time of the combustion process; otherwise uncontrolled gas leakage will result in variable delay times.

Gassy Delay Compositions

Gassy delay compositions are relatively cool systems because heat is removed from the combustion front by the gaseous reaction products. This means that the burning rate and hence the delay interval produced by the system is relatively unaffected by thermal losses to its combustion environment. Depending on the formulation, gassy compositions generate oxides of carbon and nitrogen and solid, particulate residues, producing between 200 and 400 mL of permanent gas for each gram of composition consumed. This derives from the nature of the fuels and oxidisers used in this type of composition. The fuel for a reliable gassy delay composition must meet certain requirements. It should:

- not be hygroscopic
- be chemically stable
- be compatible with the surrounding components
- be easily ignited
- consolidate well
- produce gaseous reaction products
- produce minimal solid residues that can obstruct the exit of gas and pressurise the system

The most common gassy delay composition is Black Powder, a homogeneous substance consisting of potassium nitrate, charcoal and sulphur, however the sulphurless type is usually employed in military applications due to its improved chemical compatibility. Other gassy formulations contain carbonaceous fuels such as lactose, tetranitrocarbazole (TNC), tetranitrooxanilide (TNO), ascorbic acid or chlorinated fuels such as polyvinylchloride.

Although many of the above requirements can also be placed upon the oxidisers, in practice the choice is more restricted, with potassium nitrate being mostly used. Potassium nitrate also has the advantage that it produces delay columns of high mechanical strength and it is sometimes used in conjunction with barium nitrate to make slower burning formulations.

Gasless Delay Compositions

Gasless delay systems are based on the exothermic reaction between a powdered metal and a metal oxide typical of the Goldschmidt oxidation-reduction reaction. Characteristics of the combustion process include the formation of condensed phase products and the relative regularity of the burning rate under varying pressures. While the reaction is notionally gasless, a small quantity (about 5–10 mL/g) of permanent gas (i.e., existing in the gas phase at STP) is usually formed due mainly to impurities in the chemical ingredients. However, it is important to be aware that temporary gases may be also formed during the high temperature combustion process, often resulting from the vaporisation of a portion of the metal fuel or metal oxide products or simply from the thermal expansion of air entrapped in the system. Though only temporarily in the gas phase, these species can pressurise the burning front during combustion and alter the burning rate. Although gasless delay compositions can burn in hermetically sealed systems, it is normal practice to provide a small volume, or *free space* between the igniter and the pressed column of composition to avoid excessive internal pressurisation and potential ejection of the igniter which seals the tube.

The range of fuels suitable for the manufacture of gasless delays is quite wide (Table 1), but the choice of oxidisers (Table 2) is limited to those that produce minimal gaseous decomposition or combustion products when burnt with the selected fuel or fuels.

Table 1. Some Examples of Fuels Suitable for Gasless Delay Compositions.

Fuels
Aluminium
Antimony
Boron
Chromium
Manganese
Molybdenum
Selenium
Silicon
Tellurium
Titanium
Tungsten
Zirconium
Zirconium/nickel alloy

The range of compositions that can be formulated with these ingredients is obviously quite wide and each mixture has its own characteristics that are suitable for particular applications. Several such composition systems are shown in Table 3.

For a given application, the choice of a delay composition is determined by a range of factors, one of which is the burning rate. Table 4[5] shows how a range of burning rates might be achieved by varying the percentages of the ingredients of a particular type of delay composition.

Table 2. Examples of Oxidisers Suitable for Gasless Delay Compositions.

Oxidisers
Barium chromate
Barium peroxide
Bismuth oxide
Calcium chromate
Chromic oxide
Copper oxide
Iron oxide
Lead chromate
Lead oxides
Molybdenum oxide
Potassium dichromate
Potassium perchlorate
Potassium permanganate

Table 3. Typical Gasless Delay Compositions.

Barium chromate
Potassium perchlorate
Zirconium/nickel alloy

Burning rate range = 1.7–25 mm/s

Boron
Barium chromate

Burning rate range = 7–50 mm/s

Potassium dichromate
Boron
Silicon

Burning rate range = 1.7–25 mm/s

Boron
Bismuth oxide
Chromic oxide

Burning rate range = 7–50 mm/s

Another of the other major considerations (particularly in applications related to safety and arming) influencing the choice of composition for a delay element is its mechanical strength as a consolidated column. A column that can be disintegrated as a result of rough handling during transport or thermal or mechanical stresses prior to or during operational deployment cannot produce a reliable delay time and the safety of the system into which it is incorporated may be compromised. Many potential gasless delay compositions formulated with the ingredients shown in Table 2 will not consolidate well. For this reason, the choice of oxidisers has largely been limited to ionic compounds such as barium chromate or potassium dichromate. Experience has shown that ionic solids tend to exhibit superior strength characteristics on pressing to covalently bonded substances. However, in recent years, occupational health and safety (OH&S) issues related to the use of some of the ingredients used in delay compositions has initiated research on new formulations which do not incorporate toxic or carcinogenic chemicals. Of particular concern are

Table 4. Burning Rates of a Tungsten Fueled Delay Composition System.

Ingredient	Percentage in Composition					
Tungsten (7–10 µm)	27	33	49	63	80	58
Barium chromate	58	52	41	22	12	32
Potassium perchlorate	10	10	5	5	5	5
Diatomaceous earth	5	5	5	10	3	5
RLBR (s/cm)	15.8	11.4	3.9	1.4	0.6	0.4
Equivalent burning speed (mm/s)	0.6	0.9	2.6	7.1	16.7	25.0

compounds containing bismuth, chromium(VI) or lead (i.e., the oxidisers used in most of the current gasless delay systems!)

Chemistry of Gasless Delay Compositions

Gasless delays are similar to thermites in that their combustion chemistry is based on the Goldschmidt reaction:

$$M_1 + M_2O \rightarrow M_1O + M_2 + \text{heat} \qquad (5)$$

where metal M_1 is oxidised to M_1O by a metal oxide, M_2O, which is, in turn, reduced to its metallic form M_2. Over the years, many delay compositions have been developed for particular applications and some likely chemical reactions of the simpler systems are:

$$2\ Si_{(s)} + Pb_3O_{4(s)} \rightarrow 2\ SiO_{2(s)} + 3\ Pb_{(l)} \qquad Q_2 = 1.49\ \text{kJ/g} \qquad (6)$$

$$2\ B_{(s)} + Bi_2O_{3(s)} \rightarrow B_2O_{3(s)} + 2\ Bi_{(l)} \qquad Q_2 = 1.43\ \text{kJ/g} \qquad (7)$$

McLain[3] notes that for a boron/barium chromate system, the oxidation product at the reaction temperature might predominantly be a gaseous sub-oxide such as BO rather than the expected oxide, B_2O_3. It is probable that sub-oxides do form as a result of these notionally gasless reactions, and this further stresses the need to check theory (or assumption) with practical experimentation, particularly when attempting to determine the stoichiometry of a system prior to deciding upon ingredient formulation.

Effect of Pressure on Gasless Delay Compositions

Gassy delays, which must burn vented to the atmosphere because their burning rates are often exponentially related to increasing pressure, tend to be extinguished in low-pressure environments.

Gasless delay compositions however, will burn reliably at a relatively reproducible linear rate at both high and low pressures. Although gasless delays are normally burnt in a sealed system (that is, independent of the external environment), high internal pressures can be generated at the burning front by the hot reaction products from the igniter or from the combustion of the composition itself. Gasless delays are affected by pressure but unlike gassy systems, the burning rate usually slows at moderate to high pressures and tends to achieve a region where further pressure increase has little effect on the burning rate. In spite of this, the burning rate dependence on pressure of a sealed gasless system must still be considered if accuracy and time reproducibility are to be attained. The burning rate of most pyrotechnic compositions increases with pressure according to Vieille's law:[9]

$$R = R_o P^n \qquad (8)$$

where R is the burning rate at elevated (or reduced) pressure, P is the pressure (in atmospheres) and R_o is a constant (the burning rate at atmospheric pressure). The value n is specific to the system and varies from about 0.1–0.6, depending on the amount of gas produced by the combustion reaction. While this relationship has potential use in predicting the theoretical burning rate of pyrotechnic systems including gasless delays, the specific reaction dynamics

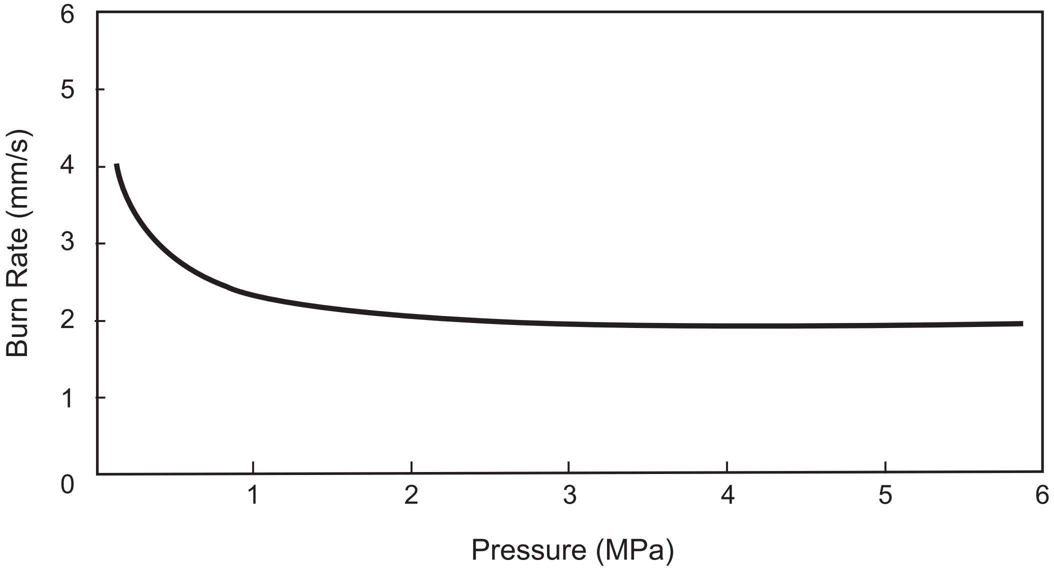

Figure 6. Burning rate vs pressure curve for B/BaCrO$_4$.

of certain types of composition may introduce over-riding factors that, over certain pressure ranges, produce unpredictable changes in the burning rate. This means that the burning rate/pressure relationship for a particular delay formulation may need to be determined experimentally over a wide range of pressures.

As examples, Figure 6 shows the experimentally determined burning rate/pressure relationship for a fast gasless delay composition containing boron and barium chromate (5/95 by weight). It can be seen that the curve, after a gradual slowing of the burning rate due to pressure increase, reaches a plateau region and further elevation of the combustion pressure to between 1.5–6 MPa has only a marginal effect on the burning rate. This classic relationship exhibits good agreement with Vieille’s law over this pressure range. This composition would be ideal for an internally pressurised delay element with a moderate free space.

The relationship in Figure 7 however, is more

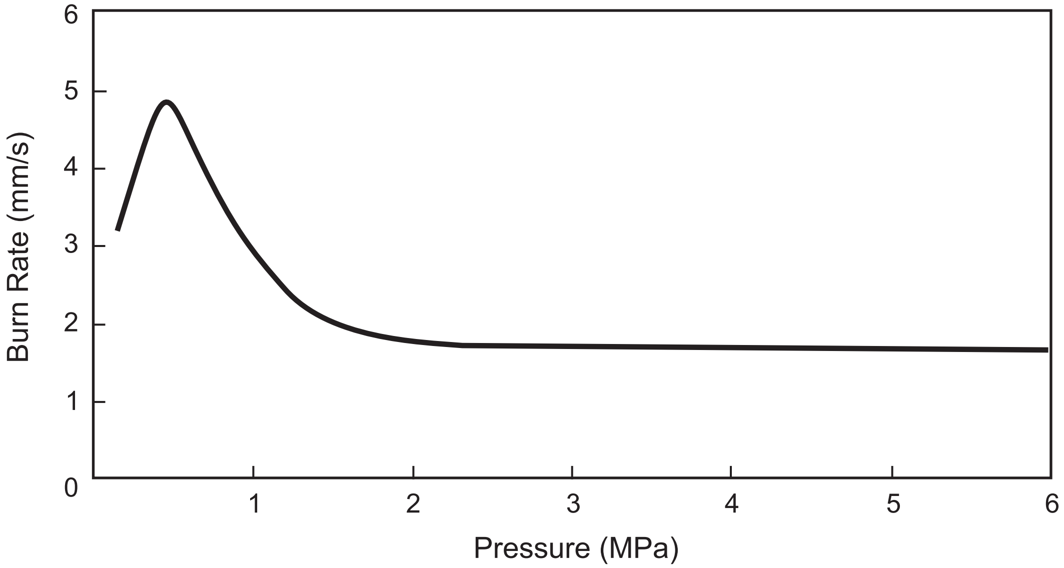

Figure 7. Burning rate vs pressure curve for B/Si/K$_2$Cr$_2$O$_7$.

complex, particularly over the pressure range up to about 2 MPa. This curve is for a relatively slow burning gasless delay formulation containing boron, silicon and potassium dichromate (4/5/91), a composition that has been used in very accurate delay detonators for missiles. It can be seen that there is a sharp increase in the burning rate between 0.1 and 0.4 MPa; thereupon the burning rate slows until a minimum is reached at about 2 MPa. Beyond this level, the burning rate is relatively unaffected by further pressure increase. The peculiar behaviour of this composition is thought to be caused by the sealing effect of the molten oxidiser (MP 398 °C) and the differential pressures developed within the consolidated column as a consequence.[10]

In the illustrated system, if the free space or the ignition source chosen by the designer were such that the internal pressure was between 0.1 and 2 MPa, the delay element could not be expected to yield a reproducible time interval. It is therefore important to select a gas-producing igniter or set the free space above the delay column in accordance with the burning rate/pressure relationship of the particular delay composition, or to choose a composition in which the dependence is not as critical.

The pyrotechnic composition database for the burning rate dependency on combustion pressure is very limited; therefore, each composition must usually be tested according to the intended application and evaluated according to the general principles outlined above.

The Pyrotechnic Delay Element

In its simplest form, the gassy pyrotechnic delay element may consist of a length of Bickford fuse potted for example, into a container of flash composition. The fuse may be ignited directly with a match or struck upon a matchbox if primed with a match composition. The fuse burns from one end to the other; the product gases exit the end of the fuse case, which is usually made of hemp coated with pitch or plastic. Black Powder burns at a defined RLBR (about 0.7 s/cm); therefore, the resulting delay interval is dependent upon the cut length of the fuse.

In more complex designs, the formulation of the Black Powder itself can be altered if required to slow the burning rate and produce longer times from a given column length. This can be achieved by the addition of modifiers such as excess charcoal, lactose or other sugars, or acaroid resin to the mealed form of Black Powder, which is then pressed into a tube.

A simple gasless delay element consists of a metal tube into which the delay composition is directly pressed at high compaction pressure to form a column. The tube is fitted at the ignition end with an ignition source (a percussion primer in the illustrated case in Figure 8). Beneath this is the free space; unless this volume is provided, combustion gases can overpressurise the system and eject the primer. A mechanical seal at the opposite end completes the assembly; this is normally designed to vent the combustion products from the tube upon delay burnout to provide an ignition transfer stimulus.

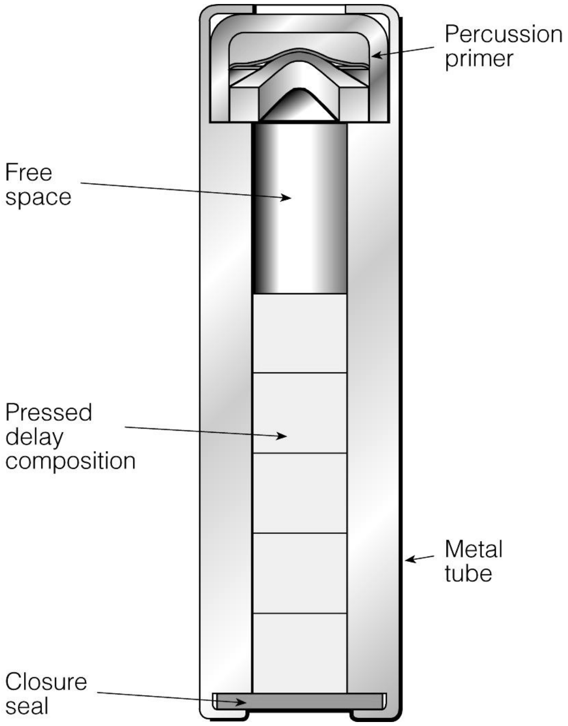

Figure 8. A typical pyrotechnic delay element.

When the primer is struck, ignition is transferred to the top surface of the delay composition (which may be primed in the case of slow burning delay compositions) and it commences to burn along the length of the column. As the burning front approaches the end, the closure seal reaches a point where it can no longer withstand the internal pressure and temperature. It fails and the hot combustion products, which are usually molten or incandescent species, are ejected from the tube. The time between primer strike and the ignition transfer stimulus is the delay interval, which is mainly determined by the type of composition and the length of the column.

Thermal Sources

Pyrotechnic delay systems are examples of the irreversible solid-solid interactions of fuels and oxidisers that are the basis of all pyrotechnic reactions, however as has been said, other types of composition are deliberately designed to produce a hot molten slag that can be used for specific purposes. Such compositions are usually called thermites; the original thermite reaction was first patented by Goldschmidt[11] in 1895:

$$8\ \mathrm{Al} + 3\ \mathrm{Fe_3O_4} \rightarrow 4\ \mathrm{Al_2O_3} + 9\ \mathrm{Fe} \qquad Q_2 = 3.68\ \mathrm{kJ/g} \qquad (9)$$

The characteristics that distinguish a thermite reaction from other pyrotechnic reactions are:

- an almost complete absence of gaseous reaction products after combustion
- a high reaction temperature (typically 2000–3000 °C)
- the formation of a molten slag that can be used to burn, cut or weld

Chemistry of Thermites

In a Goldschmidt reaction, the thermal energy produced is the total heat of formation of the products minus the total heat of formation of the reactants, minus the heat losses associated with physical effects such as latent heats of fusion and vaporisation of the products. If the heat produced is greater than about 2.23 kJ/g, the reaction is likely to go to completion.[12] While organic binders can be used in thermite compositions for special applications, some of the heat from the reaction will be lost due to the formation and ejection from the burning front of endothermic gaseous products such as carbon dioxide, water and nitrogen.

Because the basic reaction is relatively simple, it is possible to calculate the temperature of the reaction quite accurately. This is an invaluable tool because a thermite formulation can be designed to match a particular requirement. The technique is as follows:[13]

Using the reaction

$$2\ \mathrm{Al_{(s)}} + \mathrm{Fe_2O_{3(s)}} \rightarrow \mathrm{Al_2O_{3(s)}} + 2\ \mathrm{Fe_{(l)}} \qquad (10)$$

Heat of Reaction, $\Delta H°$

$$= \Delta H° \text{ (Products)} - \Delta H° \text{ (Reactants)}$$

$$= (-1675.7) - (-824.2)$$

$$= -851.5\ \mathrm{kJ/mol}$$

It is possible to estimate the maximum theoretical combustion temperature of a thermite reaction using the equation:

$$Q = m\,S\,(T_o - T) \qquad (11)$$

where Q is the heat of the reaction, m is the number of atoms in the final product, T is the final temperature, T_o is the initial temperature and S is the specific heat at constant pressure. For the sake of simplicity, the specific heat is given a value of 27.2 J/mol/deg,[13] which corresponds to the average specific heat of the metal up to its boiling point. This means that the specific heat of the oxide formed is not considered in this calculation. Using data from equation 10

$$298 - T_{max} = -851.5 \times 1000/(27.2 \times 7)$$

therefore $T_{max} = 4770$ K.

which is comparable to the temperature of 4382 K determined by Fischer and Grubelich.[14]

Uses for Thermites

The military uses of thermites as incendiaries have largely been superseded by liquid incendiary materials. However thermites are currently being used for the safe disposal of explosive ordnance whether used as a powder, putty, cast or pressed pellet form. Typical examples of thermite devices include incendiary grenades and the pyrotechnic torch (thermal lance).

In the industrial sphere, technology based on this reaction has been used to repair castings and to carry out butt-welding of railway lines.

Alumino-thermic reactions have also been used to produce pure carbon-free metals such as chromium and manganese by the use of the appropriate oxidiser. For example:

$$4\ \mathrm{Al} + 3\ \mathrm{MnO_2} \rightarrow 2\ \mathrm{Al_2O_3} + 3\ \mathrm{Mn} \qquad Q_2 = 4.86\ \mathrm{kJ/g} \qquad (12)$$

Recently this technology has been expanded to include not only the manufacture of pure metals but also alloys (aluminides, nickelides), refractories (borides, carbides, nitrides, silicides), complex oxides (niobates, tantalates, ferrites, cuprates), hydrides and phosphides. The process is called self-propagating, high-temperature synthesis (SHS).[15] The few examples following demonstrate the versatility of the SHS process:

$$2\ \mathrm{B_2O_3} + \mathrm{C} + 6\ \mathrm{Mg} \rightarrow \mathrm{B_4C} + 6\ \mathrm{MgO} + \text{heat} \qquad (13)$$

$$3\ \mathrm{NiO} + 5\ \mathrm{Al} \rightarrow 3\ \mathrm{NiAl} + \mathrm{Al_2O_3} + \text{heat} \qquad (14)$$

$$24\ \mathrm{Fe} + 2\ \mathrm{BaO_2} + 17\mathrm{O_2} \rightarrow 2\ \mathrm{BaO{\cdot}6\ Fe_2O_3} + \text{heat} \qquad (15)$$

Ingredient Selection

Fuels

When designing a thermite composition it is important to select a fuel:

- with a high heat of combustion
- that forms an oxide of low melting point and high boiling point.

When chemical stability, cost and availability are considered along with the above criteria, aluminium is the optimum fuel (Table 6). However magnesium is often added to improve ignitability, and titanium or zirconium included to achieve a showering incendiary effect.

There is another class of fuel that is occasionally used for heat production, the intermetallic compounds such as: 'magnalium' (a 50/50 alloy of magnesium and aluminium), aluminium/nickel, aluminium/palladium, zirconium/nickel, titanium/boron, titanium/carbon, and calcium/silicon. The purpose of these fuels is usually system-specific and one of the alloying components usually serves a function other than as a fuel in the reaction.

Oxidisers

When choosing an oxidiser, the following characteristics are important:

- a low heat of formation
- minimum oxygen content of 25%
- a high density
- the ability to reduce to a metal with a low melting point and high boiling point

From Table 7, the best oxidisers for use in thermites are the oxides of iron, manganese and copper. Iron oxides are the cheapest to use but the slag formed in the Goldschmidt reaction has relatively low fluidity—this can be improved by the addition of sulphur or sulphides.[12]

Improvements in Ignitability

Alumino-thermic compositions have been found to be difficult to ignite and must be primed to ensure ignition transfer. There are also a number of other ways in which thermites can

Table 6. Key Characteristics of Some Thermite Fuels.[16]

Fuel	Melting Point of Oxide (°C)	Boiling Point of Oxide (°C)	Specific Gravity of Fuel (g/cm^3)	Formula of Oxide	Heat of Formation of Oxide (–kJ/mole)	Stoichiometric Formula of Thermite (%) Fuel	Oxidiser (Fe_2O_3)	Thermal Output (kJ/g)
Al	2054	3000	2.7	Al_2O_3	1675.7	25	75	3.98
Mg	2826	3600	1.7	MgO	601.6	32	68	4.22
Ca	2899	> 2899	1.5	CaO	634.9	43	57	3.86
Ti	1843	> 2500	4.5	TiO_2	944.0	31	69	2.56
Si	1713	2950	2.3	SiO_2	910.7	21	79	2.68
B	450	~ 1860	2.3	B_2O_3	1273.5	12	88	2.48

Table 7. Characteristics of Some Oxidisers Used in Thermites.[16]

Oxide	Heat of Formation (–kJ/mole)	Oxygen Content of Oxide (%)	Specific Gravity of Oxide (g/cm^3)	Melting Point of Metal (°C)	Boiling Point of Metal (°C)	Stoichiometric Formula of Thermite (%)		Thermal Output (kJ/g)
						Fuel (Al)	Oxidiser	
B_2O_3	1273.5	69	1.8	2075	4000	44	56	3.25
SiO_2	910.7	53	2.2	1414	3265	37	63	2.15
Cr_2O_3	1139.7	32	5.2	1907	2671	26	74	2.60
MnO_2	520.0	37	5.0	1246	2061	29	71	4.59
Fe_2O_3	824.2	30	5.1	1538	2861	25	75	3.98
Fe_3O_4	1118.4	28	5.2	1538	2861	24	76	3.68
CuO	157.3	20	6.4	1084	2562	19	81	4.11
Pb_3O_4	718.4	9	9.1	327	1749	10	90	2.00

be made to ignite more reliably, the final choice depending on cost and the intended application.

General

The original Goldschmidt reaction was based on the use of *hammerscale*, an oxide of iron (rust) of inconsistent composition. This formulation was particularly difficult to ignite; the problem was largely overcome by the use of the well-defined forms of iron oxide (including synthetic forms) and better control of oxidiser particle size. In recent times, most thermite applications have been limited to incendiary, explosive ordnance disposal (EOD), and cutting technology. For these alumino-thermic devices, an ignition system has often had to be developed.

Inclusion of Copper or Manganese Oxides into Iron Oxides

Experimental observations have indicated that thermite compositions containing Fe_3O_4 are easier to ignite than those containing Fe_2O_3. The reason is thought to be related to the crystal structure of the oxide, Fe_3O_4 having an inverse spinel structure of the general classification AB_2O_4.[17]

The inclusion of copper and manganese oxides as part of or all of the oxidiser content will also improve the ease of ignition of a thermite; one technique reported includes the copper oxide (CuO) and/or the manganese oxide (MnO_2) in the crystal lattice as a ferritic structure. For example, the ferrite, $CuFe_2O_4$, can be prepared by heating a mixture of $CuSO_4{\cdot}5H_2O$ and $FeSO_4{\cdot}7H_2O$ in the appropriate ratios.[18] McLain[19] reports the calorimetrically measured heat of reaction for a 50:50 mix of $CuFe_2O_4$ and Ti as 5.7 kJ/g, whereas for Fe_2O_3 and Ti, the heat of reaction was only 3.67 kJ/g.

Inclusion of Metal Oxides of High Specific Gravity

The inclusion of oxidisers such as molybdenum oxide (MoO_3), tungsten oxide (WO_3) and lead oxide (Pb_3O_4) can be used to produce highly reactive thermite mixtures. These systems can be very expensive and there may be OH&S concerns with their preparation, but their rapid burning rate ensures their use in very fast delays and in the ignition systems of infrared decoy flares. Examples include B/MoO_3, Zr/WO_3 and Si/PbO_2.

Inclusion of Salt Oxidisers - Thermates

The addition of oxidisers such as nitrates and peroxides increases the heat of combustion and improves the mechanical strength of the pressed compositions. These oxidisers also introduce flame to the combustion (because of the amount of gas evolved) and usually make the composition more sensitive to mechanical stimuli such as impact and friction.

The inclusion of a nitrate oxidiser, usually barium nitrate, into a thermite improves both the ignitability of the formulation and increases target penetration due to gas production and the consequent projection of molten slag. Such a formulation is called a *thermate*. These have

Table 8. Explosive Sensitiveness Data for Typical Thermite Compositions.

	Hazards Assessment Data			
Type of Thermite Composition (%)	F of I[a]	T of I (°C)	Friction[b]	Ignition by electric spark
Mg/Fe_2O_3 (30/70)	> 200	> 400	0-0-0	Nil at 4.5 J
Plastic Thermite[20]	> 200	> 400	0-0-0	Nil at 4.5 J
Thermate $Mg\text{-}Al/Ba(NO_3)_2$ (40/60)	50	> 400	100-100-50	Nil at 4.5 J
$Si/PbO/Bi_2O_3$ (15/52/33)	120	> 400	0-0-0	0.01 J

a Figure of Insensitiveness (RDX = 80).

b Temperature of Ignition.

c Mallet Friction Test (Boxwood mallet on: Yorkstone-hardwood-softwood anvils, % ignitions from 10 tests).[21]

been widely used in incendiary grenades, particularly for explosive ordnance demolition (EOD) applications.

Explosives Safety Hazards

There is a misguided belief that thermite compositions are explosively insensitive. This is far from the truth and the variability of explosives hazards assessment data for a range of different types of thermite compositions is emphasised. Refer to Table 8. The burning rates of some thermite-type compositions are exceedingly rapid and the entire mass may explode upon initiation.

From the data in Table 8 a magnesium-fuelled thermite could be considered to be relatively insensitive to most stimuli but the thermate composition is friction-sensitive and by contrast, the $Si/PbO/Bi_2O_3$ system is electrostatically sensitive.

Conclusion

The technology associated with the design of pyrotechnic delays, which are used to provide reliable time intervals, has been described in detail. The different practical applications of the two basic types of delay composition, ‘gassy’ and ‘gasless’, have also been outlined.

The reaction chemistry of gasless delays is similar to that of thermite compositions. Both systems are based on the Goldschmidt reaction, but a thermite mixture, containing a metal and a metal oxide, is specifically formulated to burn and liberate high amounts of thermal energy.

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The Chemistry of Colored Flame

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Introduction

The focus of this chapter is the basic chemistry of colored flame. However, without first understanding physically what colored light is, how it originates, and the classical laws of additive color mixing, a discussion of the chemistry would be of limited value. Accordingly, approximately the first half of this chapter is devoted to presenting such background information. Readers already possessing such basic information are encouraged to skip to later sections.

This chapter is an update of two articles written by the authors more than 20 years ago.[1–2] It also draws heavily on the excellent work of many others.[3–32] Additionally, this chapter includes much information that can be found in a host of general physics and chemistry texts. However, only where the information in this chapter is attributed to a small number of authors has an attempt has been made to provide specific references.

The Nature of Light

Understanding the basic nature of light is one of the important prerequisites, and taking an historical approach is a useful way to structure this discussion.

Before the seventeenth century, light was generally believed to consist of streams of tiny particles, or corpuscles, traveling between the light source and one's eye. According to this corpuscular theory of light, the way a person saw things was that light corpuscles bounced off objects and then traveled to their eye. Being particles, light corpuscles had to travel in straight lines, unless acted on by outside forces, such as gravity. However, beginning in the mid-seventeenth century, experiments began to reveal properties of light that could not easily be explained using the corpuscular theory of light. For example, in both refraction and diffraction, beams of light bend away from their original straight lines, yet there were no known forces acting on them. If, however, light consisted of waves, then the properties of refraction and diffraction would not only be allowed, they would be expected. Thus the wave theory of light gradually replaced the earlier corpuscular theory.

The wave theory seemed satisfactory for about 200 years, until near the end of the nineteenth century. At that time, the wave theory still served well to explain all the properties of light concerned with its propagation from place to place. However, there were newly observed properties, concerning the ways in which light was emitted and absorbed, that could not be explained if light consisted of simple waves. For example, when the spectrum of light emitted by incandescent bodies was analyzed in a precise manner, it was found to be different from that predicted by the wave theory. However, the death blow for the wave theory (and what won Albert Einstein a Nobel Prize) was the explanation of the photoelectric effect. In the wave theory, the energy of light is proportional to the amplitude of the waves, yet in explaining the photoelectric effect it was clear that the energy of light was proportional to its frequency and not its amplitude. This was so far from being allowed by the wave theory that the simple wave theory had to be abandoned.

The observations regarding the photoelectric effect are consistent with light being discrete packages of energy, with the energy of each packet being proportional to frequency. The idea of these light packets sounds a lot like light corpuscles, but with a new twist; these packets now have a frequency—and therefore a wavelength—associated with them. This is something like a cross between a particle and a wave. That is to say, these light packets have some properties that are wave-like (they have a frequency and wavelength) and some properties that are particle-like (they exist as discrete entities—each with their own discrete energy). This is the quantum theory of light, in which:

- Light is emitted and absorbed as if it consisted of discrete entities, now called *photons*;
- Light is propagated from place to place as if it consisted of waves with a definite frequency and wavelength; and
- Photons carry an amount of energy that is proportional to their frequency.

There is no analog to photons in everyday experience. Figure 1 is a simplistic attempt to represent the packets of wave energy (photons) of the quantum theory of light. Quantum theory is the current theory of light and is also the basis for understanding the atom.

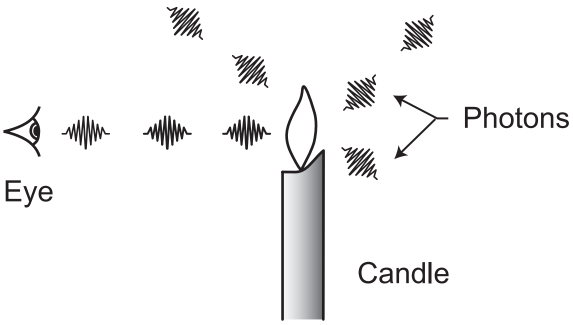


Figure 1. An attempt to illustrate the quantum theory of light.

As a matter of convenience, in the early portions of this chapter, photons will most often be described in terms of the energy they possess; whereas later they will generally be described using their wavelength. This is acceptable because a photon's energy (E_p), frequency (ν) and wavelength (λ) are uniquely related by the equation:

$$E_p = h\nu = hc/\lambda, \qquad (1)$$

where, h is a constant (Planck's constant, which equals 6.63×10^{-34} Joule second) and c is the speed of light (3.00×10^{8} meters per second). After specifying any one of the three properties of a photon (energy, frequency, or wavelength), the others are fixed and can be calculated if desired.

Light is often considered to be only that to which one's eyes respond (i.e., those photons of the necessary wavelength to evoke visual sensations). However, the definition could be expanded to include invisible light: infrared and ultraviolet light. Infrared light photons are less energetic (have somewhat longer wavelengths) than visible photons, and ultraviolet photons are more energetic (have shorter wavelengths) than visible photons. There are no fundamental differences between infrared, visible and ultraviolet light photons; they just have different wavelengths, and those wavelengths are continuous (i.e., there are no wavelength gaps between what are called infrared, visible and ultraviolet light photons).

The world is full of photons with substantially longer wavelengths than infrared (e.g., microwaves and radio waves) as well as photons with wavelengths shorter than ultraviolet (e.g., X-rays and gamma rays), see Figure 2. All these photons are fundamentally the same thing (packets of electromagnetic wave energy), and one would be justified in calling them all by the same name. However, for this chapter, light shall be defined as only those photons that are usually termed infrared, visible and ultraviolet light.

Note that for radio waves the amount of energy carried by a single photon is extremely small and the wavelength is huge. It would be practically impossible to detect a single radio wave photon. Consequently radio waves are found to behave mostly like waves, not particles. Conversely single gamma-ray photons carry a comparatively enormous quantity of energy. A single gamma ray photon can easily make its presence felt, but the wavelength is so small that the wavelike properties are very difficult to discern. Thus gamma rays behave essentially like energetic particles. Light photons are in between radio waves and gamma rays; individual photons carry enough energy to make their presence felt (e.g., photo-electric effect and photochemistry), but the wavelength is still sufficiently long for the wavelike properties to be evident (e.g., refraction and diffraction).

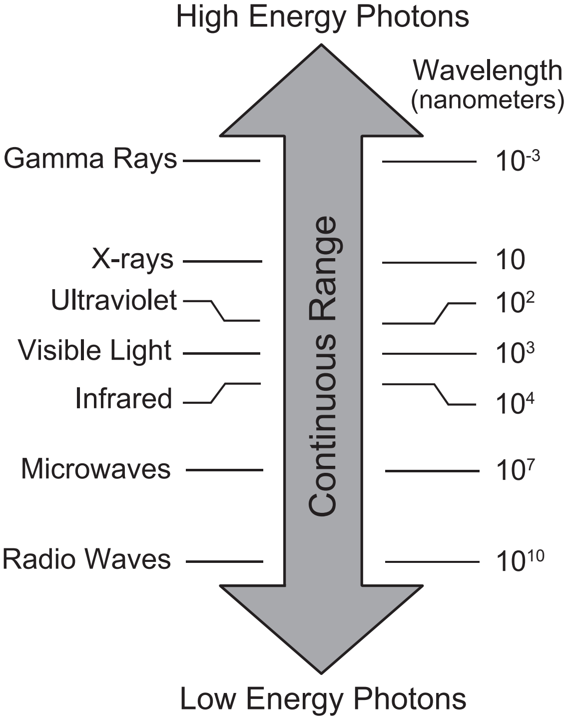


Figure 2. An illustration of the continuous range of photon wavelengths and the descriptive terms for those photons.

More Quantum Theory

Beyond explaining the nature of light, quantum theory is basic to our current understanding of physics, especially atomic physics. In particular, quantum theory provides the explanation of the mechanism through which light is generated, including colored light from pyrotechnic flames.

One of the major tenets of quantum theory is that all *bound systems* are *quantized*. Bound systems are systems that are constrained to stick together in some manner. Some examples of bound systems are electrons whirling about an atom, a rotating fireworks wheel, and the moon orbiting the Earth. In each case, some force holds the system together: electrostatic attraction between electrons and the nucleus of an atom, tension transmitted through the spoke(s) of the fireworks wheel, and gravity between the Earth and moon. Quantum theory establishes that each of these bound systems is *quantized*. That is, bound systems cannot have just any amount of energy; rather they can only have certain “allowed” amounts of energy. In terms of energy, this is a little like climbing a ladder, where one’s potential energy increases as one advances up the ladder. In this analogy, one can stand on any rung they wish and can have that amount of potential energy, but one cannot stand half way between two rungs. If one were to try, they would immediately fall to the next lower rung. It is the same way with bound systems; each can have any of a number of allowed energies but none of the energies between those allowed. In this way, the range of energy values for bound systems is discrete (quantized) and is not continuous.

When a bound system has one of its allowed energies, it is said to exist in a particular *energy level* or *energy state*. Energy levels are often described using energy level diagrams, like the one illustrated in Figure 3. The lowest energy level is called the *ground state* and levels with higher energies are called *excited states*. The system being described in the energy level diagram can have energies corresponding to any of the allowed states, but it is “*forbidden*” to have any of those energies between the allowed energy states. If we try to provide the system with enough energy to raise it to one of the forbidden energies, the system will accept only enough energy to reach the next lower allowed state. Bound systems also normally exist in the lowest possible energy state. Thus, if a system is given enough energy to reach an excited state, generally it will soon give up that energy, dropping to lower energy states.

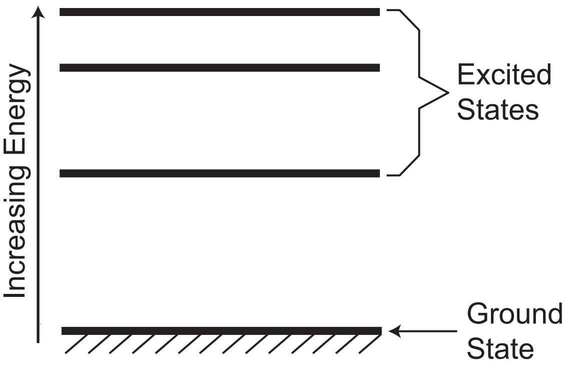


Figure 3. An illustration of an energy level diagram for a bound (quantized) system.

When a system gains or loses energy, it is called an *energy transition*. In energy level diagrams, energy transitions are typically shown as arrows between the energy levels involved. Figure 4 is an illustration of the energy level diagram of a bound system, including a series of energy transitions beginning with the system in its ground state. The first transition (shown as a bold upward arrow) goes from the ground state to the uppermost excited state. Thereafter the system loses energy through two energy transitions (shown as bold downward arrows in Figure 4), dropping back to the ground state. Note that it is not necessary for the system to pass through each intermediate energy state during an energy transition. In this example, the first transition (upward) skipped two intermediate levels and the final energy transition passes from the second excited state directly to the ground state, without passing through the first excited state.

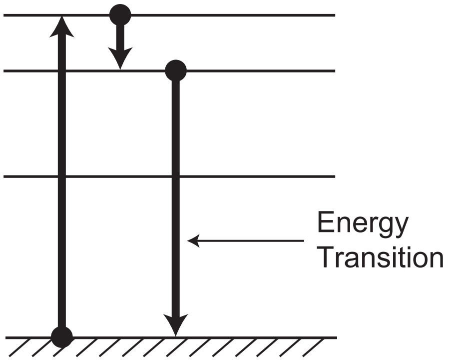


Figure 4. Illustration of transitions between energy levels.

In the discussion thus far, systems have been described as having energy, without specifying the form of that energy. The energy can be in the form of motion within the system—as in a whirling fan blade (kinetic energy), and it can be in the form of stored energy—as in a compressed spring (potential energy). Using an example from fireworks, consider a simple wheel. The fireworks wheel is a bound system because it is constrained from flying apart by the connecting spokes between its propulsive drivers. If quantum theory is correct, then the energy of this system must be quantized and can have only certain allowed values. In the case of a fireworks wheel, its energy is kinetic energy in the form of its spinning motion, and the amount of energy is a function of its rate of spinning. Accordingly, quantum theory predicts that only certain allowed rates of spinning are possible and that spin rates between the allowed rates simply are not possible. This seems to contradict what is observed in everyday experience. It appears that the wheel can be made to spin at whatever rate one wishes and that the rate of spinning varies continuously, not in steps. For this fireworks wheel, it is not that the allowed energies and the steps between them do not exist; it is just that for objects as large as a wheel, the allowed energies are so very close together that one cannot observe the energy steps even with the most sensitive scientific instruments. For all bound systems large enough to be seen with one's eyes, the quantum energy steps are so small as not to be directly observable.

If one can never hope to directly observe quantum effects on those objects in the world about us, one might wonder what use is quantum theory. In the submicroscopic world of atoms and molecules, the quantum steps between allowed energy levels can be relatively enormous, and quantum effects are not only observable but are paramount. It is in the submicroscopic world of atoms and molecules that light is generated. To understand and work effectively with light generating processes in pyrotechnics, it is necessary to have at least a general understanding of quantum theory.

Atomic Line Spectra

Consider the example of an atom of hydrogen as illustrated in Figure 5. (Note: in Figure 5 the relative size of the nucleus has been greatly exaggerated, and the electron orbitals have been grossly simplified.) The hydrogen atom is the simplest of all atoms. It has a nucleus that consists of a single proton with a positive charge. Traveling about this proton is a single electron with a negative charge. The electron is not free to travel just anywhere, rather it is constrained by an electrostatic force of attraction between the opposite electron and proton charges. Accordingly the hydrogen atom is a bound system, and its energy states will be quantized. The region in the space around the nucleus where an electron can reside is called an *orbital*. The size (and shape) of these orbitals is a function of the energy possessed by the electron. In the absence of external influences, the electron in a hydrogen atom resides in the lowest or ground state. As energy is supplied to the atom, the electron can occupy higher energy excited states, by moving to orbitals that are on average farther from the nucleus. In pyrotechnics, this energy would usually be supplied as thermal energy produced by chemical reactions in a flame. (This energy is transferred to an electron as a result of collisions between the various atoms and molecules in the flame.) To give an idea of just how large an energy step exists between hydrogen's ground and first excited states, it would require a flame temperature approximately twice as great as that generated in a typical pyrotechnic flame to readily supply the energy for this transition. Unlike the fireworks wheel example, quantum effects were not observable, where the quantum effects for a hydrogen atom simply cannot be ignored!

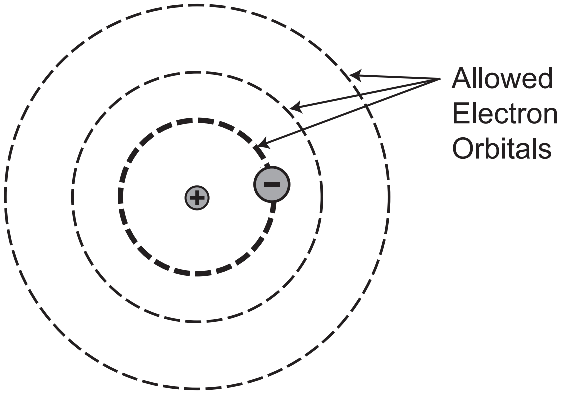


Figure 5. A greatly simplified illustration of a hydrogen atom.

If a hydrogen atom has received enough energy to have reached an excited state, providing more energy were available, it could absorb an additional amount of energy to move its electron to an even higher excited state. This corresponds to the electron moving to an orbital even further from the nucleus. The energy required for a transition to each successively higher excited state is less than that required for transitions between lower excited states. (For atoms, as a general rule, the gaps between each successively higher excited state become less as suggested in Figure 4.)

However, rather than the hydrogen atom absorbing additional energy, it is more likely that the hydrogen atom will experience a transition back to a lower energy state instead. This can happen in either of two ways: the atom can transfer its energy to another atom or molecule in a collision, or occasionally the released energy will be carried off in the form of a photon of light. In the energy level diagram of Figure 6, the light photon emitted—as the atom decays back to its ground state—is shown as a wavy arrow to the side. The energy of this photon (E_p) is equal to the energy difference between the two energy levels involved in the transition (i.e., energy is conserved during transitions between energy levels).

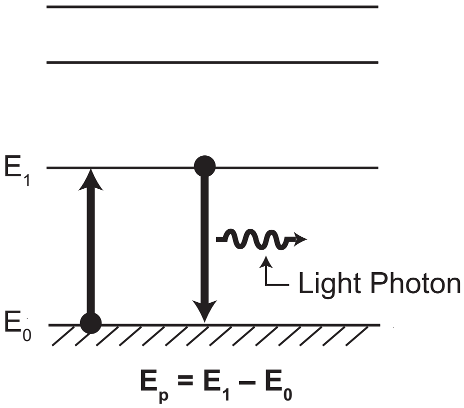


Figure 6. Light being emitted by an excited atom when it decays to a lower energy state.

If a hydrogen atom is in its second excited state, it has some alternatives regarding possible transitions back to the ground state. The transition could go directly to the ground state emitting a single photon, or it might transition as a two step process, passing through the first excited state, thus potentially emitting two lower energy photons, see Figure 7. This process of atoms emitting light photons is typical of one type of light production in pyrotechnic flames. In this process, atoms absorb thermal energy from a flame causing some of their electrons to occupy excited states; then as the electrons drop back to lower energy states, light photons may be generated. In each case, the energy of an emitted photon is exactly equal to the energy difference between the energy levels involved in the transition, as shown in Figure 7.

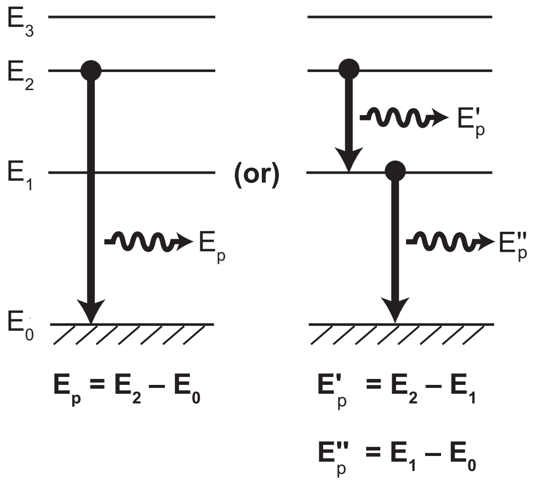


Figure 7. Competing atomic transitions between energy levels.

While atoms of **different** chemical elements each have a **different** set of allowed energy levels, the energy levels of all atoms of the same chemical element will have exactly the **same** set of precise values. If a sample containing a large number of atoms of one chemical element is supplied with sufficient excitation energy, electron transitions will occur and photons will be emitted. If an instrument were used to analyze the number and energy of the emitted photons, and if a graph were to be made of that data, something like Figure 8 would be produced. At most energies, it would be observed that no photons are emitted (corresponding to zero photons on the graph). Only at a relatively small number of very precise energies are photons observed, and those energies correspond to the differences between that type of atom's allowed energy states. It is because all of the photons emitted by that chemical element have one of a specific set of very precise energies, that gives the appearance of vertical "lines" in an otherwise empty graph. The length of each vertical line depends on the relative number of photons emitted with that energy, which will generally differ from line to line. (The intensity of the individual lines depends on details of quantum theory that are beyond the scope of this chapter.)

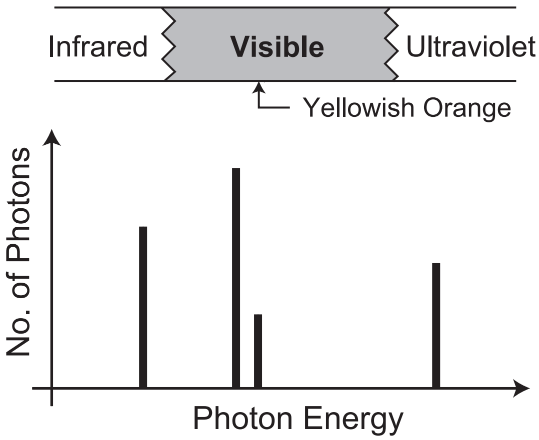


Figure 8. An illustration of a hypothetical atomic line spectrum appearing yellowish orange in color.

Had a different chemical element been used, the graph would appear somewhat similar; however, the energies at which photons are observed would not be the same because the set of allowed energy levels would not be the same. A graph such as that in Figure 7 is a representation the spectrum of light emitted by atoms of that element and is usually referred to as an *atomic line spectrum.*

If a sufficient number of the photons emitted by excited atoms have energies that fall in the range of visible light, then an observer would see those emissions. If the emitted photon energies fall predominately in one part of the visible light spectrum, the light will appear colored to the observer. For example, in Figure 8, there are four lines in the spectrum. The lowest and highest energy photons fall in the infrared and ultraviolet portions of the light spectrum; thus they are not visible to an observer. (In the upper portion of Figure 8, the squiggly lines used to separate the visible spectral region from the ultraviolet and infrared regions are intended to indicate that the limits of the range of photons that are visible do not cut-off sharply but rather fade gradually to invisibility.) The other two spectral lines in Figure 7 fall about one third the way through the visible region. These emissions would be seen and, as will be discussed later, would appear yellowish-orange in color.

Molecular Band Spectra

The most useful sources of colored flame emissions in pyrotechnics originate from molecules, rather than atoms. Thus it is necessary to continue the discussion of quantum theory with a look at molecules. Figure 9 is a greatly simplified illustration of a molecule of hydrogen gas (H_2), where the protons (nuclei) of the two hydrogen atoms are bound together by the forces produced by the pair of electrons occupying an orbital around the two nuclei. Similar to atoms, the electrons in molecules can be excited to higher orbitals and can emit photons as the electrons decay back to lower energy states. While the basic mechanism of light production is the same as with atoms, there is an important difference in the spectrum of photons emitted by molecules. Whereas the energies of emitted photons by atoms have precise values giving rise to **lines** in their spectra (spectra is the plural of spectrum); in molecular spectra the energies of emitted photons have numerous values that cluster tightly in groups giving rise to **bands** in their spectra.

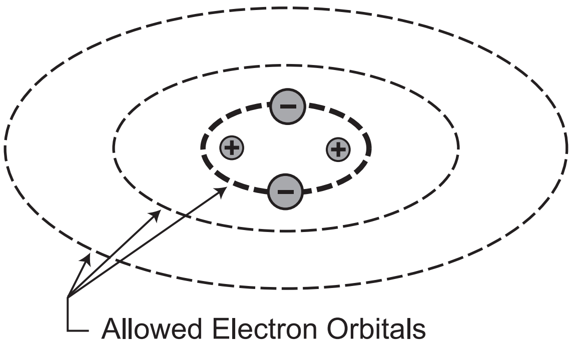


Figure 9. A greatly simplified illustration of a hydrogen molecule.

Like the lines in an atomic spectrum, the bands in a molecular band spectrum can be understood using quantum theory. In a molecule of hydrogen, in addition to the electrons being bound to the atoms of the molecule, the atoms are bound to each other in an arrangement somewhat like the fireworks wheel discussed earlier. Like the wheel, the hydrogen molecule can rotate (see Figure 10A). However, unlike the wheel with its rigid framework, the molecule is flexible. It is possible to conceptualize the chemical bond between the two hydrogen atoms as something like a spring, as suggested in Figure 10B. Like a spring, the hydrogen molecule can also bend and stretch, giving rise to these types of vibrational motion, as suggested in Figure 10C.

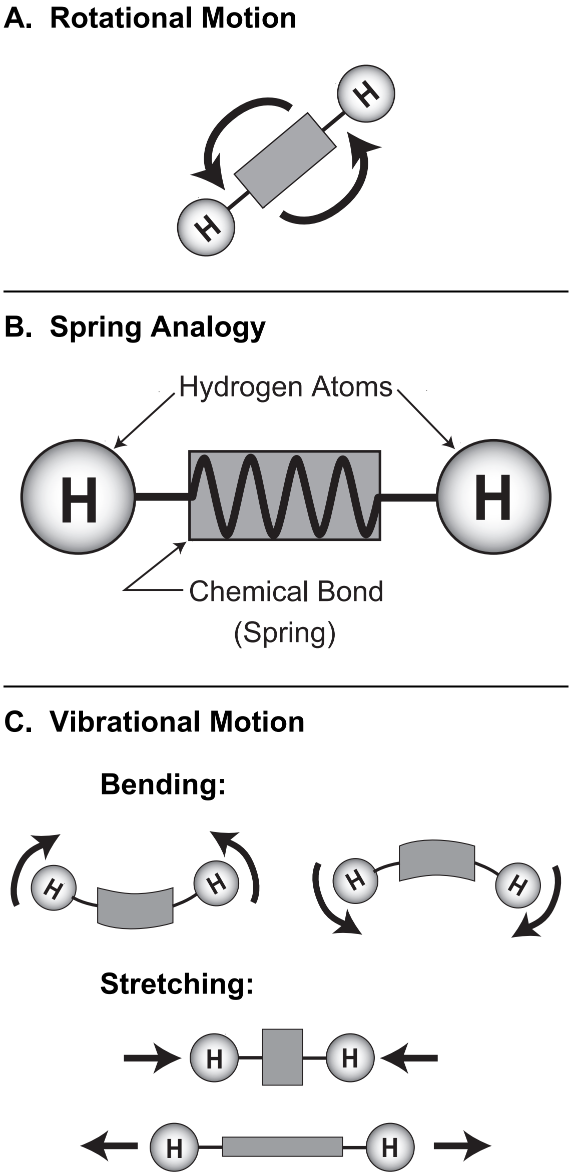


Figure 10. An illustration of a hydrogen molecule, with the chemical bond conceptualized as a spring and showing rotational and vibrational motions.

Because the pair of hydrogen atoms of the molecule are bound to each other, they also constitute a bound system. Thus their rotational and vibrational motions are quantized and can only take on certain allowed amounts of energy. The molecule can vibrate (or rotate) a little and be in a low energy vibrational (or rotational) state, or it can move more vigorously and be in higher energy states. Just as an energy level diagram can be drawn showing electron energy levels, energy level diagrams can also be drawn showing rotational and vibrational energy levels. However, the spacing between the three types of energy levels is significantly different. Recall that the spacing between the electron energy levels started out quite large but got smaller as one progressed to higher levels. In contrast, the spacing between vibrational energy levels is much less than the spacing between electron energy levels and the spacing remains approximately constant as one progresses to higher energy levels. The spacing between rotational energy levels is even less than that between vibrational levels, and the spacing increases as one progresses to higher energy levels.

Like an atom, a molecule must always be in one of its set of allowed electron energy states: the ground state or one of its excited states. However, a molecule must also be in one of its set of allowed vibrational energy states and in one of its set of allowed rotational energy states; with the overall energy of the molecule being the sum of its electron energy, plus its smaller vibrational energy, plus its even smaller rotational energy. Thus an energy level diagram for a molecule will still have ground and excited electron states with spacings similar to those in an atom, see the left side of Figure 11. However, independent of its electron energy state, the molecule can exist in any number of vibrational energy states. Accordingly, added to each electron state in the energy level diagram will be a set of vibrational energy levels, each with slightly different energies. The center of Figure 11 is an attempt to show an expanded view of one electron level, with that electron energy level seen to be broken into a number of relatively closely spaced vibrational energy levels. Similarly, added to each vibrational energy level is a set of rotational energy levels. At the right in Figure 11 is an expanded view of a single vibrational level, with that vibrational level further broken down into a set of rotational energy levels. The net effect of having a set of very narrowly spaced rotational energy states added to each vibrational state and that added to each electronic state, is to have a series of allowed energy bands (very closely spaced energy levels), with each band starting with the energy of one of the electron energy levels.

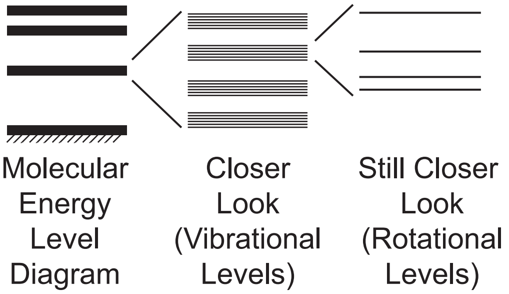


Figure 11. An expanded view of molecular energy levels (bands) composed of electron levels that each have added to it a series of vibrational levels and each of the vibrational energy levels have a series of rotational levels.

When a molecule receives energy and is raised to an excited state, it can occupy any of the energy levels within one of these bands of closely spaced levels. Similarly, when the molecule loses energy in a transition back to a lower energy state, it can also occupy any of a large number of energy levels in that band, see Figure 12. Photon energies given off during transitions to lower energy states are still equal to the energy difference between starting and ending states. However, because there are numerous slightly different starting and ending energy levels possible for any energy transition, a very large number of photon energies, differing only very slightly from each other, will be observed. For example, consider an energy transition that occurs between a level near the bottom of a band of excited states and the top of the band of lower states. The photons produced will have a little less energy (E_p) than had the transition ended at an energy level near the bottom of the band of lower energy levels (E'_p). Further, had the transition started from an energy level near the top of the band of excited states and ended at the bottom of the lower level, the energy of the emitted photon (E''_p) would have been a little greater yet, see Figure 12.

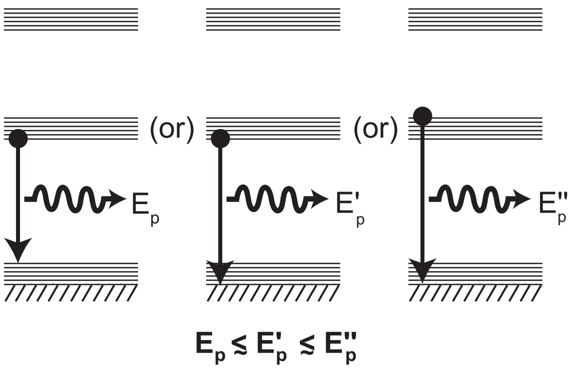


Figure 12. Energy transitions in molecules produce photons with a range of closely spaced energies.

While each **different** type of molecule has a **different** set of energy levels, the energy levels for all molecules of the **same** chemical species have exactly the **same** set of energies. If a sample containing a large number of molecules of one type is supplied with sufficient excitation energy, electron transitions will occur and photons will be emitted. If an instrument were used to analyze the number and energies of the emitted photons, a graph of those results would look something like Figure 13.

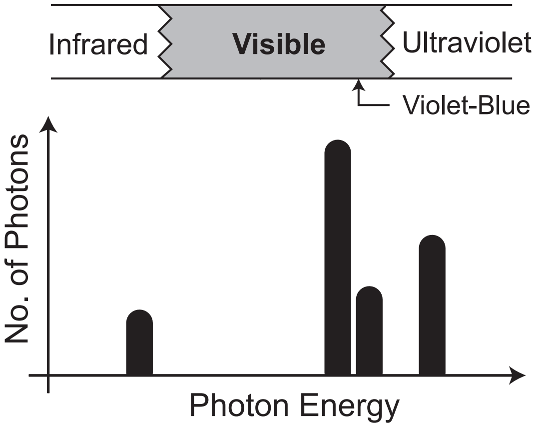


Figure 13. Illustration of a hypothetical molecular band spectrum appearing violet-blue in color.

Similar to what is seen for atoms, at many energies, it would be found that no photons are emitted (zero on the graph). In regions around a relatively small number of different energies, photons are observed, with energies corresponding to the differences between allowed energy states for that type of molecule. (That photons are emitted in bands of slightly differing energy is in contrast with atoms where the photons all have one of a set of precise energies.) A graph such as Figure 13 is a representation of the type of light spectra emitted by molecules and is usually referred to as a *molecular band spectrum*. The photons have ranges of energies that give the appearance of bands in an otherwise empty graph.

Had a different type of molecule been used, the graph would appear somewhat similar; however, the energies at which the photons are observed would not be the same because the specific set of allowed energy levels are different for different molecules.

If sufficient numbers of photons are emitted by the excited molecules, and they have energies that fall in the range of visible light, then an observer would see the emissions. If the emitted photon energies fall predominately in one part of the visible light spectrum, that emitted light will appear colored. For example, in Figure 13, there are four lines in the spectrum. The lowest and highest energy photons fall in the infrared and ultraviolet portions of the light spectrum, and thus are not visible to an observer. The other two molecular bands fall in the visible region, near the ultraviolet end. These emissions would be seen and, as will be discussed later, would appear violet-blue in color.

Sources of Continuous Spectra from Flames

With regard to fireworks, the two light generating mechanisms discussed thus far have the desirable characteristic of being able to produce intensely colored light. Unfortunately, two other light generating mechanisms operate in flames that have a deleterious effect on color quality. These result from the generation of light photons with a continuous and wide range of energies generally throughout the visible spectrum. The effect of these continuous emissions is a washing-out of flame color, possibly ruining an otherwise excellent colored flame effect. (The reason for this washing-out of color is discussed later in this chapter.)

The first mechanism for generating a continuous spectrum in a flame can be understood using energy level diagrams similar to those used to explain the origin of atomic line and molecular band spectra. When discussing the energy level diagram for atomic hydrogen, it was mentioned that the separation between each successively higher electron energy level decreased. The energy gaps between the levels continue to decrease until the gaps vanish at some limiting value. This limiting value is called the *ionization energy* for the atom (or molecule). If the atom acquires enough energy for one of its electrons to exceed this ionization energy, that electron is energetic enough to escape the atom completely, see Figure 14. (Ionization of an atom can be conceptualized as something vaguely like a space ship breaking out of Earth orbit.) The result of ionization is a *free electron* (no longer bound to the atom) and an *ion* (a charged atom). What was originally a completely bound atomic system has become unbound with regard to the free electron. As a result, the energy of the free electron is no longer quantized and it is able to possess any of the continuous range of energies, shown as the shaded area in Figure 15.

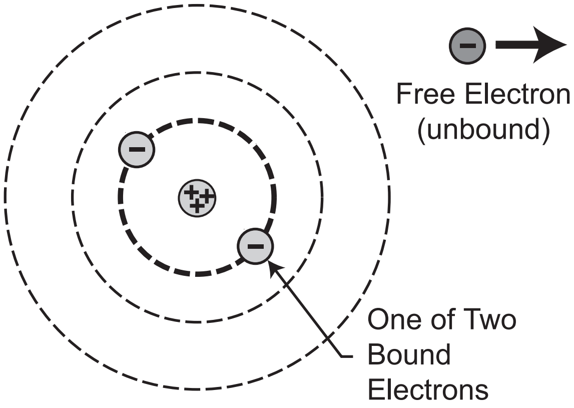


Figure 14. A much simplified illustration of an ionized lithium atom.

As mentioned above, atoms do not normally persist in excited electron states; they quickly undergo transitions to return to their ground state (de-excitation). Similarly, free electrons and ions tend to recombine, thus dropping to lower energy states. Upon their recombination, the energy can be carried off in the form of photons, but with one important difference. Because the free electrons were initially unbound, their starting energy was not quantized. Accordingly, upon their recombination, even though the re-formed atom ends-up in quantized energy states, the energy of photons produced will not be unique, see Figure 16. The result is that the photon energies can range widely with absolutely no gaps in the energy they possess. Thus the spectrum from ion-electron recombination is continuous, rather than a line or band spectrum such as produced by atoms and molecules, respectively.

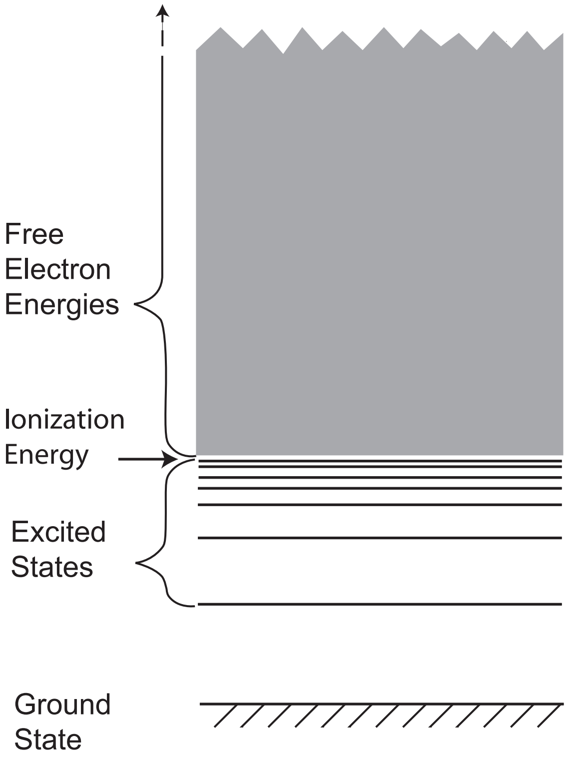


Figure 15. An illustration of an energy level diagram for a lithium ion

While on the subject of ions, it should be mentioned that ions are still quantized systems for those electrons that remain bound to the ion's nucleus. Everything that was said about atoms and molecules still applies to electron transitions within atomic and molecular ions. It is only when ions recombine with free electrons that continuous spectra result.

The second mechanism by which continuous spectra are generated is through incandescence. To explain incandescence properly, it would be

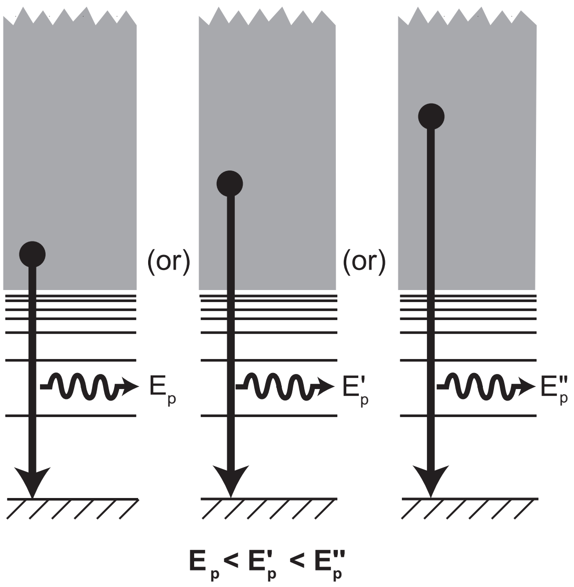


Figure 16. Ion recombination starts with free electrons possessing energies that are not quantized, resulting in a broad and continuous range of possible photon energies.

necessary to expand the discussion of quantum theory significantly. Fortunately, it is not necessary to understand the quantum origin of incandescence. It is sufficient to know that it occurs and a little about how it manifests itself. At the temperature of pyrotechnic flames, gases do not incandesce (glow), only solids and liquids incandesce. Such objects are seen to glow because they are emitting photons that are in the visible range. As the temperature of the incandescent body increases, two things happen; it glows brighter and the average energy of the emitted photons increases. In pyrotechnics, any non-vaporized material that is present in flames will incandesce, producing a continuous spectrum that can seriously wash-out flame color.

Even the extremely tiny bits of reaction products that finally end up as smoke particles consist of many billions of atoms collectively bound together. When this is the case, it is no longer appropriate to treat the individual atoms of such enormously large clusters of atoms as individual entities in the solid. Rather quantum theory treats the particle as a whole. The net effect of having a system consisting of many billions of atoms is a near complete merging of the individual energy levels of the atoms in the particle. It might be conceptualized as an extreme example of what happens when two hydrogen atoms combine to form a hydrogen molecule. Recall that what started out as relatively few precisely defined energy levels for hydrogen atoms, became bands of energy levels when just two atoms combined to form a hydrogen molecule. Now consider a smoke particle with billions of atoms bound together. The result is not just a slight broadening of the atomic energy levels, but rather the introduction of many billions of additional energy levels that effectively merge into a continuum, see Figure 17. Accordingly, when a smoke particle is thermally excited and there are transitions back to lower states, the smoke particle can assume any of these myriad of states. The result is that the emitted photons can have essentially any energy whatsoever; creating a continuous spectrum, see Figure 18. (The reason for the shape of the continuous spectrum is beyond the scope of this chapter.)

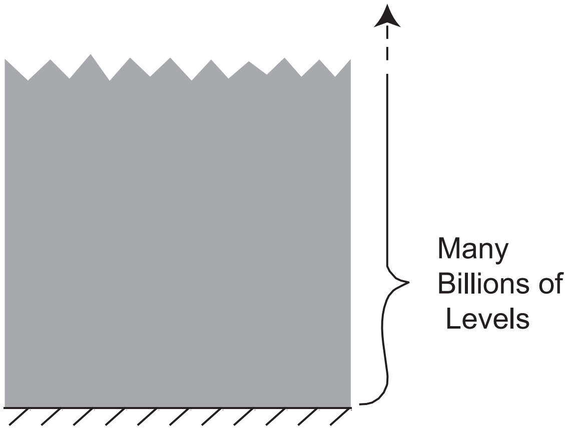


Figure 17. An illustration of what the energy level diagram of an incandescent particle might look like.

Because the range of emitted photons is both continuous and broad, at typical flame temperatures, it is not possible for the light emissions from incandescence or ion recombination to predominate in any one portion of the visible spectrum. Accordingly, at these temperatures it is not possible for incandescence or ion recombination to contribute to producing richly colored flame emissions. These types of emission can only serve to weaken (wash-out) flame color.

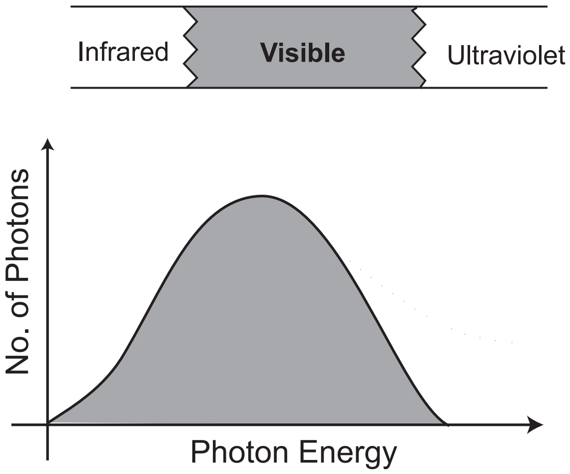


Figure 18. An illustration of a continuous spectrum such as might be produced by a high temperature incandescing particle.

A Further Introduction to Color and Spectroscopy

To conform to a common practice in spectroscopy, in the remainder of this chapter, light photons will generally be characterized by their wavelength rather than their energy as was done in the previous sections. This is acceptable because, as you may recall from the discussion about the nature of light, there is a unique one-to-one relationship between a photon's wavelength and its energy. Also, what might be called a classical approach will be taken in discussing pyrotechnic flame color, even though there is a relatively recent theory of the perception of color[32–34] that expands the understanding of color perception beyond the classical treatment. This was done because the classical approach correctly predicts the perception of color in most situations, and it provides a relatively simple framework from which to discuss colored flames.

In the seventeenth century, Newton observed that a beam of white light falling on a prism could be made to separate into a continuous series of colors, now called the visible light spectrum, see Figure 19. While he was at a loss to explain the physical basis for his observations, his work laid the foundation for understanding color, and he developed the first laws of additive color mixing.

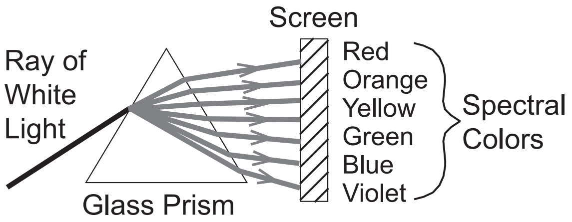


Figure 19. An illustration of Newton's observation that a prism can be used to separate the color components of white light.

The colors that Newton saw in his experiments ran from violet (bent most by the prism) through blue, green, yellow and orange, to red (bent least). The colors were continuous; there were no gaps and they graded smoothly from one color to the next. If the colored light from the prism were made to fall on a white screen, a more conventional view of the color spectrum results, see Figure 20. Squiggly lines have been added to denote the approximate limits to the various spectral colors as might be perceived by a typical observer. These squiggly lines are artificial and do not appear in a real spectrum. They are used to help make the point that different individuals are likely to disagree as to exactly where the colors change, for example from yellowish-orange to orangish-yellow. Approximate wavelengths corresponding to the various colors are also included in Figure 20 and are summarized in Table 1. The wavelengths are given in nanometers (one billionth of a meter and abbreviated as nm).

It is important to understand what the prism has done. It has not changed white light into colored light; the light that originally appeared white was already a combination of the different colors (wavelengths). What the prism did was to cause the variously colored components of white light to be bent at different angles as the light passed through the prism. This resulted in the various colored components diverging from each other and falling on different parts of the screen. That is to say, no single wavelength (energy) of light photons will appear white to an observer. Whenever we see something as white, it is because our eyes are receiving the proper combination of colored light to be mentally interpreted as white.

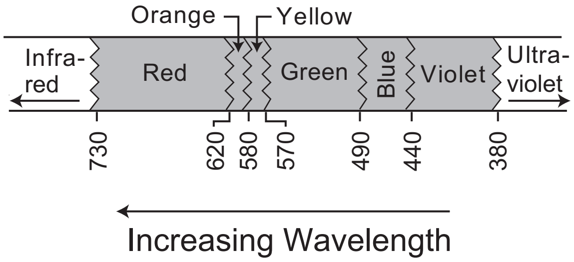


Figure 20. An illustration of the colors of the visible light spectrum. (Wavelengths are approximate and to the nearest 5 nm.)

Table 1. Approximate Wavelength Range for Spectral Colors. (To the nearest 5 nm.)

Perceived Color	Wavelength Range (nm)
Red	730 to 600
Orange	600 to 585
Yellow	585 to 570
Green	570 to 490
Blue	490 to 455
Violet	455 to 380

Beyond the short wavelength limit of violet and the long wavelength limit of red, Newton observed the spectrum to fall dark. These are the ultraviolet and infrared regions of the light spectrum, respectively. It is not that there are no light photons that fall in these dark regions; it is just that our eyes are not sensitive to light of these wavelengths.

For the purpose of this chapter, color will be defined as *those visual sensations produced in the brain of an observer when viewing any combination of light sources having wavelengths in the visible region of the spectrum*. As such, color is defined as a psychological reaction to a visual stimulus and truly only exists in the mind of the viewer. There are two reasons why this subjective definition was chosen rather than attempting a precise physical definition involving specific photon wavelengths. First, this definition is consistent with our modern understanding of how individuals perceive color.[33–35] Second, it is possible to produce most color sensations in many different ways, using combinations of different wavelengths of light. Accordingly, contrary to what might seem to be implied by Figure 20 and Table 1, most colors are not uniquely quantifiable in the sense of being able to characterize color based on a unique set of physical properties (e.g., photon wavelengths).

The fact that **most** color sensations are not uniquely related to the wavelength of light entering one's eyes is especially important in understanding color flames and dealing with the problem of improving their quality. This can be confusing to grasp because for **some** special color sensations there is a unique relationship between perceived color and wavelength. This paragraph will try to explain this more clearly. It is true that all photons have definite measurable wavelengths (energies). Further, if an emission source produces photons that all have the same (single) wavelength in the visible range, they can be seen by an observer and will appear deeply colored. In this special case, where all the photons have the same wavelength, the color that is observed does depend on their wavelength as suggested in Figure 20 and Table 1. The longest wavelength (lowest energy) photons in the visible range produce a color sensation of red; the shortest wavelength (highest energy) photons in the visible range produce the color sensation of violet. Sources of single wavelength photons, having wavelengths between those of red and violet, produce the color sensation corresponding to one of the other colors Newton saw when using his prism. These special colors are called *spectral colors*, and they are special because there is a unique relationship between color and photon wavelength. However, these spectral colors represent only a tiny fraction of all possible colors. The vast majority of color sensations, including those evoked by the emissions from colored pyrotechnic flames, are produced by various combinations of many different wavelength photons. For this vast majority of color sensations there is no unique relationship between color and photon energy, and the exact same color sensation can be created using a large number of combinations of different wavelength light photons. (This will become more clear later in this chapter.)

Newton's prism was a rudimentary form of a visible light spectroscope, and it could be used to crudely analyze sources of colored light. Newton used a circular hole in his window shutter as his source of light. His spectrum was thus made up of a series of overlapping colored images of that circular hole. Later, researchers developed a prism spectroscope in which the light from the source passed through a narrow slit on its way to the prism. The observer then viewed the slit through a telescope pointed at the prism, resulting in spectra with higher resolution.

At this point, it might be useful to consider what atomic-line, molecular-band and continuous spectra would look like with a spectroscope. If the light coming from an atomic light source passed through the spectroscope, the photons of different wavelengths (colors) would be separated one from another. If they were projected onto a screen, they would appear as a series of colored lines separated by dark spaces. Figure 21A is an example of what might appear on the screen for a hypothetical atomic emitter. (Note: the images in Figure 21 are negative images, where dark actually means bright.) Each colored line on the screen corresponds to one of the lines in the graph of photon energies in Figure 8. (The infrared and ultraviolet lines included in Figure 8 do not appear in Figure 21A because they are not visible to an observer.) In Figure 8, the length of the line was used to indicate the intensity of that wavelength (energy) photon. In Figure 21A, each colored line is equally long, and the intensity of each colored line must be determined by observing its brightness.

Figure 21B is an example of what might appear if we were observing a hypothetical molecular source of light. In this case the spectroscope would produce bands of color with dark regions in between. These colored bands correspond to the bands in the graph of photon energies in Figure 13; and the brightness of the bands corresponds to their intensity. If the spectroscope were used to observe a high temperature incandescent light source, which emits a continuous spectrum, it would produce something like the visible light spectrum in Figure 21C; various colors of light would fall throughout much or all of the color spectrum and there would be no gaps between any of the colors present. Again the brightness along the length of the spectrum corresponds to the intensity of the various wavelength emissions.

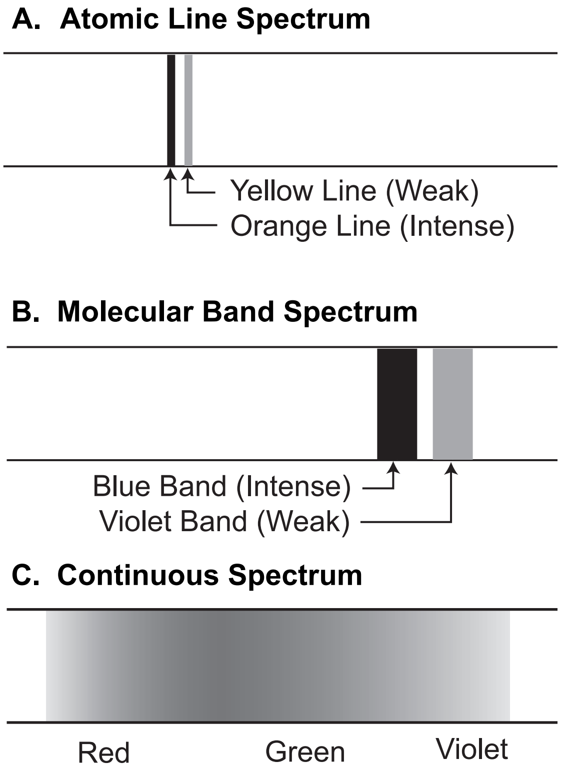


Figure 21. An illustration of how hypothetical atomic-line, molecular-band and continuous spectra might appear using a rudimentary spectroscope. (Actually this is a negative image where dark means bright.)

Quantifying Color Sensations

Newton observed that it was possible to generate a range of colors (*spectral colors*) by passing a ray of white light through a prism. Also he discovered that a very large number of new colors (including white) (*composite colors*) could be generated by blending sources of the spectral colors: red, green and blue. To deal efficiently with the subject of composite colors, it was necessary to find some way of quantifying one's observations. An obvious possibility would be to use a three dimensional graph, with each of the three axes representing one of the three primary colors (red, green and blue). Then each of the composite colors produced would be represented as a point in three dimensional color space. However, while this would work, it would be cumbersome and would not reproduce accurately on two dimensional paper.

Fortunately, a much simpler, two dimensional method was developed to represent both spectral and composite colors. This was made possible by the discovery that if the brightness of all three primary light sources were varied proportionately (e.g., if the intensities of each source were doubled), then the composite color observed remains unchanged except for its brightness (which in this example is also doubled). This meant that only the fractional intensity of the three primary colors determines their composite color. (And their combined intensity determines the brightness of that color.) It is only necessary to specify two of the three fractions to describe the mixture completely. For example if a composite color is made using red, green and blue light sources, and one were told that 1/3 red and 1/3 green light have been used, then because the total of the three fractions must equal one, obviously the amount of blue light being used must also have been 1/3. Thus a convenient method to represent color is to specify just two of the three

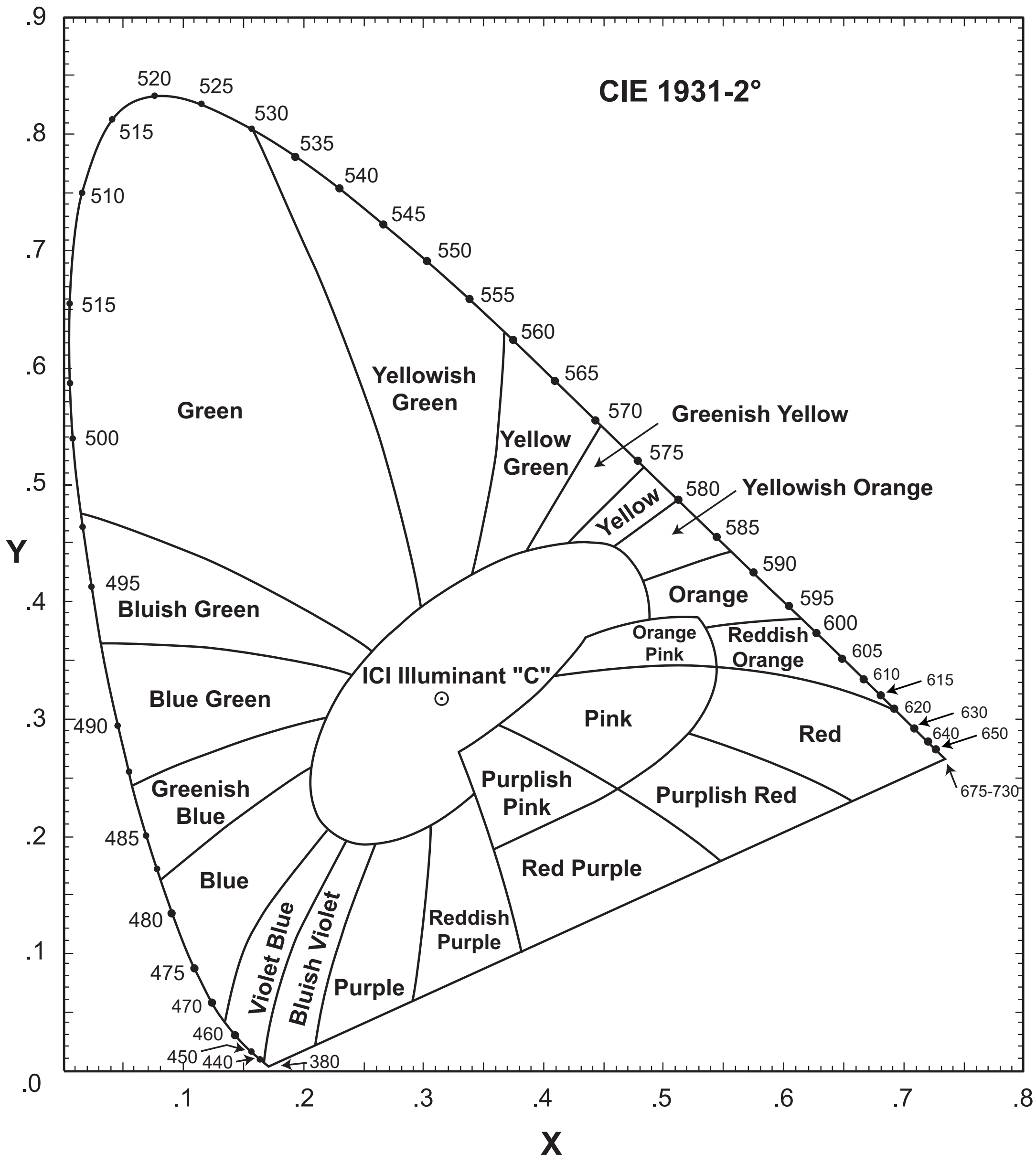


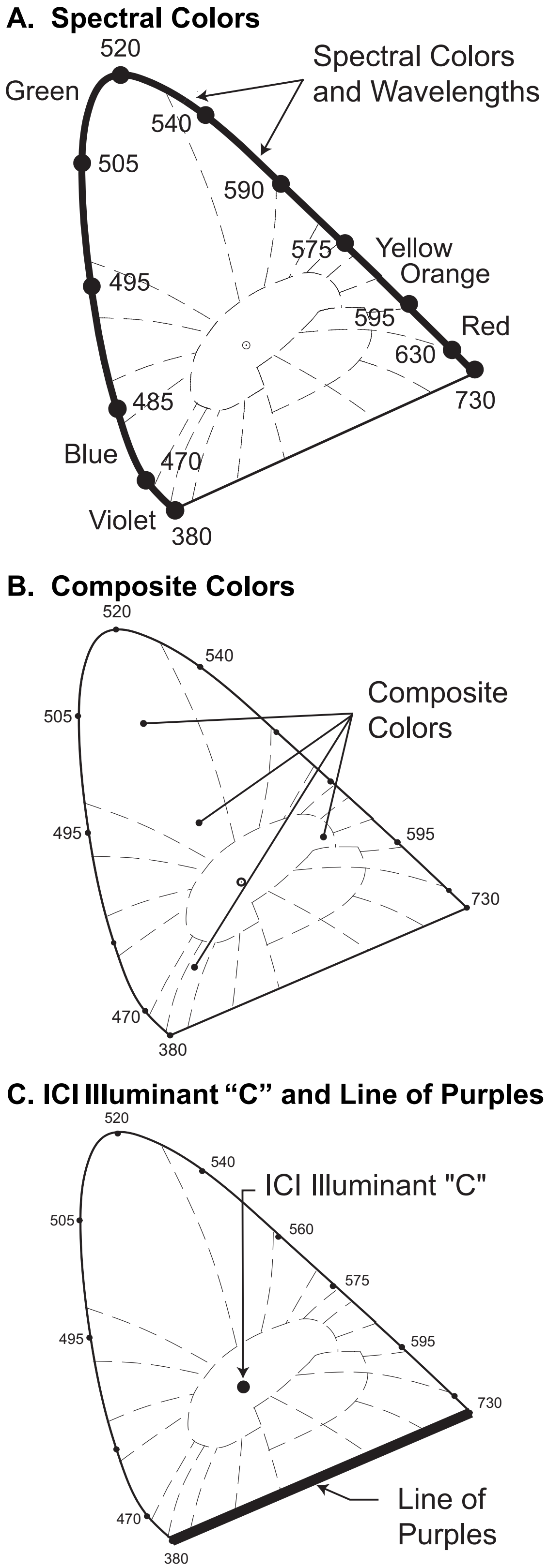
Figure 22. A non-color rendition of a chromaticity diagram. (This version was developed in 1931 by the International Commission on Illumination.)

primary color fractions, and this can easily be done using a graph in just two dimensions. When color fractions are plotted for all colors, the result is what is commonly referred to as a *chromaticity diagram*, see Figure 22.

In Figure 22, the vertical (Y) axis is the fraction of a source of special green light used, the horizontal (X) axis is the fraction of a source of special red light used, and the fraction of blue light is implicit (and can be calculated if desired). The spectral colors (those pure colors for which a unique relationship exists between color and wavelength) lie on the outer periphery of the tongue-shaped region as highlighted in Figure 23A, and for which the corresponding wavelengths (in nanometers) are listed.

All possible composite colors lie inside the tongue-shaped color region of the chromaticity diagram (Figure 23A). The color names listed in the chromaticity diagram, Figure 22, are those that a typical observer of the composite colors would use to describe them. The colors grade gradually from one to the next. The lines separating each of the color areas have been added as a convenience and only serve to indicate the approximate boundary at which an observer would typically call the colors by some other name (for example, where an observer might stop calling a series of gradually changing bluish-green colors and start calling them blue-green).

The straight line across the bottom of the tongue shaped region, highlighted in Figure 23C, is called the *line of purples*. The colors lying on this line are as pure as spectral colors, but they are not spectral colors. These colors can only be produced using various combinations of the reddest of the possible red light sources and the most violet of the possible violet light sources. (This will become more clear in the discussion below.) Because these colors must be made using photons of two different wavelengths, there is not a single (unique) wavelength that can be associated with them, and there are no wavelengths listed along the line of purples. The point near the center of the chromaticity diagram labeled ICI Illuminant "C" (or sometimes just "C") is the color point for a standard light source. This standard was chosen because it is a good approximation for average



A. Spectral Colors

B. Composite Colors

C. ICI Illuminant "C" and Line of Purples

Figure 23. Illustrations identifying key features of the chromaticity diagram.

daylight at noon and is taken as constituting white light.

The shape and orientation of the tongue-shaped color region depend on the choice of the three primary colors. If negative fractions of the primary colors are allowed (e.g., –1/2, 3/4, and 3/4) then almost any three different colors make satisfactory primaries. In fact, even if we choose the spectral colors of red, green and blue, it is not possible to make all of the composite colors without occasionally using negative amounts of those primary colors. (This too will be discussed further below.) On a mathematical level using a negative amount of light is okay, but it is confusing conceptually and is impossible to do in reality. How can one use less than zero of a primary color, which is what a negative amount represents?

To eliminate the necessity of using negative color fractions and to standardize the diagrams, an International Commission on Illumination (ICI) was assembled in 1931. Their solution was to invent three new (slightly unreal) primary colors. Remember, chromaticity diagrams were created just to make it easier to deal with the subjective science of additive color; so there is nothing sacred about chromaticity diagrams or the primary colors on which they are based. If three slightly unreal primary colors will help to make working with color easier, they should be allowed, providing everyone uses the same chromaticity diagram based on those same primary colors.

Since 1931, the International Commission has developed additional chromaticity diagrams, and a strong argument could have been made to use one of their more recent chromaticity diagrams. However, there is nothing intrinsically wrong with the 1931 diagram, and it is still the one most frequently used in discussing colored pyrotechnic flames. Accordingly, the chromaticity diagrams used in this chapter are based on that established by the 1931 International Commission on Illumination.

In the illustrations for the following sections of this chapter, only simplified versions of the chromaticity diagram have been used, thus it may occasionally be helpful to refer back to the complete diagram in Figure 22.

Classical Laws of Additive Color Mixing

For the most part, the laws of color mixing were derived as the result of subjective observation using people as the primary measuring instruments. Remember, color is a psychological response to a physical stimulus; thus while the sensation of color is real, it literally only exists in one's mind. For almost all colors, in particular those produced by pyrotechnic flames, there is no unique set of physical attributes that can be used to quantify (measure) perceived color. Accordingly, the use of the subjective observations of people in designating the colors of a chromaticity diagram and in developing the laws of additive color mixing not only appropriate, it was necessary.

The classical color mixing laws are a systematic expression of our everyday observations of color. As such, they have been quite useful. Research[33–35] has demonstrated that these simple laws are not always satisfactory and that the brains of observers can be made to perceive color sensations that the classical laws say are not possible. However, the classical laws are sufficient to provide a basic understanding of colored pyrotechnic flames, and they will be quite useful when discussing colored flame chemistry. Therefore the simpler classical laws will be discussed in some detail and will be used in the remainder of this chapter.

The first of the classical laws of color mixing can be stated as: *every source of colored light is represented by a definite point located in the color region of the chromaticity diagram.* All of the slightly different colors one might call green will have color points falling somewhere in the vicinity of point A in the chromaticity diagram in Figure 24. Similarly, all light sources one would call red have color points somewhere near point B, and white light sources have their color points in the vicinity of point C (which is the color point for ICI Illuminant "C").

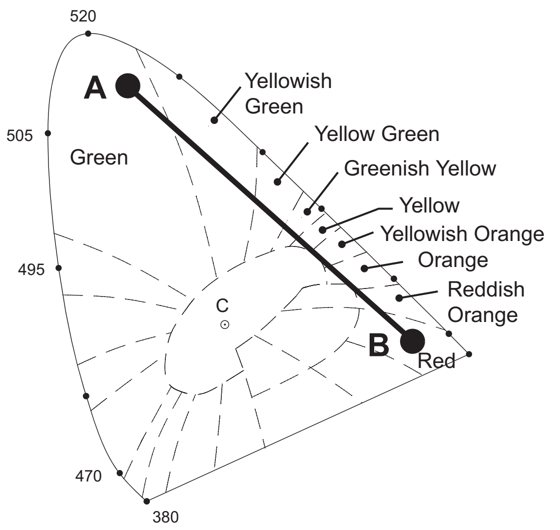


Figure 24. The first and second laws of additive color mixing: color points and lines.

The second law of color mixing can be stated as: *when the light from two color sources are combined (added together) in various proportions, the resulting color points will lie a proportional distance along the line connecting the two original color points*. For example, if green and red sources of light (color points A and B in Figure 24) are mixed in various proportions, the resulting color will lie somewhere along the line AB. By varying the relative amount of green and red light used, all of the colors from green, through yellowish green, yellow green, greenish yellow, yellow, yellowish orange, orange, reddish orange to red are possible. Further, the location of the combined color point on line AB is equal to the proportion of each of the light sources. In Figure 25, color points are shown for three different combinations of light from sources A and B. When 50% A and 50% B are used, the resulting color point D will be located at the midpoint of the line AB. If the ratio is 75% A and 25% B, the color point D' will be the result. If the ratio is 10% A and 90% B, the color point D" will be the result.

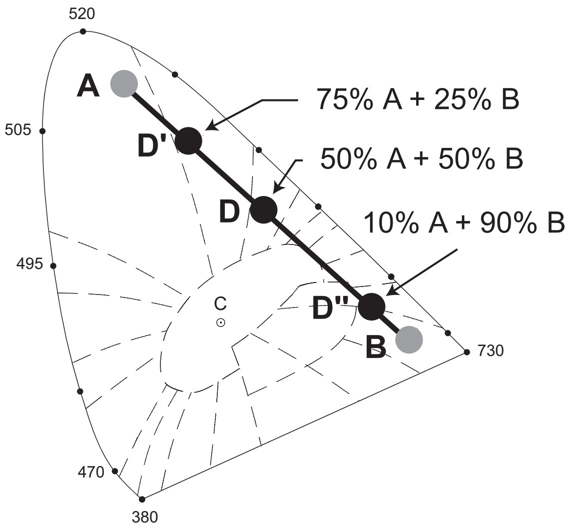


Figure 25. The location of color points produced by combining varying proportions of light sources **A** *and* **B**.

Implicit in the second law of additive color mixing is that using **only** colored light sources A and B, **only** those colors on the line AB are possible. It is not possible to make blue or violet by mixing sources of green and red light. Also implicit is that only the proportion (relative amount) of the two light sources determines the color. For example, equal amounts of the light sources A and B can be combined to produce color point D. If the brightness of both light sources (A and B) is doubled, the color produced is still that of color point D; however, the color will now be twice as bright (intense).

The third law of color mixing can be stated as: *every color, except pure spectral colors, can be made using any of a large number of combinations of different color sources, and those colors will appear indistinguishable to an observer*. For example, if it were desired to make white light (Illuminant "C") from pairs of non-white light sources, one possibility would be to mix bluish-green light (color point E in Figure 26) and pink light (color point F). By varying the relative proportions of the two colors, all the colors along the line EF can be made. Observe that the color point for Illuminant "C" falls on this line. Thus white light can be made using the correct proportion of sources of bluish-green and pink light. Other possibilities to make ICI white are to mix reddish-purple and yellowish-green (color points G and H), or violet-blue and greenish-yellow (color points I and J) in the proper proportions. In fact, by choosing different starting colors, the number of possibilities to produce white light is essentially unlimited. If observers, using only their eyes, compared the standard daylight source, Illuminant "C", to each of the three combined sources just described, they would not be able to discern any difference.

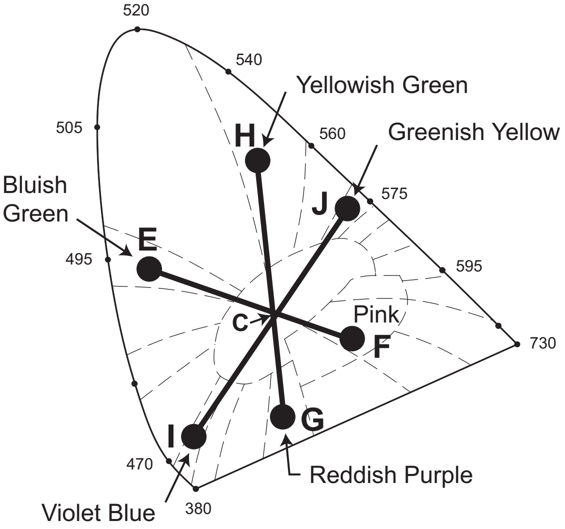


Figure 26. A few of the many color combinations that can produce white light.

Using the laws of color mixing, it is now possible to demonstrate why the spectral colors red, green and blue can be used in various combinations to make most, but not all, of the composite colors. To do this, first consider a source of spectral blue light (color point K in Figure 27 with a wavelength of 470 nm). If spectral red light (color point L, 730 nm) is added to the blue light, in varying proportions, any of the colors along the line KL can be made. Next, imagine that a small amount of spectral green light (color point M, 520 nm) is turned on and its intensity held constant. With just this little green added to the original blue color, the blue–green color point will move along the KM color line to reach color point N. Similarly with this little green added to the original red color, the red–green color point will move along the color line LM to reach color point O. Now by varying the ratio of blue to red, any color along the color line NO can be made. Next, if the amount of green is increased a little more, and the process of varying the ratio of blue to red is repeated, any color along the line PQ can be made. As the process of increasing the amount of green light is continued, it will eventually be possible to make all of the colors inside the triangle KLM.

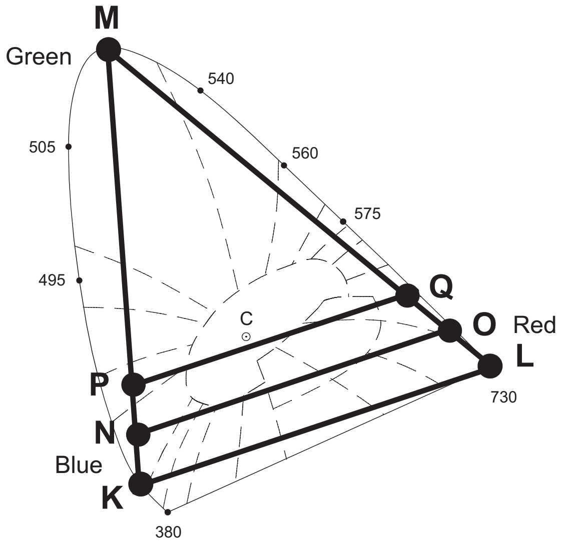


Figure 27. An illustration of how the spectral colors of blue, red and green can be used to make most of the possible composite colors.

The colors inside the triangle KLM constitute most, but not all, of the colors in the chromaticity diagram. For example, consider the color at point R in Figure 28. Using just the blue (K) and green (M) light sources, those colors along the line KM can be made, and point S is the color closest to point R. After adjusting the blue and green light sources to reach color point S, when red is now added, color points along the line SL can be reached. As more red is added, the closer the composite color point moves toward the red color point L. Thus, adding any red at all moves the composite color point farther from the desired point R. To reach point R, it would be necessary to add less than no red at all (i.e., a negative amount of red). From a practical standpoint, this is impossible. The color at point R is one of those colors that cannot be made using spectral red, green and blue; similarly, none of the other colors outside the triangle KLM can be made using these primary colors.

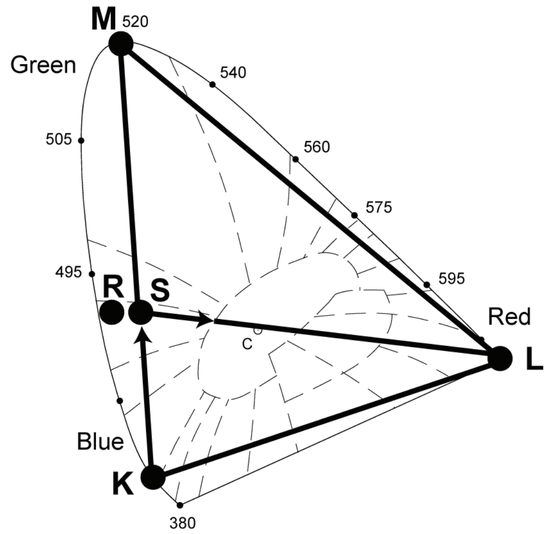


Figure 28. An illustration of why some composite colors cannot be made using combinations of spectral blue, red and green light.

Having introduced the classical laws of additive color mixing, only one topic remains before this chapter can turn its attention to a discussion of colored flame production. That last remaining topic is the method used to measure (quantify) perceived color such that the light produced by various colored flames can be compared.

The Measurement of Color

The basis for the measurement of color follows from the third law of color mixing, from something that might be called the *principle of equivalent color*. Even though there are many ways of combining colored light sources to produce the same color sensation, they are all equivalent as seen by an observer. Therefore, a precise physical description of any of those various methods of producing the color sensation will serve to define the perceived color completely. For example, it was previously described how three different combinations could create the color of Illuminant "C" (Figure 26). If one were to describe any of these methods precisely, then the color of Illuminant "C" would be completely defined. This somewhat arbitrary process for defining (measuring) color is acceptable, but it would be improved if the method used by everyone were standardized so that everyone used the same method. Fortunately, there is such a standardized method.

The standard method is based on the observation that most color points on the chromaticity diagram can be reached using a combination of white light (Illuminant "C") and one of the spectral colors. For example, the color point T in Figure 29 can be reached using a combination of white light and the spectral color with a wavelength of 490 nm. In this case, color point T is approximately 65% of the way from Illuminant "C" to the spectral boundary. Thus, if both the wavelength of the spectral color and the percentage of the distance along the line from Illuminant "C" to the spectral color are specified, then the color point is completely defined. The wavelength of the spectral light used to do this is called the *dominant wavelength*. The percentage of the distance along the line from point C is called *purity*, with color point C having 0% purity and spectral colors having 100% purity. In the example of color point T, the dominant wavelength is 490 nm and its purity is 65%. Similarly, the color point U in Figure 29 has a dominant wavelength of 565 nm and a purity of 90%.

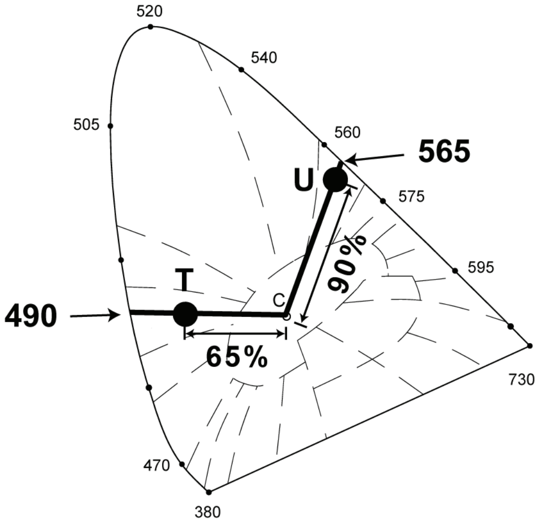


Figure 29. An illustration of the standardized method for the measurement of color.

In effect, by using this method to measure color, a researcher in one location is giving other researchers the recipe for them to reproduce the same exact perceived color. Color researchers can purchase light sources producing the white light of ICI Illuminant "C". Then using a device called a monochrometer and an incandescent light, spectrally pure light of various wavelengths can be generated. Based on the second law of additive color mixing, if one wanted to reproduce the color of point T, one could mix a spectral light source of 490 nm with an Illuminant "C" light source in a ratio of 65 to 35. The result would be a composite color in every way equivalent to color point T.

The standard method of measuring color must be modified slightly for those colors inside the triangle CVW of Figure 30. These colors, called *nonspectral composite colors*, cannot be made by combining white light and one of the spectral colors. For example, consider the color point X. When a line is drawn from ICI "C" through color point X until it intersects the boundary of the chromaticity diagram, it does so along the line of purples (VW), for which there are no spectral wavelengths. Thus the color point X does not have a dominant wavelength as described above. It does, however, have what is called its *complementary wavelength*. This can be found by extending the line XC upward until it intersects the line of spectral colors in the upper portion of the chromaticity diagram. In this case, the color point X has 550 nm as its complementary wavelength. To indicate that this is the color point's complementary wavelength, the prefix C is added (e.g., C–550 nm). The purity of the color is determined as previously and is the length of the line CX, expressed as a percentage of the distance from point C to the line of purples. Thus, the color at point X would be measured as having a dominant wavelength of C–550 nm and a purity of approximately 50%.

Colors are completely defined by specifying their dominant wavelength and purity. However, colored light sources have another attribute that must be specified, that of brightness. The brightness of a light source is measured as *luminous flux*, or for the purposes of this chapter, simply as intensity. Light sources in pyrotechnics are completely described using only dominant wavelength, purity and intensity.

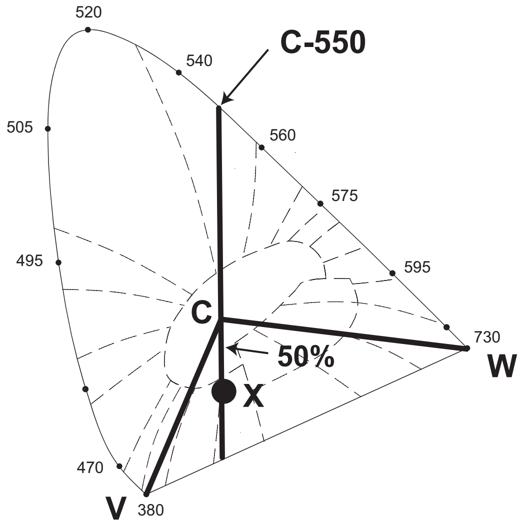


Figure 30. Illustration of the method for measuring non-spectral colors.

Color Theory Applied to Pyrotechnic Flames

At this point, it is appropriate to apply some of the theory already discussed to the subject of colored pyrotechnic flames. It was said that atomic line spectra have the desirable characteristic of being able to produce deeply colored flames, and this is true. Consider the hypothetical case of some chemical element whose atoms produce spectra with only one spectral line falling in the visible region. In this case the color point corresponding to those electronic transitions in this atom will fall somewhere along the outer edge of the color region of the chromaticity diagram. This spectral color, by definition, has a purity of 100%. If this is the only emitting light source in the flame, the flame will be very deeply colored. The particular color generated will depend on the wavelength (energy) of the spectral line. In the example shown in Figure 31, first consider only the one spectral line that produces color point A. It has the dominant wavelength of approximately 460 nm, and of course it has a purity of 100%.

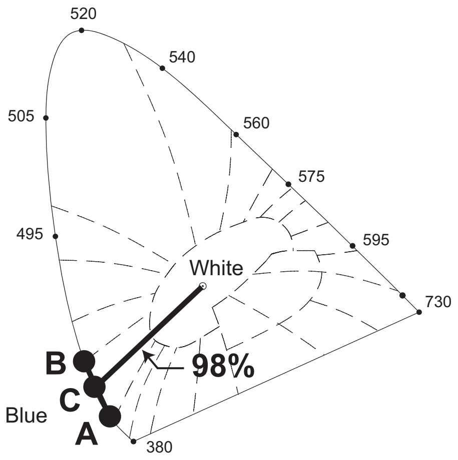


Figure 31. An illustration of a hypothetical case where multiple atomic lines would produce a high purity colored flame.

Unfortunately, in a pyrotechnic flame, many different chemical species will be present, each potentially contributing their own spectral lines. Consider next a slightly more realistic case, one in which there are additional spectral lines in the visible spectrum. If just one additional spectral line is present in the spectrum and one is extremely fortunate, it is possible that the second color point would lie close to spectral source A, such as color point B in Figure 31. The composite color must lie somewhere along the line AB connecting the spectral color points in the chromaticity diagram. The exact position of the composite color will depend on the relative intensity of the two spectral lines. If it is assumed that the intensities are equal, the composite color point will lie at C, midway between points A and B. The composite color will still be very pure, about 98% in this example. The most noticeable effect will be a slight shift in dominant wavelength to a value between that for A and B. To an observer, the effect will be a slight change in color, but the flame will still be seen as deeply colored.

An even more realistic case is that the second spectral line has a dominant wavelength quite different from the first; then real problems can result. Consider the case where the added spectral line (color point D in Figure 32, with a dominant wavelength of 560 nm) lies somewhere across the chromaticity diagram from the first color point. The composite colors that could be produced will lie along the line AD. If one were fortunate and this second spectral line (D) only had about two-tenths the intensity of the first, the composite color point will fall at point E. Color point E has about the same dominant wavelength as when only the spectral line of point A is present. However, the purity of color point E has dropped to approximately 60%. An observer will see a slight change in color, similar to that in the first example. However, because of the reduced purity, the color will now appear noticeably washed-out. Even worse, had the two spectral lines been of equal intensity, the composite color would appear at the color point F. The dominant wavelength of this composite color has changed substantially, and its purity has fallen to less than 20%. This light source will appear almost white to an observer, a devastating loss of flame color.

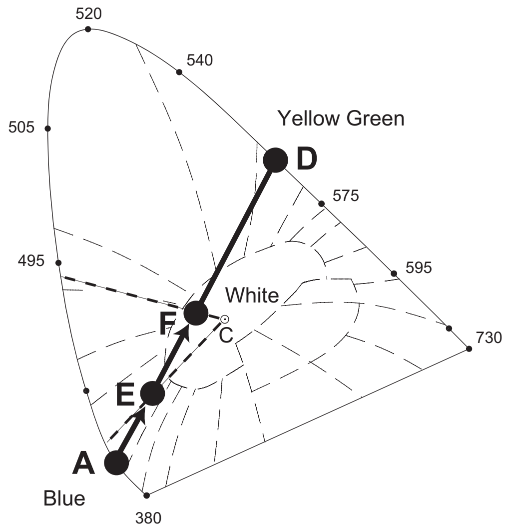


Figure 32. An illustration of a hypothetical case where multiple atomic lines could produce a low purity colored flame. Heavy dashed lines show the dominant wavelengths for color points E and F.

Thus far only flames producing atomic line spectra have been considered; however, molecular band spectra are much more common in pyrotechnic flames. A molecular band spectrum with just a single band will produce a deeply colored flame just as in the example of Figure 31. Recall that a molecular band is just a collection of very closely spaced lines that give the appearance of being a continuous band. On a chromaticity diagram, it is as though there were a large collection of color points in one spectral region. The collection of equally intense color points running from approximately 460 to 480 nm, as shown in Figure 33, will produce a composite color with the dominant wavelength of about 470 nm and having approximately 99% purity. Thus molecular bands can be treated in much the same way as atomic lines were (i.e., a molecular band can be treated as if it were an almost pure spectral line with its dominant wavelength about midway through the band). Then everything that was said above for atomic line spectra, applies equally to molecular band spectra or to mixtures of atomic and molecular spectra. The important thing to remember is that the wider the molecular band, the less pure (more washed-out) the color will appear.

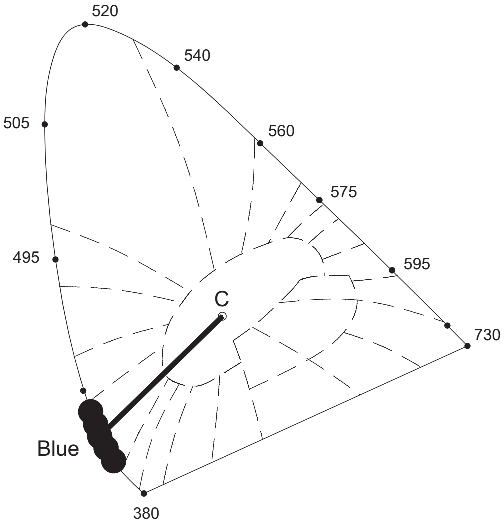


Figure 33. An illustration of a hypothetical case of a single molecular band producing a high purity colored flame.

Now consider the effect of continuous spectra, which can be treated as little more than extremely wide molecular band spectra. However, because of the extreme width, there can be a tremendous loss of purity. Consider the example of a continuous spectrum from an extremely high temperature (10,000 °C) object. This would result in a composite color point somewhere in the vicinity of G in Figure 34, not far from the white color point of Illuminant "C". For lower temperature incandescing objects, the color points will fall somewhere along the curved line GH, with the color points for the lowest temperatures being near color point H. (Depending on the exact nature of the incandescing material, it is possible for the color points to extend more or less into the yellow region than is shown for the line GH.[7a]) The perceived brightness of the light emitted by incandescing material is also a function of temperature, with low temperatures producing low levels of brightness (appearing dim) and high temperatures producing high levels of brightness. Table 2 lists the approximate color of incandescing material (liquids and solids) and their brightness as would be perceived by an observer.

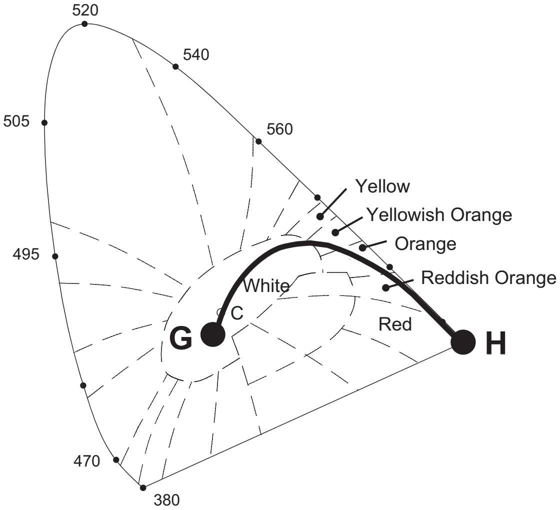


Figure 34. An illustration of the color points produced by incandescing material as a function of their temperature.

Table 2. The Perceived Color and Relative Brightness of Incandescing Material.

Temperature (°C)	Perceived Color	Relative Brightness(a)
500	Red	1
850	Reddish orange	4
1500	Orange	7
2200	Yellowish white	9
3000	White	10

a) Based on information from references 7a, 34a, and 36.

Although not particularly well documented, typical colored flame temperatures range from 2100 to 2500 °C.[7b] At these temperatures, incandescing material will be bright and near white. Thus incandescent sources (solids and liquids) that are present in colored flames can be quite detrimental to the color produced. This is because the bright and nearly white light they produce can act to significantly reduce the color purity of the flame, making it appear washed-out. While this is true for all colors, it is especially true for blue, as illustrated in Figure 35. For example, even if it were possible to produce spectrally pure blue emissions from some emitting species in the flame (color point I), but there were incandescing solid or liquid particles in the flame (color point J) whose emissions were only 40% as strong as the blue emissions, composite color point K (appearing bluish-white) would be produced. The addition of the emissions from incandescing particles has seriously reduced the purity of the flame color.

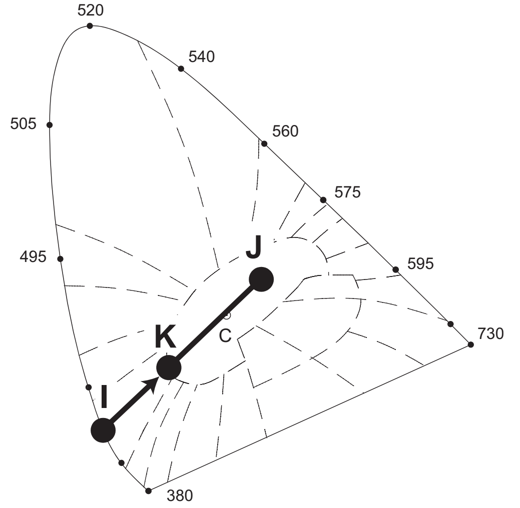


Figure 35. An illustration demonstrating the deleterious effect incandescence can have on otherwise high purity colors.

As a final example, consider the case of high purity purple colored flames, which are relatively difficult to produce. A high purity purple flame is one that would have its color point L somewhere inside the shaded region in the chromaticity diagram in Figure 36. To produce high purity purple flame color, one needs the proper combination of spectral emissions from the extreme opposite ends of the spectrum, color points M and N. Finding such sources is at least difficult and, in the case of the high purity violet emitter, it is probably impossible. However, what makes the problem of high purity purple even more difficult is that the presence of only 20% of a spectral green emitter (color point O) moves the composite color point from L to P (i.e., from high purity purple to near white).

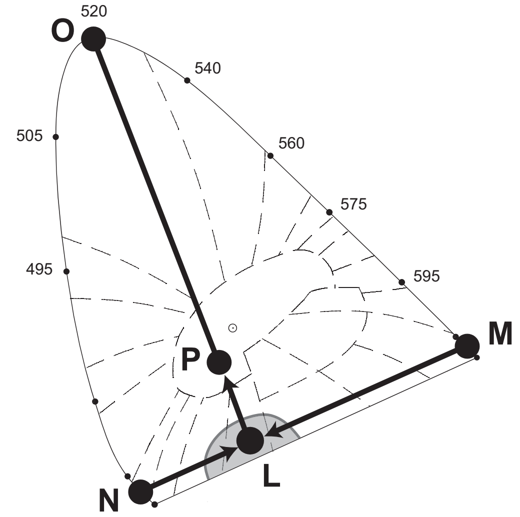


Figure 36. An illustration of why it is especially difficult to produce a high purity purple flame.

In the real world of colored pyrotechnic flames, there will generally be very many different chemical species present in the flame and many of those species will emit interfering wavelengths of light. The net effect is to reduce the purity of the desired flame color. This is demonstrated in Figure 37, where the points of the smaller triangle represent the color points for what are approximately the best formulations for traditional red green and blue fireworks stars,[21,30] and these are probably somewhat better than typical commercial fireworks formulations. Of these best traditional formulations, only red is of reasonably high purity and at nearly the ideal wavelength, see Table 3. The green has moderate purity but is yellowish green. The blue is actually slightly closer to ICI white in color than spectral blue. This inner color triangle is not large in comparison with the full range of possible colors in the chromaticity diagram. Even more significantly, it must be recalled that much of its central region is that portion of the chromaticity diagram allocated to shades of white light.

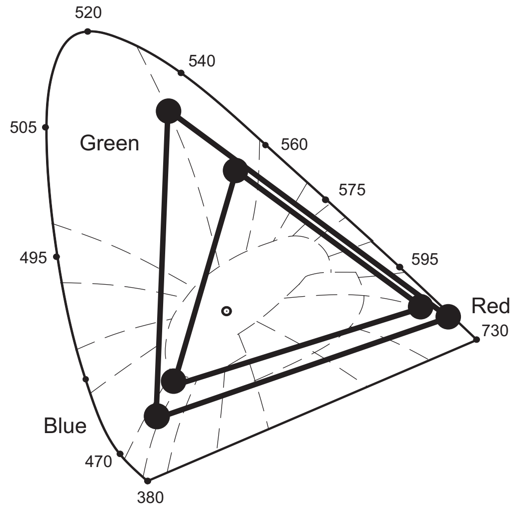


Figure 37. A demonstration of the color points for the "Best-Traditional" (smaller triangle) and the "Best-Yet" (larger triangle) color star formulations.

In the past few years, researchers have developed formulations providing improved color.[19,21] The approximate red, green and blue color points for the best of these are shown as the points of the larger triangle in Figure 37. The dominant wavelengths and purities for these were calculated and are also listed in Table 3. In each case, the color points have been shifted closer toward the optimum wavelength and the purities have improved. (However, it should be acknowledged that there are problems associated with using these new best-yet formulations that will make it somewhat difficult to use them commercially.)

Pyro-Chemical Flames for Color Production

As discussed above, the most common process for colored light production is to supply an atomic or molecular species with sufficient energy to cause the elevation of their electrons to excited states. Thereafter, as the electrons drop back to lower energy states, photons of light may be produced (possibly see again Figure 6). This process can be summarized by the following generalized chemical equations:

$$\{CS\} + \text{Heat Energy} \rightarrow \{CS\}^* \qquad (2)$$

$$\{CS\}^* \rightarrow \{CS\} + \text{Photon} \qquad (3)$$

where {CS} is the color species (an atom or molecule), and {CS}* represents the color species with an electron in an excited state.

In pyrotechnics, the source of the energy needed to begin the light production process is thermal energy manifested as a flame. (Essentially all of the desirable color-emitting species that are used in pyrotechnics are molecules and not atoms; accordingly, for convenience in most of the remainder of this section, color emitting species will generically be referred to as molecules.)

Table 3. Dominant Wavelength and Purity for the "Best-Traditional" and the "Best-Yet" Color Star Formulations.

Chromaticity Diagram		Best-Traditional[a]		Best-Yet[b]	
Color	Wavelength (nm)[c]	Dom. Wave. (nm)	Purity (%)	Dom. Wave. (nm)	Purity (%)
Red	650	617	89	640	98
Green	505	556	72	532	82
Blue	475	450	49	470	67

a) Calculated based on data in references 21, 30 and 37a.

b) Calculated based on data in references 19 and 21.

c) This is the wavelength that corresponds to the approximate center of the range for the specified color.

As a practical matter, "We have a pretty clear idea of what is meant by a flame, but it is very difficult to give the word a precise meaning."[36] Probably the most fundamental characteristic used to determine whether something is a flame is its emission of light. Other characteristics such as its flickering, radiating heat and its apparent chemical nature seem less important. Consider Figure 38, an illustration of a typical flame being produced by a burning pyrotechnic composition. The greatest single difference between points B and C (just inside and just outside the flame envelope) is that the molecules at point B are emitting visible light and those at point C are essentially not. For the most part, the same kinds of molecules are present at both points, and while the temperature at point C is lower than at point B, it is not radically lower.

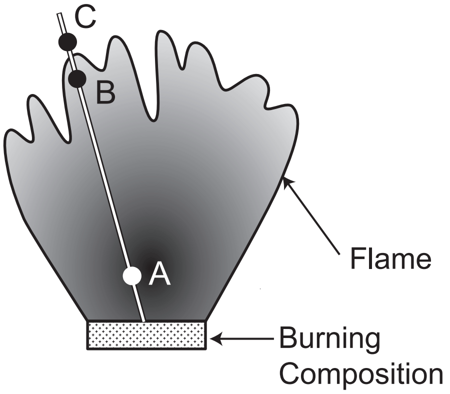


Figure 38. An illustration of a typical pyrotechnic flame.

Even though the temperature difference between B and C is not great, it is sufficient to account for the molecules at point B emitting light while those at point C essentially are not. (The molecules at point **C** are actually producing a small amount of visible light, but so little as not to be readily seen by an observer.) Recall that the energy carried off by the photon (i.e., its wavelength) is determined by the difference in energy between the electron-energy levels involved in a transition to lower energy states. When the available energy in the flame (i.e., flame temperature) is great enough to cause sufficient numbers of electrons to reach energy levels such that the resulting photons have wavelengths in the visible range, then the molecules at that point will be seen to emit light. At some point in the flame the temperature will fall to a level such that the available energy is no longer high enough to excite a sufficient number of electrons to levels that produce visible light photons, and then no light will be seen to be emitted. Figure 39 is a generalized graph of temperatures along the line in Figure 38 on which points A, B and C fall.[7b,38] Included in Figure 39 is a line intended to correspond to the approximate flame temperature necessary for the production of a visually discernable quantity of light from the molecules present. At point A the temperature is well above that value, at point B the temperature is only slightly above that value, and at point C the temperature of the flame has dropped to a value slightly below that needed for the production of visibly observable light. For the most part, the molecular species that are present at point B are also present at point C. As far as light generation is concerned, the only important difference is temperature and that difference is not particularly large. For the purpose of this chapter, the definition of a flame is *that region surrounding a source of chemically generated heat energy where the temperature is sufficient to cause the emission of visibly observable light from those chemical species present*.

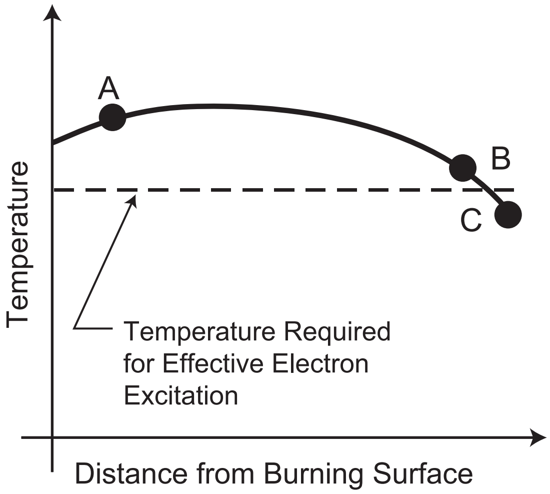


Figure 39. An illustration of flame temperature as a function of distance from the burning surface for a hypothetical burning pyrotechnic composition.

In addition to supplying the heat energy necessary to excite electrons, pyrotechnic chemical reactions must provide the heat energy needed to vaporize the color agent and chemical reaction products. Recall that solid particles and liquid droplets can only emit undesirable continuous spectra. Accordingly, to produce relatively pure flame colors, it is important that the color agent and the various reaction products all be vaporized in the flame. The source of the needed heat energy is the class of exothermic chemical reactions called combustion, which can be represented with the generalized formula:

$$\text{Oxidizer} + \text{Fuel} \rightarrow \text{Combustion Products} + \text{Heat} \qquad (4)$$

where the fuel and oxidizer combination is sometimes referred to as the *pyrogen*. Relatively few pyrotechnic compositions are formulated for the sole or even primary purpose of producing thermal energy. For example, in this chapter the compositions are intended to produce colored flame. In that case, while thermal energy production is necessary, in addition to the pyrogen, a number of other chemical components (additives) must be present to produce the colored light. Accordingly, in addition to its ability to produce thermal energy, the choice of the pyrogen must be such that it does not otherwise interfere with the chemistry of colored light production.

Given the central role of pyrotechnic combustion reactions in the production of colored flames, it is appropriate to consider briefly how the heat energy of combustion is produced and why different fuels and oxidizers generate differing amounts of heat. When atoms come together to form molecules, chemical bonds form between the atoms, thus holding the atoms together as a molecule. It requires the input of energy to break chemical bonds, and energy is released when new chemical bonds form. Stronger bonds require more energy to break them, and more energy is released when strong bonds are formed. The strength of the chemical bond between atoms in a molecule depends on the type and number of atoms forming the molecule.

During a combustion reaction, first chemical bonds must be broken within the fuel and oxidizer, and then new bonds are formed within the reaction products. If heat is to be produced during a chemical reaction, then on average, the chemical bonds formed must be stronger than those broken. This is the case with pyrotechnic combustion; oxidizers and fuels have relatively weak chemical bonds as compared with the chemical bonds of the reaction products. Table 4 lists the most common pyrotechnic fuels and oxidizers used in colored flame formulations. When various combinations of fuels and oxidizers are used, different numbers of bonds will be broken and formed between different kinds of atoms. Thus it should be expected that different amounts of energy will be produced in the combustion reactions involving different fuels and oxidizers.

Table 4. Common Pyrotechnic Fuels and Oxidizers Used in Colored Flame Compositions.

Fuel	Formula
Aluminum	Al
Lactose	$C_{12}H_{22}O_{11}$
Magnesium	Mg
Magnalium (alloy)	Mg/Al
Red gum (Accroides)	$C_6H_6O_{2.6}$ [(a)]
Shellac	$C_6H_{9.6}O_{1.6}$ [(a)]
Sulfur	S

a) From reference 39.

Oxidizer	Formula
Ammonium perchlorate	NH_4ClO_4
Barium chlorate	$Ba(ClO_3)_2$
Barium nitrate	$Ba(NO_3)_2$
Potassium chlorate	$KClO_3$
Potassium nitrate	KNO_3
Potassium perchlorate	$KClO_4$
Sodium nitrate	$NaNO_3$
Strontium nitrate	$Sr(NO_3)_2$

The energy released by some common oxidizers upon their reacting with carbon to produce carbon dioxide (CO_2) is listed in Table 5, where the unit kJ/g_{ox} (kilojoule per gram of oxidizer) is used as a measure of the thermal energy produced in the reaction (called *enthalpy of reaction*). The oxidizers have been divided into high energy and low energy groups, wherein the high energy oxidizers (perchlorates and chlorates) produce approximately twice the energy per gram, as compared with the low energy oxidizers (nitrates). It may be of interest to note that ammonium perchlorate and potassium perchlorate produce more thermal energy than potassium chlorate. This is typically true and is not an isolated result caused by using carbon as the fuel. For the most part, this is the result of perchlorates containing one additional oxygen atom per formula unit, in comparison with potassium chlorate. This additional oxygen atom is available to form an additional strong bond with a carbon atom, thereby releasing more energy. The result is that perchlorates are the more potent generator of heat energy. This may seem to contradict the common experience with formulations using potassium chlorate, which tend to burn more violently than similar formulations using potassium perchlorate. While these observations are accurate, this is not the result of potassium chlorate being the better heat producer.

Table 5. Enthalpy of Reaction for Various Oxidizers Reacting with Carbon.

Oxidizer	Enthalpy of Reaction (kJ/g_{ox}) [(a,b)]
Ammonium perchlorate	–6.1
Potassium perchlorate	–5.7
Potassium chlorate	–5.1
Strontium nitrate	–2.8
Barium nitrate	–2.1
Potassium nitrate	–1.8

To convert from kJ/g to kcal/g, divide by 4.18.

a) These results were calculated using data published in reference 41 and assuming carbon dioxide was the product. Note that negative values indicate that heat was produced in the reaction.

b) Enthalpy of Reaction was formerly called Heat of Reaction.

The energy released by some common fuels upon their reaction with oxygen are listed in Table 6. Again it is possible to divide the list in terms of energy production, with the combustion of metal fuels producing greater thermal energy than the non-metal fuels listed.

Table 6. Enthalpy of Combustion for Various Fuels Reacting with Oxygen.

Fuel	Enthalpy of Combustion (kJ/g_{fuel})(a,b)
Aluminum	–31
Magnalium	–27(c)
Magnesium	–25
Red gum	–22
Lactose	–16
Sulfur	–9

To convert from kJ/g to kcal/g, divide by 4.18.

a) These results were calculated using data published in references 40 and 41. Note that negative values indicate that heat was produced in the reaction.

b) Enthalpy of Reaction was formerly called Heat of Reaction.

c) This value was estimated.

Considering Tables 5 and 6, it is apparent that the choice of fuel and oxidizer for the pyrogen can have a large effect on the amount of thermal energy produced. Flame temperatures are a function of the amount of energy released in a pyrotechnic chemical reaction. All else being equal, the more thermal energy that is produced, the higher the flame temperature will be. Table 7 is a compilation of maximum flame temperatures produced by a collection of oxidizers reacting with shellac. Note that the order of flame temperatures produced by the oxidizers follows the same general order as the amount of energy produced when they are reacted with carbon (listed in Table 5). Similarly, while the published data do not facilitate a direct comparison, it is apparent that the use of metal fuels can result in significantly higher flame temperatures.[7b]

Table 7. Maximum Flame Temperatures of Oxidizers Reacting with Shellac.[7b]

Oxidizer	Ox. (%)	Fuel (%)	Flame Temp. (°C)(a)
Potassium perchlorate	74	16	2250
Ammonium perchlorate	76	14	2210
Potassium chlorate	77	13	2180
Potassium nitrate	72	18	1700

a) Temperatures are rounded to the nearest 10 °C.

Note: All mixtures contained 10% $Na_2C_2O_4$ to allow for measurement of flame temperature.

Color Generating Chemical Species and Their Production

Table 8 is a list of metals commonly associated with the production of colored pyrotechnic flames. Also included are the chemical species actually responsible for the emitted color. Note that in all cases except sodium, it is molecular compounds (not the metal atoms) that are the color generating species. Consider the red emissions from strontium, the color generating species are strontium monochloride ($SrCl^\bullet_{(g)}$) and strontium monohydroxide ($SrOH^\bullet_{(g)}$). Not only do strontium atoms not produce red light, they also potentially interfere with the production of intensely colored red flames; strontium atoms emit violet-blue light. Note also that both strontium **mono**chloride and strontium **mono**hydroxide are not combined in the normally expected (1 to 2) ratios of strontium chloride ($SrCl_2$) and strontium hydroxide ($Sr(OH)_2$).

The strontium monochloride and strontium monohydroxide color species are individual *free radical* molecular species (a single strontium atom combined with a single chlorine atom or a single hydroxide unit) that exist in the vapor state (as a gas). (Free radical is the term generally applied to an atom or group of atoms in an arrangement that results in there being an unpaired electron in the atom or molecule. The presence of the unpaired electron normally results in free radicals being especially reactive chemically. The superscript dot symbol "$^\bullet$" is used to indicate that something is a free radical.) That strontium monochloride and strontium monohydroxide are molecular free radicals in the vapor state is in strong contrast with strontium chloride and strontium hydroxide, which are ionic compounds [assemblages of tremendous numbers of strontium (2+) ions combined with twice that num-

Table 8. List of Metals Commonly Used to Generate Colored Pyrotechnic Flames.

Element	Color Generating Species	Color	Dominant Wavelength (nm)(a)	Purity (%)(b)
Strontium	$SrCl^\bullet_{(g)}$	Red	636	100
	$SrOH^\bullet_{(g)}$	Red orange	614	100
Barium	$BaCl^\bullet_{(g)}$	Green	522	96
	$BaOH^\bullet_{(g)}$	Green	507(c)	80
Copper	$CuCl^\bullet_{(g)}$	Violet-blue	465	88
	$CuOH^\bullet_{(g)}$	Yellowish-green	548	92
Calcium	$CaOH^\bullet_{(g)}$	Reddish-orange	600	100
	$CaCl^\bullet_{(g)}$	Reddish-orange	609	100
Sodium	Na (atoms)	Orange	589	100

a) Data from reference 31, based on the CIE 2° chromaticity diagram.

b) Purity is to the nearest 2%.

c) BaOH is a relatively weak emitter in comparison with the other species.

ber of chloride (1–) ions or hydroxide (1–) ions] existing in the solid or liquid states.

Because all of the emitting species in Table 8, with the exception of sodium, are molecules, they emit band spectra. More importantly, their spectra consist of a series of bands that generally span a substantial range of wavelengths. For example, Figure 40 presents the spectra from the monochlorides of strontium, barium and copper. Table 9 is a compilation of the observed spectral bands for the emitters listed in Table 8. Figure 41 is a chromaticity diagram showing the location of the color points for each of the color species listed in Table 8. Because of the range of their spectral emissions, the color species constitute composite colors that are described in terms of their dominant wavelength and purity (see the last two columns of Table 8).

In the past, some have suggested that the monochlorides were plus one molecular ions and not free radicals (neutral species). However, the neutral character of these species has been confirmed.[32]

Unfortunately the *color species* listed in Table 8 are not the *color agents* that are used in colored flame compositions. For example, the source of strontium is usually strontium carbonate or strontium nitrate. For the most part, the reason for this is simple, the color emitting molecules—strontium monochloride and strontium monohydroxide—do not exist at room temperature, so they cannot be used in a formulation. Further, the use of strontium chloride and strontium hydroxide as starting chemicals is impractical because they are far too hygroscopic for general use. Table 10 is a listing of the most common color agents used in pyrotechnics.

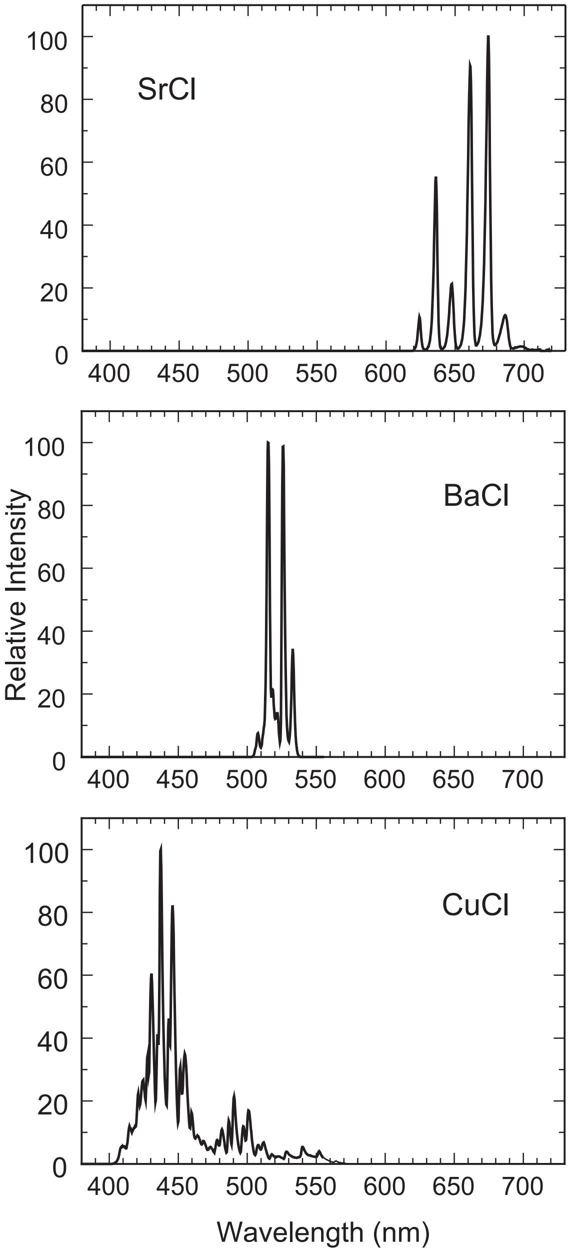


Figure 40. Spectral emissions of the monochlorides of strontium, barium and copper.[31] (The Y-axes are relative intensity.)

Table 9. Spectral Bands for the Emitting Species Listed in Table 8.[31]

W. L.(a)	R. I.(b)	W. L.(a)	R. I.(b)
SrCl		**BaOH (cont.)**	
624	11	513	100
636	55	524	86
648	21	745	47
661	90	488	72
674	100	502	30
687	11	513	100
700	1	524	86
SrOH		745	47
606	59	**CuCl**	
620	2	412	6
626	2	415	12
649	13	419	12
659	33	421	22
671	70	426	27
682	100	428	35
707	9	431	61
722	1	435	41
CaCl		436	100
581	3	443	46
593	45	446	82
605	11	449	31
608	14	452	35
619	99	460	16
621	100	465	9
633	9	469	7
635	8	476	5
CaOH		479	7
555	45	482	11
572	1	485	13
594	7	489	21
600	11	496	12
604	14	498	17
625	100	509	6
645	10	512	6
665	1	515	3
BaCl		526	4
507	8	538	5
514	100	552	4
517	21	**CuOH**	
521	14	505	46
524	99	512	44
532	34	524	75
BaOH		533	84
488	72	546	100
502	30	605	10

(a) W. L. is wavelength to the nearest nanometer.

(b) R. I. is relative intensity normalized to 100 for the strongest peak.

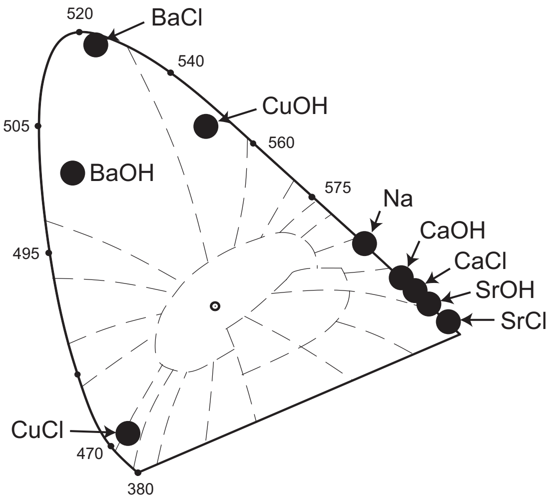


Figure 41. Location of the color points for the color species listed in Table 8.[31]

Table 10. List of Color Agents Commonly Used in Pyrotechnic Compositions.

Color	Color Agent	Formula
Red	Strontium carbonate	$SrCO_3$
	Strontium nitrate	$Sr(NO_3)_2$
	Strontium oxalate	SrC_2O_4
	Strontium sulfate	$SrSO_4$
Green	Barium carbonate	$BaCO_3$
	Barium nitrate	$Ba(NO_3)_2$
	Barium sulfate	$BaSO_4$
Blue	Copper(I) chloride	$CuCl$
	Copper(II) carbonate	$CuCO_3$
	Copper(II) oxide	CuO
	Copper(II) oxychloride	$CuCl_2O \cdot 3Cu(OH)_2$
Orange	Calcium carbonate	$CaCO_3$
	Calcium oxalate	CaC_2O_4
	Calcium sulfate	$CaSO_4$
Yellow	Cryolite	Na_3AlF_6
	Sodium nitrate	$NaNO_3$
	Sodium oxalate	$Na_2C_2O_4$

As a practical matter, it is necessary to create the actual color generating molecules within the pyrotechnic flame. In general, the first step in this process is to break apart the color agent. Then, by providing a source of the proper nonmetal atoms or atom groups, the desired chemical species may be formed. This is discussed in more detail for red colored flames in the next section of this chapter.

Red Colored Flame Chemistry

This discussion of red colored flame chemistry lies somewhere between fact and plausible speculation. This is because some details of the production of the red color emitting molecules has not been rigorously proven, and in other cases the actual chemistry is more complicated than can be represented in simple chemical equations. The reason such an explanation has been included is that it is reasonably correct and sufficiently thorough to be used as a basis for understanding how and why adjustments to formulations can be expected to affect red flame color.

The likely process of producing the color species for red flames[37b] can be represented as described in equations 5 through 8:

$$SrCO_{3(s)} \rightarrow SrO_{(s)} + CO_{2(g)} \qquad (5)$$

$$SrO_{(s)} + HX_{(g)} \rightarrow SrOH^{\bullet}_{(g)} + X^{\bullet}_{(g)} \qquad (6)$$

where HX is water, a hydrocarbon, an alcohol, etc. Then if a source of chlorine atoms is available, the monochloride can be produced:

$$SrOH^{\bullet}_{(g)} + Cl^{\bullet}_{(g)} \rightarrow SrCl^{\bullet}_{(g)} + OH^{\bullet}_{(g)} \qquad (7)$$

As an alternative to equation 7, if the species HX in equation 6 is hydrogen chloride, the monochloride may form directly from strontium oxide:

$$SrO_{(s)} + HCl_{(g)} \rightarrow SrCl^{\bullet}_{(g)} + OH^{\bullet}_{(g)} \qquad (8)$$

Essentially all pyrotechnic compositions contain at least one carbohydrate (e.g., dextrin or starch) and other ingredients that burn to produce water vapor as a product. For example, equation 9 shows potassium perchlorate reacting with dextrin.

$$3\ KClO_4 + C_6H_{10}O_5 \rightarrow 3\ KCl + 6\ CO_2 + 5\ H_2O \qquad (9)$$

Accordingly, with the availability of water vapor in a flame, the production of strontium monohydroxide in colored flames is no problem (eq 6). However, it is necessary to consider the potential sources of chlorine atoms and hydrogen chloride molecules (in eqs 7 and 8). This is especially important because generally the monochlorides are the preferred color emitting species (the dominant wave length is 636 nm for strontium monochloride rather than 614 nm for the monohydroxide). Chlorine is present in the most common colored flame oxidizers (in the chlorates and perchlorates); however, this is generally not considered a sufficiently effective source of chlorine atoms for use in producing strontium monochloride. To see why, consider the following two possible equations for potassium perchlorate reacting with carbon:

$$KClO_4 + 2\ C \rightarrow KCl + 2\ CO_2 + 5.8\ kJ/g_{ox} \qquad (10)$$

$$4\ KClO_4 + 7\ C \rightarrow 2\ K_2O + 7\ CO_2 + 4\ Cl^{\bullet} + 2.2\ kJ/g_{ox} \qquad (11)$$

Equation 10 produces no free chlorine, but equation 11 does. Competing chemical reactions proceed along the path that provides the greatest overall reduction in *free energy*. (A discussion of free energy is beyond the scope of this chapter.) All else being equal—including entropy changes—this amounts to saying that competing chemical reactions tend to favor the one(s) that produce the most energy. Thus equation 10, with its production of 5.8 kilojoules per gram of oxidizer (kJ/g_{ox}), will tend to predominate over equation 11 with only 2.2 kJ/g_{ox} of thermal energy released. As a result, the production of free chlorine atoms from the reaction of potassium perchlorate with carbon (or other common fuels) will be minimal.

It is possible to produce chlorine gas from the reaction of chlorate oxidizers with sulfur:[38a]

$$2\ KClO_3 + 2\ S \rightarrow K_2SO_4 + SO_2 + Cl_{2(g)} \qquad (12)$$

However, while this method was apparently used in the distant past,[42] today the extreme sensitiveness of the combination of a chlorate with sulfur is considered far too dangerous to be practical.[43-47]

Today the most common method of supplying chlorine or hydrogen chloride in colored pyrotechnic flames is through the use of a *chlorine donor*, sometimes also called a *color enhancer*. This is a chlorine rich chemical compound such as hexachlorobenzene (HCB) or polyvinyl chloride (PVC) that reacts in the flame to release chlorine or hydrogen chloride, such as suggested in equations 13 and 14, respectively.

$$C_6Cl_6 + 3\ KClO_4 \rightarrow 3\ KCl + 6\ CO_2 + 6\ Cl^{\bullet} \qquad (13)$$

$$4\,(\text{–}CH_2CHCl\text{–}) + 5\,KClO_4 \rightarrow 5\,KCl + 8\,CO_2 + 4\,H_2O + 4\,HCl \quad (14)$$

Table 11 is a list of the most common chlorine donors, along with their percent chlorine by weight. Benzene hexachloride (BHC) and PVC have been identified as producing hydrogen chloride rather then chlorine,[8a] and it is suspected that the other hydrogen containing chlorine donors (Saran® resin, Parlon® and Chlorowax®) also produce hydrogen chloride upon burning. Calomel was probably the first chlorine donor but has not been commonly used for at least 40 years, because of its low percentage of chlorine and toxicity concerns.

Table 11. List of Common Chlorine and Hydrogen Chloride Donors.

Chlorine Donor	Formula	Chlorine (wt. %)
Dechlorane(a)	$C_{10}Cl_{12}$	78
HCB (hexachlorobenzene)(b)	C_6Cl_6	74
Saran® resin	$(C_2H_2Cl_2)_n$	73
BHC (benzene hexachloride)(b)	$C_6H_6Cl_6$	73
Parlon®	$(C_{10}H_{11}Cl_7)_n$	66
Chlorowax®	variable	40–70
PVC (polyvinyl chloride)	$(C_2H_3Cl)_n$	57
Calomel (mercury(I) chloride)	Hg_2Cl_2	15

a) Dechlorane is an especially poor fuel.

b) HCB and BHC are suspected carcinogens. (Benzene hexachloride is more correctly termed hexachloro-cyclohexane.)

An additional commonly used method to produce hydrogen chloride in pyrotechnic flames is through the use of ammonium perchlorate as the oxidizer. This is illustrated by its decomposition reaction.[8a]

$$2\,NH_4ClO_4 \rightarrow N_2 + 3\,H_2O + 2.5\,O_2 + 2\,HCl \quad (15)$$

As a summary of the discussion thus far, high purity red light can be produced as suggested in the following somewhat simplified series of chemical equations. (In the equations that follow, heat has been included for those reactions in which the production or consumption of thermal energy is an important consideration.) First a source of thermal energy is needed, such as from the reaction of potassium perchlorate with red gum (eq 16). The heat produced is used in part to decompose the strontium carbonate to strontium oxide (eq 17), which can then react with some of the water vapor produced in equation 16, to produce strontium monohydroxide (eq 18). In turn the strontium monohydroxide can be converted to the monochloride if a source of chlorine atoms is provided (eq 19). Having now formed the preferred color species, if there is sufficient thermal energy available in the flame, the strontium monochloride molecules can reach an excited electron state (eq 20), which when it de-excites, produces the red light photons being sought (eq 21).

$$3.1\,KClO_{4(s)} + C_6H_6O_{2.6(s)} \rightarrow 3.1\,KCl_{(s)} + 6\,CO_{2(g)} + 3\,H_2O_{(g)} + \text{Heat} \quad (16)$$

$$SrCO_{3(s)} + \text{Heat} \rightarrow SrO_{(s)} + CO_{2(g)} \quad (17)$$

$$SrO_{(s)} + H_2O_{(g)} + \text{Heat} \rightarrow SrOH^{\bullet}_{(g)} + OH^{\bullet}_{(g)} \quad (18)$$

$$SrOH^{\bullet}_{(g)} + Cl^{\bullet}_{(g)} \rightarrow SrCl^{\bullet}_{(g)} + OH^{\bullet}_{(g)} \quad (19)$$

$$SrCl^{\bullet}_{(g)} + \text{Heat} \rightarrow SrCl^{\bullet}_{(g)}{}^{*} \quad (20)$$

$$SrCl^{\bullet}_{(g)}{}^{*} \rightarrow SrCl^{\bullet}_{(g)} + \text{Photon}_{[636\text{ nm}]} \quad (21)$$

There is another slightly different way in which colored light can be produced in pyrotechnics. It is possible for the color species to be produced already in an excited state, as opposed to their starting out in the ground state and having to use flame energy to reach the excited state as suggested in equation 20. This alternative process is called *chemiluminescence* and may be an especially important source of colored light production in some cases. (A proper discussion of chemulescence is beyond the scope of this chapter.)

If reality were as simple as suggested in equations 16 through 21, producing high purity colored flames would be quite easy. Unfortunately, there are a number of complicating factors, only some of which are illustrated in Figure 42. (Note that for clarity, most reactants and products for the chemical equations of Figure 42 have not been included.) The preferred red emitting color species ($SrCl^{\bullet}_{(g)}$) is located

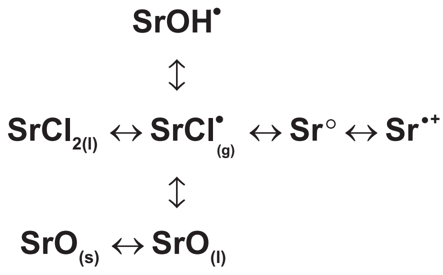


Figure 42. A representation of some of the possible reactions for strontium monochloride in a flame (based on reference 4a).
NOTE: To simplify the figure, most reactants and products are not explicitly shown.

near the center of the figure. All of the other chemical species shown there are undesirable (with the possible exception of strontium monohydroxide). The double headed arrows are used to indicate that these chemical reactions are reversible (i.e., the reactions can go either way depending on the conditions in the flame at the time). Table 12 is a list of the detrimental effects produced by these undesirable species. Moving to the left from strontium monochloride, if the temperature of the flame falls, condensed (liquid) strontium chloride droplets can form to produce continuous spectra from incandescence. This has the effect of reducing the purity of the red color as the resulting composite color point moves toward ICI white in the chromaticity diagram. Moving upward in Figure 42, it is possible that the monochloride will react with water vapor in the flame to form the monohydroxide. This is the least detrimental effect; however, the photons produced by the monohydroxide are perceived as slightly reddish-orange (614 nm) in color rather than the red of the monochloride (636 nm). Moving downward, it is possible that the monochloride will react with oxygen in the flame to form strontium oxide, which produces photons perceived as orange in color. Further, if the flame temperature is reduced, the strontium oxide can condense to produce continuous emissions from incandescence. Moving to the right in Figure 42, if the flame temperature rises too high, the monochloride will decompose with the resulting strontium atoms producing emissions perceived as violet-blue in color. Further, the strontium atoms can ionize to produce violet emissions from the excitation of the ion, plus continuous emissions from ion recombination. (Note that at the temperature of colored flames the predominant charge state of strontium ions will only be one plus and not two plus.)

Table 12. Undesirable Strontium Flame Species and Their Detrimental Effects

Species	Detrimental Emissions
$SrCl_{2(l)}$	Continuous spectrum
$SrOH^{\bullet}$	Reddish-orange
$SrO_{(g)}$	Orange
$SrO_{(l)}$ or $_{(s)}$	Continuous spectrum
Sr^{0} (atom)	Violet-blue
$Sr^{\bullet+}$ (ion)	Violet & continuous spectrum

As can be seen from Figure 42, even after one is successful in producing the desired color species, there is much that can still go wrong. Unfortunately, there is even more that can go wrong in the process of producing the desired color species. To avoid the production of those chemical species that seriously reduce color quality and to optimize the production of useful species, it is necessary to attempt to fine tune (control) the reactions taking place in the flame.

Control of Red Flame Chemistry

As a result of the chemical equilibria prevailing in the flame, all the chemical species shown in Figure 42 (and many others) will be present to some extent in a strontium red flame. Fortunately it is possible to preferentially form more of the desirable color emitting species if Le Châtelier's Principle is thoughtfully applied. Le Châtelier's Principal can be stated as:

Chemical systems in equilibrium respond to a stress in a manner that tends to relieve the stress.

For the purpose of this text it is not necessary to understand fully what chemical equilibrium and stresses on reacting systems are. In its true sense, a pyrotechnic flame as a whole is not a system in chemical equilibrium; however, if a small enough region of the flame is considered over a short enough interval of time, that region—for that time—can be considered to be in equilibrium. A stress on a reacting system is just about anything that changes one or more of the conditions existing in the flame.

Perhaps some examples will make Le Châtelier's Principal and its application to colored flames more clear. First consider the very simple system of a container of ice water. The melting of the ice can be written as the chemical reaction:

$$H_2O_{(s)} + \text{Heat} \rightarrow H_2O_{(l)} \qquad (22)$$

where heat is shown as one of the reactants. The opposite of this reaction can also occur:

$$H_2O_{(l)} \rightarrow H_2O_{(s)} + \text{Heat} \qquad (23)$$

At a temperature of 0 °C both ice and water will be present and is a case of chemical equilibrium. The amount of ice and water present will seem to be constant and unchanging; it appears that nothing is happening. However, submicroscopically things will still be happening. Every instant many molecules of ice will consume heat to become liquid (eq 22), and at the same time and in an equal number, other water molecules will release energy to become solid (eq 23). In chemical equilibrium, it is not that nothing is happening, but rather opposite reactions are occurring at the same rate, so that only externally does it appear that nothing is happening. To make this point for chemical systems in equilibrium, often the single headed arrow in chemical equations will be replaced with a double headed arrow, such as used in equation 24 and Figure 42.

$$H_2O_{(s)} + \text{Heat} \leftrightarrow H_2O_{(l)} \qquad (24)$$

In equation 24, the addition or removal of heat would be a stress on the system in equilibrium, and Le Châtelier's Principal states that the system will respond in a way to relieve the stress. If heat is added, some of the ice would melt to produce more water and in the process consume the added heat. If heat is removed, some of the water would freeze to produce more ice and in the process release heat to replace the heat that was lost.

As a second example, consider again the excitation of electrons within a color species (eq 20) and the subsequent photon emission (eq 21). This operates in much the same way as the ice water example.

$$SrCl^{\bullet}_{(g)} + \text{Heat} \rightarrow SrCl^{\bullet}_{(g)}{}^{*} \qquad (20)$$

$$SrCl^{\bullet}_{(g)}{}^{*} \rightarrow SrCl^{\bullet}_{(g)} + \text{Photon}_{[636\text{ nm}]} \qquad (21)$$

For a given amount of the color species, if additional heat is supplied by the flame, Le Châtelier's Principal suggests that more of the strontium monochloride molecules will reach an excited state (eq 20), thus leading to increased photon emission as the molecules decay back to their ground states (eq 21). The amount of heat a flame can supply is a function of its temperature, generally with higher temperature flames possessing a greater ability to supply heat energy. Thus, all else being equal, higher temperature flames produce more photons and appear brighter to an observer. (In fact the relationship between flame temperature and its perceived brightness is not linear; relatively small changes in temperature can produce fairly large changes in brightness (recall the earlier discussion about Figures 38 and 39). Considering equations 20 and 21 further, if there is an ample amount of heat available in the flame, then increasing the amount of the color species is another stress that will also result in more strontium monochloride molecules reaching an excited state to produce a greater number of photons.

Considering equations 16 to 21 again in terms of Le Châtelier's Principal, it is possible to list some of those stresses (conditions) that might be applied to this chemical system that should act to favor the production of the desired photons. This will be those factors that encourage the reactions to proceed (i.e., shift the equilibrium to the right). In equation 17, providing additional strontium carbonate and heat would be favorable stresses to produce more strontium oxide. This additional heat can be produced using more potassium perchlorate and red gum in equation 16. Assuming there is a sufficient supply of strontium oxide, if more water vapor and heat are available in equation 18, more strontium monohydroxide will be produced. If more chlorine atoms are available in equation 19, then more of the monochloride could be produced. Finally, with additional thermal energy in equation 20, more of the strontium monochloride molecules would reach their excited electronic states. These favorable conditions are summarized in Table 13.

Table 13. A List of the Favorable Conditions for Producing Red Flame from Equations 16 through 20.

Favorable Conditions for Red Light Production	Eq.	Makes More
More SrCO_3 and Heat	17	$\text{SrO}_{(s)}$
More KClO_4 and Red Gum	16	Heat
More $\text{H}_2\text{O}_{(g)}$ and Heat	18	$\text{SrOH}_{(g)}$
More Chlorine Donor	19	$\text{SrCl}_{(g)}$
More Heat	20	$\text{SrCl}_{(g)}$*

While it may sound rather simple to provide the set of favorable conditions for the abundant production of red flame photons, there is at least one catch. You cannot supply proportionately more of one ingredient without at the same time providing less of all the others. For example, the only way to provide a greater percentage of strontium carbonate is to use lesser percentages of other ingredients. Thus it is not possible to simultaneously provide more strontium carbonate (eq 17), more potassium perchlorate and red gum (eq 16), and more chlorine donor (eq 19). Even more importantly, it is necessary to consider the competing (unfavorable) reactions producing detrimental species such as illustrated in Figure 42 and whose detrimental emissions were summarized in Table 12. Some of these unfavorable monochloride reactions are expressed more completely in equations 25 to 29, wherein heat and other reactants and products are explicitly shown.

$$\text{SrCl}^{\bullet}_{(g)} + \text{Cl}^{\bullet} \leftrightarrow \text{SrCl}_{2(l)} + \text{Heat} \tag{25}$$

$$\text{SrCl}^{\bullet}_{(g)} + \text{Heat} \leftrightarrow \text{Sr}_{(g)} + \text{Cl}^{\bullet} \tag{26}$$

$$\text{Sr}_{(g)} + \text{Heat} \leftrightarrow \text{Sr}^{+} + \text{e}^{-} \tag{27}$$

$$\text{SrCl}^{\bullet}_{(g)} + \text{H}_2\text{O}_{(g)} \leftrightarrow \text{SrOH}^{\bullet} + \text{HCl} \tag{28}$$

$$\text{SrCl}^{\bullet}_{(g)} + \text{O}^{\bullet} \leftrightarrow \text{SrO}_{(l)} + \text{Cl}^{\bullet} + \text{Heat} \tag{29}$$

Considering equations 25 to 29 in terms of Le Châtelier's Principal, the favorable conditions (stresses) are those that tend to limit the extent to which the reactions occur (i.e., shift the equilibrium toward the left). In equation 25, there will be a reduced tendency for the monochloride molecules to condense to form liquid droplets of strontium chloride, if the amount of available chlorine is reduced and if a high flame temperature is maintained. In equation 26, there will be a reduced tendency for the monochloride molecules to be lost by their decomposing, if the amount of available chlorine is increased and the flame temperature is reduced. Note that this is exactly the opposite pair of conditions that were favorable for equation 25. In equation 27, as strontium atoms become ionized, there will be a decrease in the number of strontium atoms to potentially recombine with chlorine atoms to reform the strontium monochloride (eq 26). Thus the favorable conditions for equation 27 are lower flame temperature and more free electrons in the flame. In equation 28, less strontium monochloride will be converted to the monohydroxide if less water vapor is present in the flame and more hydrogen chloride is available. To some extent this is self contradicting. The only way to have hydrogen chloride present is if the fuel (eq 16) and the chlorine donor contain hydrogen; yet if they contain hydrogen they will also produce water vapor in the flame. In equation 29, the loss of strontium monochloride because of the formation of strontium oxide, can be diminished by increasing flame temperature and to some extent by limiting the amount of oxygen in the flame (i.e., by using a fuel rich pyrogen in equation 16). However, again this is self contradicting. By using a fuel rich mixture (non-optimum fuel to oxidizer ratio) less heat would be produced, which means a lower flame temperature. Some of the favorable conditions for equations 25 to 29 are summarized in Table 14.

Table 14. A List of the Conditions for Losing Less Strontium Monochloride, from Equations 25 through 29.

Favorable Conditions for Red Light Production	Eq.
Less $\text{Cl}^{\bullet}$ and More Heat	25
More $\text{Cl}^{\bullet}$ and Less Heat	26
More e^{-} and Less Heat	27
More HCl and Less H_2O	28
Less O_2 and More Heat	29

Considering the many contradictions between and within Tables 13 and 14, it is obvious that there is no simple solution to optimizing the production of red light from strontium monochloride. However, difficult is not the same as impossible. First, it is possible is to make a series of adjustments to the pyrotechnic composition, each time seeking to optimize the color output. Second, and more importantly, it is possible to find alternatives that circumvent some of the potential problems. This will be discussed for strontium monochloride red flames in the next section.

Optimizing Red Flame Chemistry

There are two categories of approaches to optimizing colored flame chemistry; 1) things to adjust and 2) basic alternatives. When making adjustments, there is probably nothing to adjust for which more and more (or less and less) can be counted on to continue to make an improvement in flame color. The goal is to find the optimum adjustment, that for which the overall flame color quality is of the highest. This color is illustrated in Figure 43. (Note: Reference 30 presents the results of a series of experiments wherein the percent oxidizer and the percent chlorine donor were varied while noting the effect on color purity and dominant wavelength of the flames produced.)

One factor to consider adjusting is the amount of color agent used. Obviously, when no color agent is used, none of the desired color species can be produced. When more, but still too little, of the color agent is used, the amount of the desired color species produced will be quite low. While the flame may be bright because of a high flame temperature, the color will be faint because of too little of the color species. On the other hand, the decomposition and vaporization of the color agent requires thermal energy. When too much of the color agent is used, too much of the available thermal energy will be consumed in that process, which is reflected as a drop in flame temperature. Thus, in this case, even if an abundant amount of the color species is generated, the flame temperature will no longer be high enough to produce sufficient electron excitation. As a consequence, the flame will be too dim to be effective. This is summarized in the first line in Table 15. The optimum amount of color agent to use is the amount that produces an ample amount of the color species without seriously reducing flame temperature. Generally this must be determined by experimenting.

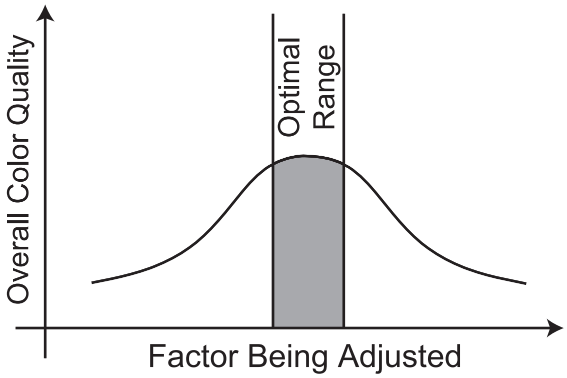


Figure 43. Illustration of the effect likely to be produced by adjusting colored flame formulations.

Table 15. Adjustments to Flame Chemistry to Optimize Color.

Factor Being Adjusted	Too Little or Too Low		Too Much or Too High	
	Effect Observed	Cause	Effect Observed	Cause
Amount of color agent	Color too faint	Too little color species produced	Flame too dim	Flame temperature too low
Amount of chlorine donor	Color too faint or too orange	Too little preferred color species produced	Flame too dim	Flame temperature too low
Fuel to oxidizer ratio	Small dim flame with reduced purity	Flame temperature low and $SrO_{(l\ or\ s)}$ forms	Large dim flame	Flame temperature too low
Flame temperature	Flame too dim	Too little energy for electron excitation	Color too weak	Color species are destroyed

A similar situation exists regarding the adjustment of the amount of chlorine donor used. With too little chlorine donor, too little of the most desirable color species (the monochloride) will be produced. While there is some potential for chlorine donors to act as fuels, they are generally poor fuels at best. Thus if a very large amount of chlorine donor is used, even if the amount of oxidizer is also increased, the total amount of thermal energy produced by the flame will be less. In turn the flame temperature will be reduced, which results in a dim flame. As when adjusting the amount of color agent, the optimum amount of chlorine donor is that which produces an ample amount of color species without causing too great a reduction in flame temperature. (See Table 15, Line 2.)

To some extent, the fuel to oxidizer ratio can be adjusted to improve the overall appearance of the flame. It is true that there is one ratio that results in the greatest release of thermal energy from the pyrogen. However, there is an additional effect worth considering. If the flame is slightly fuel rich, the flame envelope will expand somewhat because the chemical reaction of some of the fuel is delayed until sufficient atmospheric oxygen diffuses into the flame to react with the excess fuel. This larger flame envelope is thought to present a less harsh and more attractive appearance. On the other hand, an excess of oxidizer causes the flame envelope to shrink; the flame is generally thought to have a more harsh appearance plus there will be increased production of condensed strontium oxide, which will weaken flame color. (See Table 15, Line 3.)

Various combinations of fuels and oxidizers react to produce differing amounts of thermal energy (see Tables 5 and 6). Accordingly, flame temperature can be adjusted by choosing various combinations and mixtures of fuels and oxidizers. As noted above, when the flame temperature is too low, there is not sufficient energy available to excite the numbers of electrons in the color species needed to produce an ample amount of light. Generally it is thought that the flame temperature must exceed approximately 2000 °C to be effective as a source of colored light.[7b] (However, one study reporting on nitrate and non-metal fuel colored flames[14] suggests that this is not universally correct.) On the other extreme, excessively high flame temperatures are capable of supplying sufficient energy to decompose the color species, thus having the effect of producing a bright but faintly colored flame. (See Table 15, last line.)

While only so much can be done to adjust a given color formulation, this is not the full range of possibilities to produce improved flame color. Often there are alternate approaches that can be taken and which offer the possibility of substantially greater improvements in flame color. For example, color agents such as carbonates and oxalates require energy for their decomposition. This generally has the effect of limiting the amount of color agent that can be used to around 10 or 12% before the flame temperature falls too low to be effective. However, by using what might be called *double-duty* color agents, those that perform two functions, the amount of color agent used can be significantly greater without reducing flame temperature. Consider the use of strontium nitrate in the dual role of oxidizer and color agent:

$$\mathrm{Sr(NO_3)_2} + \text{Fuel} \rightarrow \mathrm{SrO} + \text{Oxidized Fuel} + \text{Heat} \quad (30)$$

In this case, the production of strontium oxide, which is used in the production of the monochloride color species (eq 18), generates heat. This is in strong contrast with it consuming heat as in equation 17.

As another example of a double-duty color agent, consider the use of strontium benzoate in the dual role of fuel and color agent:

$$\text{Oxidizer} + \mathrm{Sr(C_7H_5O_2)_2} \rightarrow \mathrm{SrO} + \text{Combustion Products} + \text{Heat} \quad (31)$$

Again, heat is generated collaterally with the production of strontium oxide. Because nitrates, as oxidizers, are not as effective as perchlorates, it will generally be necessary to use either a mixture of nitrate and perchlorate oxidizers or a fuel (or mixture of fuels) that is capable of producing more energy. (Generally, metal fuels produce the greatest amount of thermal energy (see Table 6).)

Most chlorine donors have some fuel value but it is generally significantly less than the primary fuel in the color formulation. Accordingly this puts a limit on the amount of chlorine donor that can be used before the flame temperature falls too low to be effective. One way to put more chlorine into the flame is to consider chlorine donors that contain a higher percentage of chlorine, see Table 11. However, even here there is probably a trade-off in that those chlorine donors with the highest amount of chlorine are likely the ones with the lowest fuel value. (Unfortunately this is not been well reported in the literature.) One way to compensate for using a larger amount of a chlorine donor that has a low fuel value is to use a fuel (or mixture of fuels) that is capable of producing more energy. Also, some chlorine donors (most notably, Parlon®) can double as the binder for a composition. While this can be effective in introducing a little more chlorine into a flame, there are some resultant operational difficulties. It is generally necessary to use solvents that are flammable, and the composition may be quite sticky, making it somewhat difficult to process.

After having chosen a double-duty color agent, and a chlorine donor with both a relatively high percentage of chlorine and a relatively good fuel value, there is still more that can be done. To facilitate the use of even more color agent and chlorine donor, while maintaining ample flame temperature, a relatively high percentage of metal fuel can be used. However, this can introduce some difficulties such as introducing incandescing metal oxide particles into the flame, the need to use non-aqueous binding, and difficulty with ignition. Nonetheless, it is possible to deal with these problems when necessary. (This is discussed later in this chapter.)

At this point in the discussion of red flame chemistry, it might be instructive to consider how the pyrotechnic formulations for red stars have changed over the years. Table 16 presents three formulations, the first being typical of those used around 1950. In this formulation, potassium chlorate is the oxidizer, there is a mixture of non-metal fuels, and strontium carbonate is the color agent. In this formulation there was neither an independent source of chlorine nor an effective way of effectively freeing it from potassium chlorate. Accordingly, the principal color species must have been strontium monohydroxide, with its less desirable orangish-red dominant wavelength.

Table 16. Various Red Star Formulations.

Approximate Date → Ingredient	1950	1975	1985
Potassium chlorate	66	—	—
Potassium perchlorate	—	66	—
Strontium nitrate	—	—	60
Strontium carbonate	11	12	—
Charcoal (fine)	11	2	—
Red gum (or shellac)	8	13	3
Magnalium (fine)	—	—	12
PVC	—	2	—
Parlon	—	—	25
Dextrin (or rice starch)	4	5	—
Reference	48	8c	9

The formulation that dates to around 1975 replaced potassium chlorate with the safer perchlorate alternative and added a small amount of polyvinyl chloride as a source of chlorine. While it is likely that the emissions of strontium monohydroxide still would predominate in the flame, the additional contributions from the monochloride must have shifted the dominant wavelength somewhat farther into the red.

The formulation starting to be widely used by about 1985 (at least in high level fireworks competitions) makes some important improvements. First is the use of strontium nitrate as a "double duty" oxidizer. This has the effect of introducing about four times the amount of strontium into the flame. However, because nitrates on their own do not produce a sufficiently high flame temperature to generate bright flames, magnalium (magnesium–aluminum alloy) with its high enthalpy of combustion was used as the primary fuel. The Parlon® also had multiple functions; most importantly it is the chlorine donor (probably actually a hydrogen chloride donor), but it is also a secondary fuel and the binder. By using the chlorine donor in more that one capacity, much more of it could be incorporated into the formulation; in this case providing about 15 times more chlorine than the 1975 formulation. The net result of these improvements is that the dominant flame emissions must be from strontium monochloride and the high flame temperature must make the flame brighter.

The most recent developments[19,21] in red flame formulations have made further improvements in the dominant wavelength and purity. Much of the improvement is probably the result of eliminating incandescing reaction products from the flame (mostly resulting from eliminating the use of the metal fuel present in the 1985 formulation). (The potential problems with using metal fuels is discussed later in this chapter.) While a proper discussion of these recent colored flame developments is beyond the scope of this chapter, it might be interesting to compare the spectra of one of the "best-yet" red flames with what is probably the best that is theoretically possible, a pure strontium monochloride spectrum, see Figure 44. Note that the predominant peaks in the star spectrum are the emissions from strontium monochloride. However, the star spectrum has a series of minor peaks in the range from approximately 590 to 620 nm, which would be perceived as being orange. The effect is that the dominant wavelength of the star is shifted slightly toward the orange as compared with the monochloride spectrum. In the red star spectrum, the most significant interfering contributions come from sodium present as an impurity (at 590 nm), strontium monohydroxide bands (most prominently at 606 nm), and calcium present as an impurity (most prominently at 593, 619, and 621 nm).

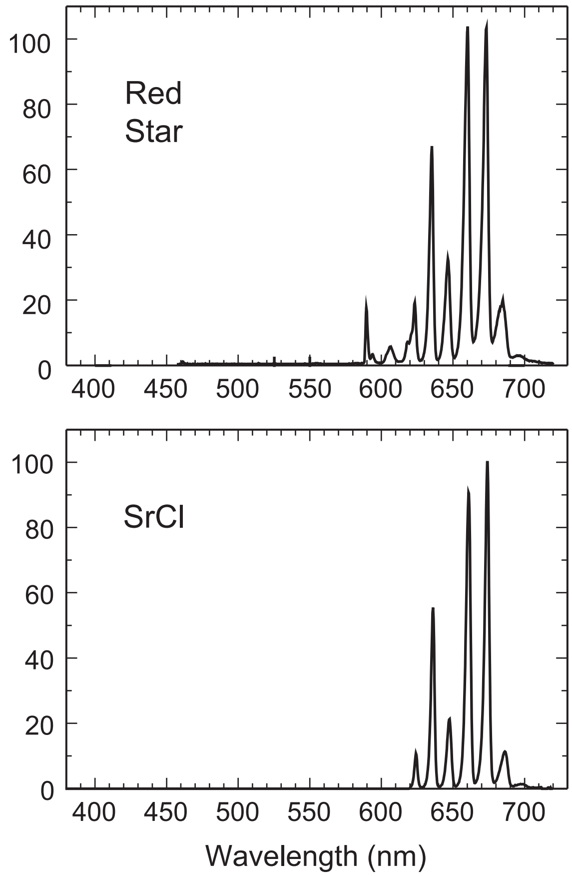


Figure 44. A comparison of the spectrum from a very high quality red star with that solely from strontium monochloride. (The Y-axes are relative intensity.)

Sodium is such a powerful emitter that even in near trace quantities it will be visible in star spectra. Considering that commercially produced colored flame compositions are made using technical grade chemicals, it is probably fortunate that the amount of sodium present as an impurity can be described as a near trace quantity. While a trace amount of sodium is expected in most of the non-metal components of a formulation, the oxidizer, which is present in the largest amount, is generally the largest contributor of sodium. In the red star spectrum, it is clear that the monochloride predominates, yet a small amount of the monohydroxide remains and is presumably unavoidable since the star formulation includes components that contain hydrogen. Calcium impurities are present presumably because it is in the same chemical group (family) as strontium, which means they both have very similar chemical properties. Accordingly, technical grade strontium chemicals are likely to contain a small amount of calcium as well.

Green and Orange Colored Flame Chemistry

Fortunately, the discussion of green and orange colored flame chemistry can be rather brief. This is because: 1) the monohydroxides and monochlorides of barium and calcium are the dominant green and orange color species, and 2) barium and calcium are in the same chemical group (family) as strontium. Virtually everything that was said about strontium red flames and about controlling red flame chemistry applies equally to barium green and calcium orange flames, and thus does not need to be said again. This section will be devoted to those few things that are different.

For barium green flames the monochloride is the preferred emitter. However, unlike strontium, the reason is not that its dominant wavelength is better. The emissions from the barium monohydroxide (507 nm) are actually somewhat more favorably located in the green color region of the chromaticity diagram than are those of the monochloride (522 nm). (However, barium monohydroxide emissions are a little lower purity than are those of barium monochloride, see Figure 41.) The main reason the monochloride is preferred is that the monohydroxide is quite a weak emitter by comparison. The difficulty with trying to use the monohydroxide as the principal emitter is that it has overwhelming difficulty competing with other interfering emissions from the flame. This has the effect of a devastating reduction of purity for the composite flame emissions. The upper spectrum in Figure 45 is from one of the "best-yet" green formulations. Note that the problem in this case is the relatively strong interfering emissions between approximately 590 and 620 nm, originating from atomic sodium (590 nm) and calcium monochloride (593 to 621 nm). In addition, there are minor interferences from the strontium monochloride (636 to 674 nm). If these impurities (especially the sodium and calcium) were scrupulously eliminated, the color would be favorably shifted toward the center of the green area of the chromaticity diagram, and the purity would be significantly increased.

For calcium orange flames, the monohydroxide is the preferred color species. This is because its dominant wavelength (600 nm) is closer to that which is perceived as orange than are those from the monochloride (dominant wave length, 609 nm). To favor the production of calcium monohydroxide, a formulation should contain no chlorine donor and should have fuels containing an abundance of hydrogen. However, even after maximizing the production of the monohydroxide, the emissions of a calcium orange composition will still appear reddish-orange. There is, however, a way to make an orange colored flame formulation whose emissions are perceived as orange, and which can be easily adjusted to accommodate producing the entire range of colors from reddish-orange to yellowish-orange[13] and beyond. The basis for this method is illustrated in Figure 46. In this case a colored flame composition is formulated to produce both strontium monohydroxide and atomic sodium as the color species. Then by adjusting the ratio of the strontium and sodium color agents, any of the colors between the two color points shown in Figure 46 can be produced. A slight modification of this approach is shown in the orange flame spectrum of Figure 47. Here the two color species used are the monochlorides of calcium and barium (with atomic sodium only present as an impurity). Using this colored flame formulation and adjusting the ratio of calcium to barium, the range of colors produced can be extended beyond orange, to yellow and yellowish-green.

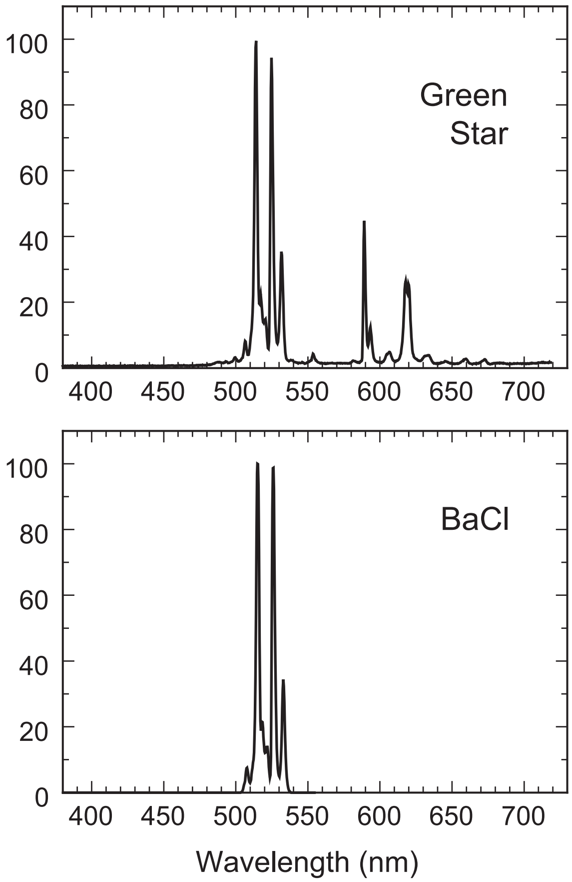


Figure 45. A comparison of the spectrum from a high quality green star with that from barium monochloride. (The Y-axes are relative intensity.)

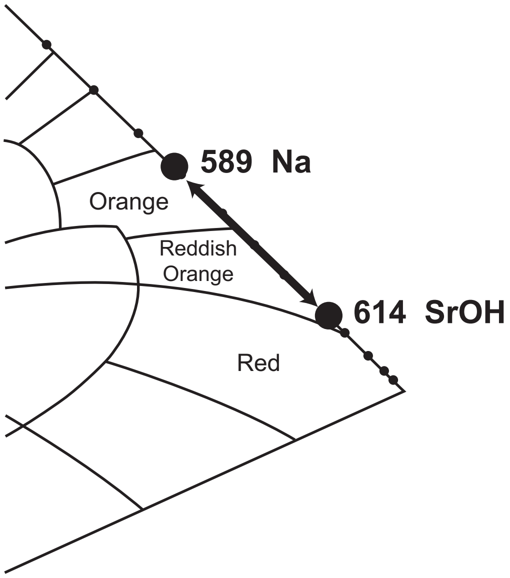


Figure 46. An illustration of the production of a range of orange colors by mixing strontium monohydroxide and sodium emissions.

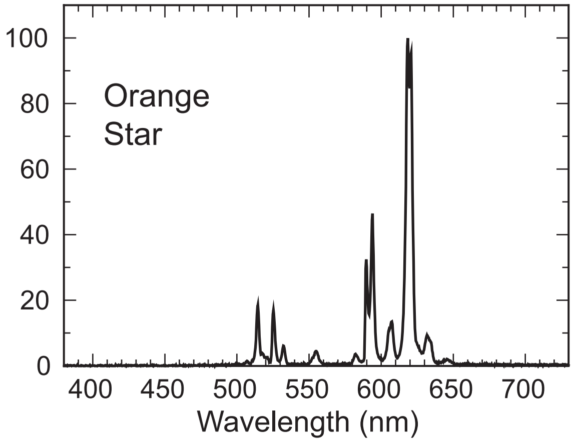


Figure 47. The spectrum of a star perceived as orange, by mixing the emissions of the monochlorides of calcium and barium. (The Y-axis is the relative intensity.)

Yellow Colored Flame Chemistry

Sodium is the only atomic color species commonly used in pyrotechnic colored flames. Its principal emissions are a pair of lines that are so close together (589.0 and 589.6 nm) that the most common types of spectrometer used in pyrotechnic research are not able to resolve them into two peaks. Thus when sodium emissions are seen in the spectra of this chapter, they appear as a single peak. Unlike what is commonly believed, sodium atoms—emitting at 590 nm—actually produce orange light. (Light perceived as relatively pure yellow will have a wavelength in the narrow range from approximately 576 to 580 nm, see Figure 22.)

In reviewing published yellow flame formulations, it seems that three different approaches are taken regarding the orange versus yellow issue. The first approach is to simply ignore the matter and have "yellow" stars that produce mostly orange light. (It might be of interest to point out that some virtually identical formulations have been described in the literature as both "yellow" and "amber" color producing compositions.[49]) The second approach is to add a source of continuous emissions to the flame. This reduces the purity of sodium's orange emissions, so that it may more nearly be perceived as yellow. One way to add a source of continuous emissions is to use a metal fuel under conditions that produce incandescent metal oxide particles in the flame. Also, the continuous emissions from the incandescence of some metals (e.g., aluminum) can have their dominant incandescent wavelength appear yellow.[7a] Another way to add a source of continuous emission is to use a moderate amount of sodium (>5% atomic sodium) and raise the flame temperature to above 2230 °C. This will cause the production of a resonance line continuum ranging from approximately 570 to 610 nm.[7b] The third, and certainly the best, approach is to add a barium compound, typically barium nitrate, to the sodium yellow composition. This is the only truly effective way to shift the color produced by sodium to a true yellow of high purity. This would be accomplished using much the same method as was discussed for orange flame color.

Before leaving the subject of sodium yellow flames, two potential problems need to be addressed. The first is hygroscopicity, the tendency for a chemical to draw moisture from the air. Many sodium compounds are too hygroscopic for general use, two examples are sodium nitrate and sodium chlorate. A better choice is sodium oxalate, and probably the best choice is cryolite (sodium fluoroaluminate).

The other problem for sodium yellow flame compositions is the potential for adverse chemical reactions between soluble sodium compounds and magnesium or magnalium that could potentially result in spontaneous ignition of damp compositions. One solution to both problems (hygroscopicity and adverse chemical reactions) can be the use of nonaqueous binding.

Blue and Purple Colored Flame Chemistry

Copper is not in the same chemical group as strontium, nonetheless, the flame chemistry of copper is similar to that of strontium. Accordingly, only those few relevant differences will be discussed in this section.

Blue flame color is reputed to be the most difficult color to produce, and based on the purity and dominant wavelength of the "best-yet" blue flame formulations, this is true (see Table 3). The only common blue emitting color species is copper monochloride (465 nm). The emissions of copper monohydroxide (548 nm) are perceived as green. Further, even the pure spectrum of copper monochloride only has a purity of 88% and it has a dominant wavelength that is perceived as violet-blue and not blue. The reason for the relatively low purity can be seen in the copper monochloride spectrum in Figure 48. In addition to the collection of bands from approximately 400 to 480 nm (perceived as violet-blue through blue), there are emissions that range from approximately 480 to 560 nm (perceived as greenish-blue through greenish-yellow). Although these detrimental monochloride bands are not strong, they are sufficient to significantly weaken the overall purity of the copper monochloride emissions (possibly see again Figure 32).

In comparing the spectra of a "best-yet" blue star and copper monochloride, three things are most noticeable: first is the presence of the sodium peak (590 nm), second is a continuum extending throughout the longer wavelength region (from at least 480 to 730 nm) and third is the presence of minor contributions from calcium (near 610 and 620 nm). All three of these features have the effect of reducing the purity of the composite color by drawing it toward white.

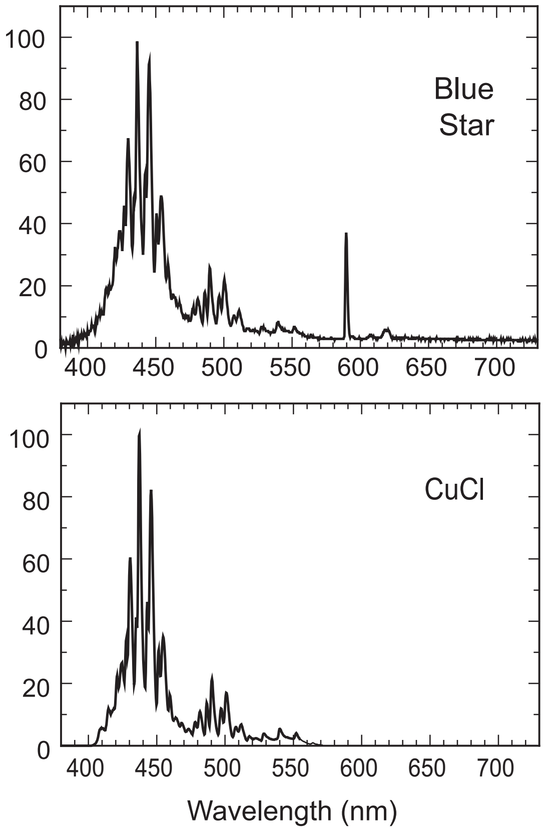


Figure 48. A comparison of the spectrum from a high quality blue star with that from copper monochloride.
(The Y-axes are relative intensity.)

It had once been suggested by the authors that a small contribution from the yellowish-green emissions of copper monohydroxide, might actually be useful in producing a flame color that is more nearly blue rather than violet blue. This argument is illustrated in Figure 49. Here the spectral emissions of the collection of copper monochloride bands produces the color point in the lower left of the chromaticity diagram, while those of the monohydroxide produce the color point near the top of the diagram. If approximately 10% of the emissions originate with copper monohydroxide, the composite color point will shift position. It will move from the violet-blue area of the chromaticity diagram, into the blue region. Although it is true that the shift in dominant wavelength is an improvement, it is somewhat difficult to accept that the accompanying loss in purity is a fair trade for the small shift in dominant wave-

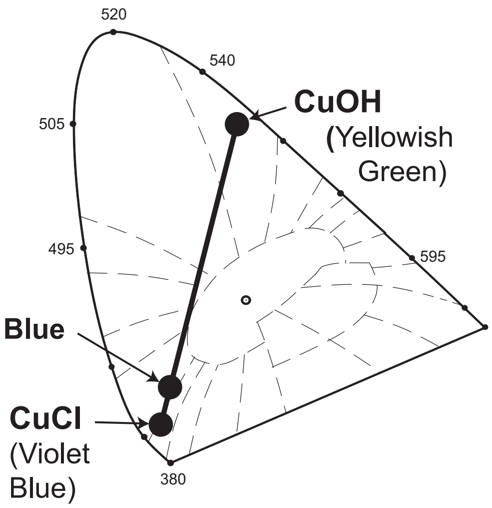


Figure 49. An illustration of the basis for the no longer accepted argument that a small contribution from copper monohydroxide is useful in improving blue flame color.

length. This is especially the case in reality because of the additional loss in purity from the three factors discussed in the preceding paragraph.

As was described much earlier in this chapter, purple is a non-spectral color, and as such it must be produced using a mixture of emissions from the extreme ends of the visible light spectrum. No one color species is known to meet this requirement and the best that can be done is to combine the spectral emissions of the monochlorides of copper and strontium (possibly see again Figure 36). Fortunately, both emitters are monochlorides and their chemistry is mutually compatible, such that their combination is practical. Figure 50 is an illustration of the possibilities regarding this. Various mixtures of emissions of the two monochlorides can be used to produce any of the colors along the line connecting their two color points near the bottom of the figure. This includes a range of purples of reasonably high purity. However, in the inevitable situation where some contribution from the monohydroxides exists, the purity of the purple color quickly decreases. Here the effect is not principally from a shift in the composite strontium color point but rather from the shift in the copper's composite color point. In Figure 50, a 20% contribution from the monohydroxides will shift the color point from purple to purplish-white. Not shown in Figure 50 is the further adverse effect that emissions from sodium and other flame species will have on the purity of a purple flame. Figure 51 is the spectrum of a "best-yet" purple star.

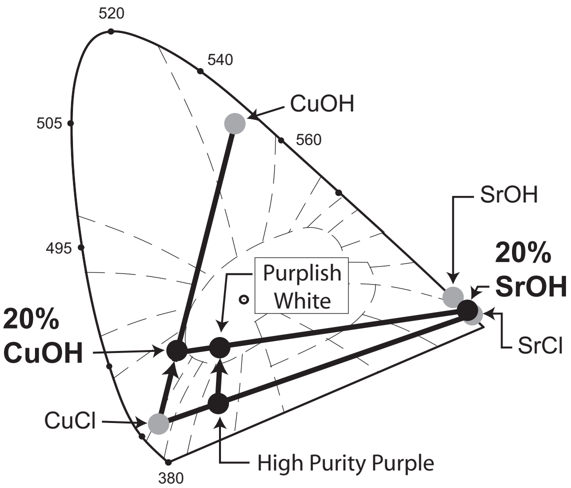


Figure 50. An illustration of forming purple from the emissions of strontium and copper color species.

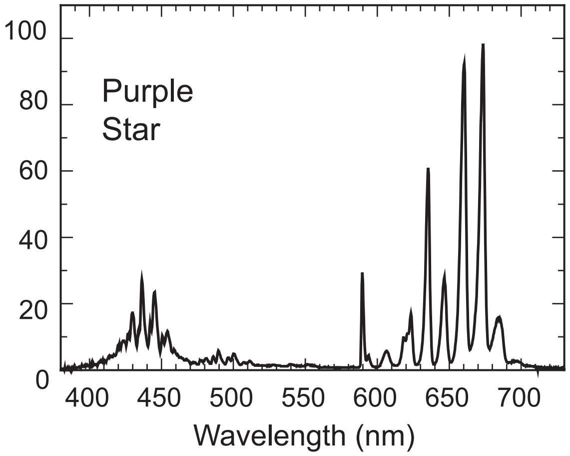


Figure 51. The spectrum of a star perceived as purple that was made by mixing the emissions of the monochlorides of strontium and copper with relatively little contribution from their monohydroxides.
(The Y-axis is the relative intensity.)

Additional Considerations Regarding Oxidizers

There are at least three good reasons for using potassium perchlorate or potassium chlorate as the oxidizer in colored flame formulations. First, potassium produces only weak emissions at 405 nm, in the extreme violet that is almost beyond the range of human vision and in the barely perceptible red at 766 and 770 nm. These lines, together with the continuum produced by the radiative recombination of potassium atoms and hydroxyl radicals,[50] are responsible for the pale violet color of potassium flames. Thus the presence of potassium does not noticeably degrade the desirable emissions of the color species. Second, potassium oxidizers are relatively inexpensive and non-hygroscopic, thus meeting practical needs in manufacturing. Third, potassium oxidizers serve as ionization buffers.[4b] Of the various metal elements involved with colored flame production, potassium has the lowest ionization energy, see Table 17. This can be important, especially at higher flame temperatures (those used to produce brighter flames). In that case, helping to prevent the loss of the color species (molecules) can be important. Since potassium has the lowest of the listed ionization energies, it will be the first of the listed metals to ionize in a flame (eq 32). This adds free electrons to the flame, which act as a desirable stress (Le Châtelier's Principle) that tends to suppress the ionization of the metal of the color species (e.g., the first ionization of strontium in equation 33). This helps prevent the loss of strontium atoms in the flame and is thus a desirable stress that acts to help prevent the loss of strontium monochloride, equation 34.

$$K^0 + \text{Heat} \rightarrow K^+ + e^- \qquad (32)$$

$$Sr^0 + \text{Heat} \leftarrow Sr^{\bullet +} + e^- \qquad (33)$$

$$SrCl^\bullet + \text{Heat} \leftarrow Sr^0 + Cl^\bullet \qquad (34)$$

Some considerable caution is warranted if one chooses to use potassium chlorate over potassium perchlorate. This is because of the heightened sensitiveness to accidental ignition of chlorate-based compositions. For example in sensitiveness testing of equivalent compositions using potassium chlorate and potassium perchlorate, it is common to find that the energy required to ignite the potassium perchlorate compositions is at least 50% greater than it is for the chlorate compositions.[7c] This is a result of potassium perchlorate having a higher activation energy barrier, see Figure 52. (The height of the activation energy barrier serves to reduce the likelihood of the accidental ignition of compositions based on potassium perchlorate in comparison with those using potassium chlorate.)

Table 17. First Ionization Energy of Some Metals of Interest.

Metal	First Ionization Energy[(a)] (kJ/mol)
Copper	744
Calcium	589
Strontium	548
Barium	502
Sodium	497
Potassium	419

a) Derived from information in reference 51.

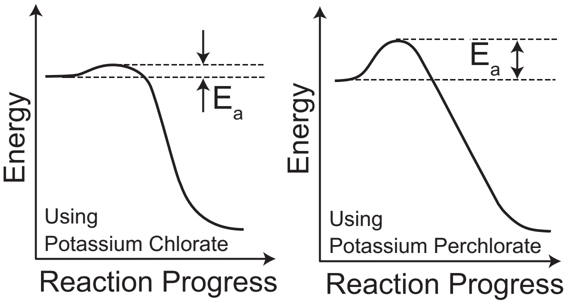


Figure 52. An illustration of the higher activation energy barrier for potassium perchlorate as compared with potassium chlorate composition.

Barium chlorate has a powerful potential advantage for use as an oxidizer in colored flame compositions. In effect it performs triple duty as an oxidizer, color agent and chlorine donor. This is because its decomposition products include barium chloride, equation 35.[8d]

$$Ba(ClO_3)_2 \rightarrow BaCl_2 + 3\ O_2 \qquad (35)$$

However, as with potassium chlorate, the ease with which an accidental ignition can occur is a problem, especially since the activation energy barrier of barium chlorate may be even lower than that of potassium chlorate.

Ammonium perchlorate has a potential advantage for use as an oxidizer for colored flame compositions because its decomposition products include hydrogen chloride, equation 15. This allows it to function as a chlorine donor in addition to its role as an oxidizer.[8e] However, the production of hydrogen chloride gas (which is odorous, corrosive and toxic) is a serious disadvantage if the composition is intended for use in indoor effects. Another potential disadvantage is that if a composition contains both ammonium perchlorate and potassium chlorate, there is the potential to form spontaneously explosive ammonium chlorate via a double replacement reaction (metathesis).

Nitrate oxidizers with non-metal fuels have been demonstrated to produce satisfactory flame colors.[14] However, while this study was quite instructive, this approach is essentially never used in practice, presumably because the flames are only of modest brightness. This not withstanding, both strontium and barium nitrates, in combination with metal fuels, can be effectively used for excellent colored flame production. This is because the oxidizers perform double duty as both the oxidizer and the color agent, and the metal fuel increases the amount of heat energy produced.

Additional Considerations Regarding Fuels

The relatively large amount of heat produced by metal fuels in colored flame formulations can be quite effective in helping to produce bright high purity colored flames. This is because their use allows increasing the percentage of color agent and chlorine donor, beyond that which could ordinarily be tolerated. The end result is the production of more of the desired color species, which can act to increase the purity of the color produced. Further, because of the increased amount of color species present in the flame, it should be possible to tolerate somewhat higher flame temperatures (brighter flames) before the decomposition of the color species reaches unacceptable levels.

Aluminum, magnesium and magnalium (magnesium–aluminum alloy) are about the only metal fuels used in colored flame formulations. However, in terms of safety, convenience and performance they are not equivalent. Aluminum is the least sensitive to accidental ignition and adverse chemical reactions because of its strong oxide coating. Magnalium with at least 30% aluminum seems to have a reasonably effective oxide coating and it places second in terms of sensitiveness. Although magnesium does oxidize, it does not provide effective protection to the metal. Thus in terms of safety, aluminum is best, followed by magnalium, then magnesium, see Table 18.

Table 18. Relative Safety, Convenience and Performance of Metal Fuels

Factor	Ranking
Safety	Al > Mg/Al > Mg
Convenience	Al > Mg/Al > Mg
Performance	Mg > Mg/Al > Al

The degree to which the surface of metal particles are not protected by an oxide coating, determines what alternative steps are necessary to sufficiently protect the metal from adverse reactions. For magnesium, generally it is necessary to apply a coating to the metal. Treatment with boiled linseed oil or potassium dichromate have been the traditional methods.[8f] However, coating with linseed oil is difficult, and there are health concerns regarding the use of potassium dichromate.[52] Recent work[53] has demonstrated the effectiveness of other more benign coatings. As an alternative to coating magnesium, it is possible to use nonaqueous binding (for example, nitrocellulose with acetone, Parlon® with a mixture of acetone and methyl ethyl ketone, and red gum or shellac with dry alcohol). By contrast, aluminum is so well protected by its oxide coating that about all that is ever considered is the addition of a small amount (0.1 to 0.5%) of boric acid to compositions to help stabilize the oxide coating. The need for coating magnalium lies between that for magnesium and aluminum. Accordingly, the trend for convenience of use follows that for safety in Table 18.

When metals are consumed in pyrotechnic flames, they form metal oxides; for the meal fuels under discussion, those are aluminum oxide, magnesium oxide, or both. These oxides have boiling points greater than the temperature of colored flames, see Table 19. These non-vaporized metal oxides, when present in colored flames, will incandesce and the continuous spectrum produced will act to decrease the purity of the composite colored light produced. Fortunately when magnesium is used, the problem of such incandescence can be overcome. At temperatures above 1950 °C, magnesium oxide will react with free carbon to produce carbon monoxide and magnesium,[54] equation 36. Since the flame temperature is well above the boiling point of magnesium, see Table 19, it would remain vaporized in the flame. Generally, the carbon particles would be supplied by the decomposition of a slight excess of an organic fuel.[8g]

$$MgO_{(s)} + C_{(s)} \rightarrow Mg_{(g)} + CO_{(g)} \qquad (36)$$

However, one would expect that magnesium oxide would tend to reform in the outer regions of the flame envelope, where the temperature is lower and oxygen from the air has diffused into the flame. Another potential disadvantage to this approach is that to the extent solid carbon is present in the flame, it will incandesce until it is oxidized in the outer regions of the flame envelope.

Table 19. Boiling Points of Metals and Metal Compounds.

Metal or Metal Compound	Boiling Point (°C)[(a)]
Magnesium oxide (MgO)	3600
Aluminum oxide (Al_2O_3)	2980
Aluminum	2467
Magnesium chloride ($MgCl_2$)	1412
Magnesium	1107
Aluminum chloride ($AlCl_3$)	d 262

d = Aluminum chloride sublimes at 178 °C and decomposes at 262 °C.

a) From reference 55.

Another approach to solving the incandescence problem is to cause the magnesium oxide to react with chlorine or hydrogen chloride to produce magnesium chloride,[8g] equation 37. Since the flame temperature is well above the boiling point of magnesium chloride (1412 °C), it will remain vaporized and thus not emit a continuous spectrum.

$$MgO_{(s)} + 2\,HCl_{(g)} \rightarrow MgCl_{2(g)} + H_2O_{(g)} \qquad (37)$$

In this case the chlorine or hydrogen chloride is likely to already be present in the flame, having been supplied by the chlorine donor. The only disadvantage of this approach is the reduction in available chlorine or hydrogen chloride in the flame, which may need to be compensated for. Nonetheless, this is a small price to pay for the elimination of the incandescence.

Aluminum oxide can also undergo the reactions in equations 36 and 37.[8g] However, empirical observations indicate that the reactions provide a lesser degree of success. Regarding the reaction with carbon, although it has not been measured, based on calculations, it is likely that the temperature needed is approximately 2140 °C,[54] or about 300 °C higher than that for magnesium. At over 2100 °C, this is likely to be at or above the maximum temperature available in some colored flames. Also, unless the flame remains above the boiling point of aluminum (2467 °C) the aluminum so produced may remain as a liquid and may continue to incandesce. Finally, if it is necessary to have the flame temperature sufficiently high to keep the aluminum from condensing, there is the problem of the color species being lost owing to their decomposition at such a high flame temperature.

In terms of the production of aluminum chloride, note in Table 19 that it decomposes at 262 °C. Apparently, based on the continuous spectral component produced, the decomposition product is not vaporized at normal flame temperatures. The incandescence that occurs when using aluminum as a fuel acts to significantly reduce color purity.

Unfortunately, in terms of performance in producing high purity colors, the trend is the reverse of those for safety and convenience, with magnesium being best, followed by magnalium and then aluminum.

While on the subject of fuels for colored flames, an additional subject deserves to be discussed. When oxygen diffuses into the outer regions of the flame envelope, some of the desired color species will be replaced with their oxides. Unfortunately, the oxides do not have emissions that are the same color as those of the color species. This has the effect of altering the color of the flame tips. The emissive colors of the oxides are given in Table 20. For strontium reds, the presence of orange flame tips would not be noticeable. However, given the high boiling point of strontium oxide (≈ 3000 °C) and the likely flame temperatures, it will condense to produce a continuous spectrum. For green and especially blue, the yellowish and pinkish flame tips, respectively, are quite noticeable to an observer at close range. It has been suggested that the use of an additional amount of a low reactivity fuel, sometimes called a *flame deoxidizing agent*, may be of benefit.[9a] Some possibilities for such fuels are hexamine, stearic acid, sulfur, asphaltum, para-dichlorobenzene, and graphite. However, while it is easy for an observer at close range to see the discolored tips of green and blue flames, it is generally quite difficult to detect the spectra of the oxides with a spectrometer. This is because the relatively weak emissions of the oxides are overpowered by the much stronger emissions from the heart of the flame envelope. Accordingly, for practical purposes it seems apparent that the emissions of the oxides in the flame tips can be ignored.

Table 20. Colors Produced by the Oxides of the Primary Color Species.

Metal Oxide	Flame Color
Strontium oxide ($SrO_{(g)}$)	Orange
Strontium oxide ($SrO_{(l\ or\ s)}$)	Yellowish-white
Barium oxide ($BaO_{(g)}$)	Yellow-green
Copper oxide ($CuO_{(g)}$)	Reddish Purple

Considerations Regarding Ignitability and Burning

The ignition and burning characteristics of colored flame compositions can be quite important. In this regard it should be mentioned that some chlorine donors (e.g., Saran® resin and Parlon®) result in compositions that are significantly easier to ignite than compositions made with some other chlorine donors (e.g., polyvinyl chloride). Similarly, not all fuels are equally easy to ignite. For example, charcoal and metals are relatively difficult to ignite when they are the only fuels in a composition, while red gum and shellac ignite easily.

The use of potassium dichromate as a burn catalyst is quite effective when used with potassium perchlorate to aid in ignition and to help stars resist being extinguished when traveling through the air at high speed. However, its use has the effect of seriously weakening the flame color produced, even when the potassium dichromate is present in relatively small amounts. The use of ammonium perchlorate facilitates the production of excellent flame colors, but its compositions tend to burn slowly and produce relatively small flames, except when catalyzed with copper compounds, whose presence is a problem for all colors except blue.

Prospects for Future Improvement

Figure 53 summarizes the state of the art with respect to colored flame production, as well as probably defining the limits on future improvements. The range of colors within the smallest of the quadrangles (shaded) represents the limits of common high quality color formulations.[21,30] This covers a relatively small portion of the chromaticity diagram, and much of that consists of what would normally be described as shades of white. It is probably quite fortunate that observers of fireworks displays do not have light sources producing bright and highly pure color available for comparison with the colors of the fireworks, which would literally pale by comparison. The small size and central location of the color triangle for typical compositions probably also goes a long way toward explaining why photographs and video recording of displays seem to reproduce the colors of the displays so poorly, unless the photographic colors are artificially enhanced.

The next larger quadrangle (not shaded) demonstrates the approximate limits of the best color formulations reported to date.[19,21] These colors are quite impressive when viewed and

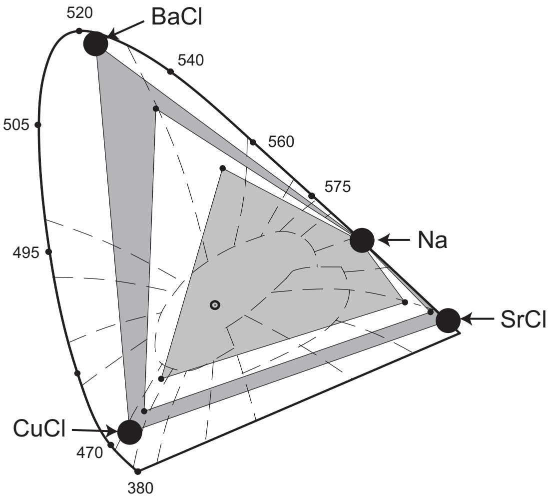


Figure 53. An illustration of the range of possibilities for colored flame production.

are readily discernable as significantly better than even the best of the commonly produced colors. (Unfortunately, there are some limitations associated with the use of these formulations in terms of cost, convenience of manufacture or burning characteristics.) Using any of the color mixing schemes,[10,11,15] even assuming the color formulations are perfectly compatible, one is constrained to produce colors no better than those inside this quadrangle.

Finally the outer quadrangle (shaded) is formed by the color points of the most desirable color species (the monochlorides of strontium, barium and copper, plus atomic sodium). Unless other, even better color species can be found (and people have looked without significant success[4,12,20,23,28]), this is the ultimate limit of what is theoretically possible. However, given that flames generally consist of very many chemical species, of which many emit in the visible region, even reaching these limits will probably be impossible. If that is the case, what is left as a practical alternative for future improvement? It may (should) be possible to improve somewhat the perception of the colors that are already possible. This would be accomplished using methods based on the current theory of color vision.[33–35] However, that discussion is beyond the scope of this chapter.

Acknowledgments

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Illuminants and Illuminant Research

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ABSTRACT

The use of pyrotechnic compositions for the production of light has a long history. Most improvements were made mainly by trial and error with many misunderstandings about the cause and effect relationships from observations. Significant advancements in the mechanisms and theory of combustion have increased the understanding of many effects and led to improved illuminants both theoretically and practically. Radiative transfer theory explained most of the observed variations in illuminant functioning. Effects of spin, liner thickness and binders have been analyzed, and application of the results has been used to improve illuminant performance and solve production problems.

Keywords: illuminant, photoflash, efficiency, magnesium, sodium, nitrate, binder, radiative transfer

Introduction

Illuminants have been a major factor in pyrotechnic applications for many years. The earliest application was the use of torches prepared with pitch or tar, ignited and used to ward off darkness. This simple application was extended with the utilization of oxidizers, such as saltpeter or niter to enhance burning. When more light was needed, it was found that sodium added to a flame produced an astonishing increase in illumination efficiency.

An early application of illumination was photoflash devices for the military. Photoflash devices released pyrotechnic compositions that burned to produce millions of candela in visible light for a fraction of a second. This allowed aircraft to fly over a region with a camera lens open and release a huge "flashbulb" to illuminate a number of square miles. This was the only way to do night surveillance. The development of airborne radar and forward-looking infrared (FLIR) has made photoflash obsolete. Photoflash compositions were based on aluminum powder mixed with potassium perchlorate with confinement until ignition which was followed by an explosive dispersion of excess aluminum reacting with the air. It should be noted that aluminum will react with both oxygen and nitrogen in the air.

The efficiency of an illuminant is given in candela per unit weight. Candela is the unit of luminous intensity equal to 1/60 of the luminous intensity per square centimeter of a blackbody radiating at the temperature of solidification of platinum (2,046 K). In jargon, it is frequently referred to as the "candlepower" of a composition. The preferred term, however, is candela. There is an approximation in efficiency that relates burning rate and intensity over a range. This relationship is shown in equation 1.

$$\text{Light Integral}\left(\frac{\text{cd}\times\text{s}}{\text{g}}\right) = \left(\frac{\text{candela}\times\text{burn time}}{\text{mass of composition}}\right) \qquad (1)$$

This equation shows that it is possible to trade burn time for candela by adjusting the burning rate of the composition without changing the formulations total energy. However, this is only true over a limited range of formulation and candle size. It can be shown that there is an ideal burning rate for a given composition to produce the most efficient output. If the burning rate is slower than the optimum rate, then radiant heat losses will reduce the efficiency. If the burning rate is faster than the optimum rate, then material will be expelled from the flare plume without complete combustion and energy will be lost.

Pressure Effect on Flame

Douda[1] published a definitive work on the effect of radiative transfer on alkali metal D-line radiation. This treatise identified several *a priori* factors that influence the resonance line broadening in pyrotechnic flames.

This author[2] extended Douda's work through flame modeling to determine the effects of these factors without *a priori* assumptions and verified the theory over a wide range of pressures, candle diameters, alkali metals, atmospheric interactions and fuels. This effort finally gave a clear understanding of the effects of combustion on illumination, including interactions with the surrounding atmosphere. This work also provided answers for many of the anomalies that had been observed, such as the increase in light output even though the theoretical flame temperature decreased with increasing magnesium content. It further showed that almost 90% of the visible light from conventional sodium nitrate-magnesium flares comes from the broadened D-line radiation.

Mixtures of magnesium and sodium nitrate, with a binder, have been well characterized. When magnesium and sodium nitrate are burned, the sodium nitrate first melts and then decomposes to release oxygen and form sodium nitrite. The oxygen released immediately reacts with the pyrolyzing binder that coats the sodium nitrate and magnesium and releases enough energy to raise the magnesium to a reactive state. This increase in energy promotes a more rapid decomposition of the sodium nitrite and the magnesium oxidizes on the surface to form a porous capsule of magnesium oxide. The magnesium oxide density is such that it cannot completely encapsulate the magnesium particle, so the internal magnesium starts to vaporize through the pores. This provides gaseous magnesium to mix and burn with the oxygen from the decomposing sodium nitrite and increases the efficiency of combustion. Thermochemical calculations readily show that the maximum temperature of the reaction of magnesium and sodium nitrate will occur at the stoichiometric composition around 46% magnesium. It is well established that the maximum candela occurs well above the stoichiometric composition with a considerable excess of magnesium present. The thermochemistry is represented by the following equations:

$$2\ \mathrm{NaNO_3(s)} \xrightarrow{\Delta} 2\ \mathrm{NaNO_3(l)} \xrightarrow{\Delta} 2\ \mathrm{NaNO_2} + \mathrm{O_2} \qquad (2)$$

$$3.5\ \mathrm{O_2} + \mathrm{C_5H_5O} \rightarrow 4\ \mathrm{CO} + \mathrm{CO_2} + 2\ \mathrm{H_2O} + 0.5\ \mathrm{H_2} + \mathrm{Heat} \qquad (3)$$

$$2\ \mathrm{NaNO_2} \xrightarrow{\Delta} \mathrm{Na_2(g)} + \mathrm{N_2(g)} + 4\ \mathrm{O_2} \qquad (4)$$

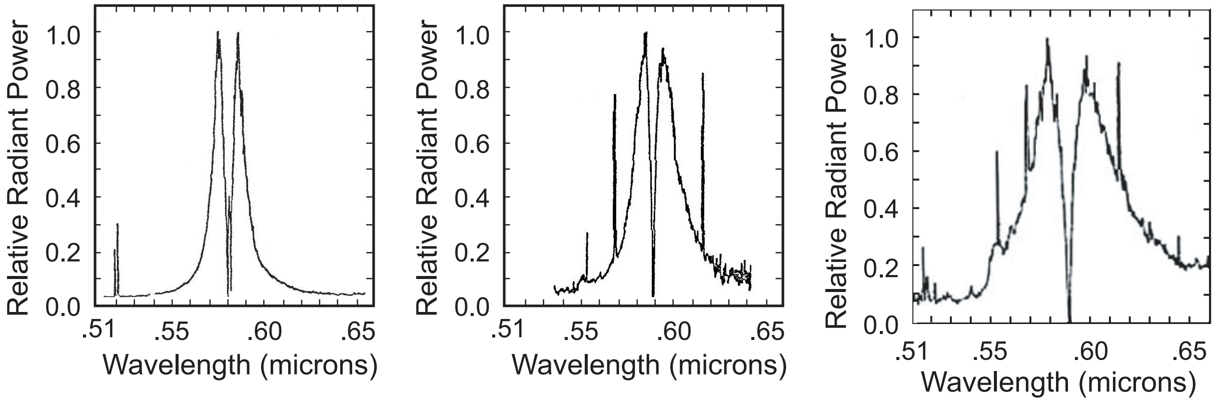
$$\mathrm{Mg(s)} \xrightarrow{\Delta} \mathrm{Mg(g)} \qquad (5)$$

$$\mathrm{O_2} + 2\ \mathrm{Mg} \rightarrow 2\ \mathrm{MgO(s)} + \mathrm{Heat} \qquad (6)$$

$$\mathrm{Na_2} \xrightarrow{\Delta} 2\ \mathrm{Na^*} \qquad (7)$$

$$\mathrm{Na^*} \rightarrow \mathrm{Na^*} + 589\ \mathrm{nm\ photon} \qquad (8)$$

The sodium nitrate first melts and then decomposes to sodium nitrite with the release of some oxygen (eq. 2). The oxygen reacts with some of the binder to form carbon monoxide, carbon dioxide and water with the release of more heat (eq. 3). The heat causes the sodium nitrite to decompose into sodium vapor, nitrogen and oxygen (eq. 4). The magnesium is heated and vaporized to provide magnesium gas for easy oxidation (eq. 5). The additional oxygen from equation 4 reacts with the remaining binder and the magnesium fuel (eq. 6). The oxidation of the magnesium provides a very high temperature (3073 K) that is adequate to dissociate the sodium vapor into individual atoms and raise them to a higher state of excitation (eq. 7). The excited sodium atoms then radiate their excess energy as sodium D-lines (a doublet at 589 nm) (eq. 8). This D-line radiation is broadened by a number of mechanisms with pressure as the strongest contributor. This can be seen from sodium vapor street lamps that use high pressure sodium vapor, excited electrically, to produce a high level of visible light. The broadening of the radiation increases the amount of light over a wider range of the spectrum, which reduces the monochromatic nature of the atomic spectra. Examples of this broadening due to increasing pressure are shown in Figures 1 a to c.



(a) *Pressure is 76 torr.* (b) *Pressure is 300 torr.* (c) *Pressure is 760 torr.*

Figure 1. Spectra showing that increased pressure results in a broadening of the D-line radiation.

Plume Effect

The plume of a burning flare entrains air as it exits the canister and the oxygen in the air reacts with the magnesium to increase the outer temperature of the plume and keep the sodium atoms at a highly excited state. A diagram of the plume of a burning flare is shown in Figure 2. When the temperature drops below about 1800 K, radiation of the sodium D-lines ceases. The more magnesium present in the flame, the longer the flare plume becomes as the magnesium continues to react with the air and bolster the surface area. The insulated central portion of the plume continues to cool by radiation and lose radiative efficiency but the overall increase in flare plume surface area compensates and provides the observed increase in candela.

Figures 3 a to c show the decrease in broadening for sodium D-lines at a fixed distance above the surface as the percent magnesium increases.

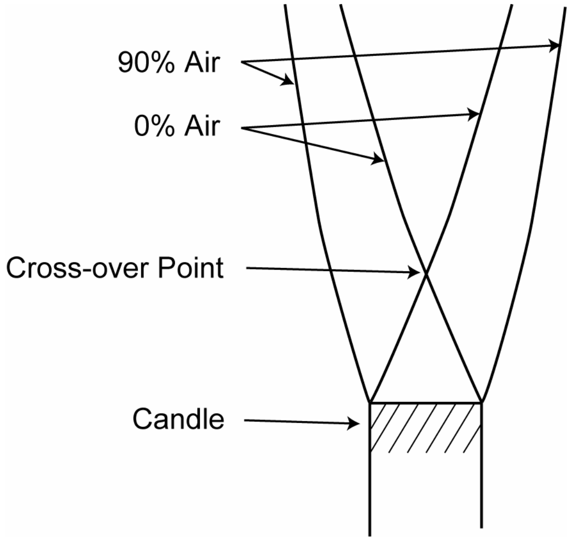
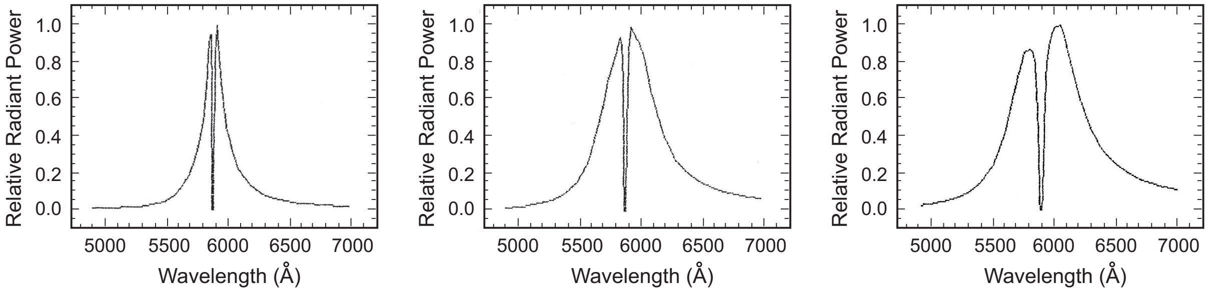
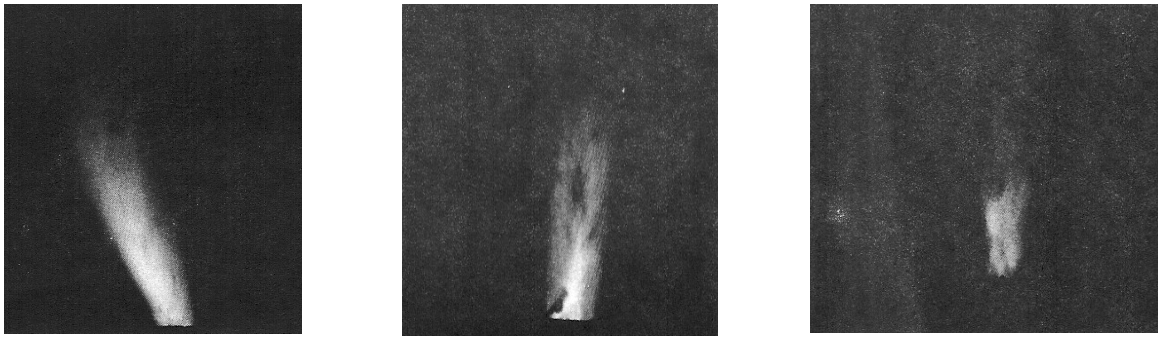


Figure 2. Plume diagram.



(a) *40% magnesium.* (b) *50% magnesium.* (c) *60% magnesium.*

Figure 3. Graphs showing that the sodium D-lines broaden as the percent of magnesium increases.



(a) in air *(b) in argon* *(c) in nitrogen*

Figure 4. Plume length effect on a stoichiometric formulation burned in (a) air, (b) argon, or (c) nitrogen.

The plume length was experimentally found to increase as a function of diameter and fuel richness so that flare surface area increases as the fuel increases. This analysis also explains the effect of candle diameter on efficiency.

As the diameter increases, the entrainment of air into the central portion of the plume is less efficient and the radiative transfer mechanisms lose efficiency.

An interesting set of tests were performed in a large chamber (6 m^3) with different atmospheres. The purpose of the tests was to determine how much the oxygen in the air was contributing to the efficiency of magnesium-sodium nitrate flares. Stoichiometric and fuel rich compositions were burned in atmospheres of air, nitrogen or argon. The results from the stoichiometric formulations clearly showed little difference in plume length and candela. See Figures 4 a to c.

With the fuel rich composition, however, the tests in air showed a much longer plume and higher candela. See Figures 5 a to c. In argon, the plume length was shorter and the candela much lower. In nitrogen, the plume was very short and the candela was very low. The argon does not react with the excess magnesium, so the lower flame temperature of the fuel rich composition results in greatly reduced D-line radiation.

The flare plumes in a nitrogen atmosphere are much shorter than the plumes in an argon atmosphere in keeping with the prediction that nitrogen is more effective in collisional de-excitation of excited sodium atoms. This is another of the radiative transfer mechanisms that is treated in the theory.

Hooymayers and Alkemade[3,4] reported measured values for quenching cross sections of various species with sodium and potassium. Their results indicated that the apparent quench-

(a) in air. *(b) in argon.* *(c) in nitrogen.*

Figure 5. Plume length effect of a fuel rich formulation burned in (a) air, (b) argon, or (c) nitrogen.

ing cross section of a species with an alkali metal would be inversely proportional to the atomic weight of the alkali metal. A higher value indicates a more efficient quenching cross section for the species. See Table 1 for a compilation of quenching cross sections for various species with sodium.

Table 1. Quenching Cross Section Values for Species with Sodium.

Species	Temperature (K)	Na Value
CO	2000	72
CO_2	1670	113
Ar	2070	2.3
H_2O	2070	1
N_2	1940	40
O_2	1885	66

Formulation Effect

Effective illumination is based on magnesium, sodium nitrate and a binder. The binders are important in the production processes of the illuminant composition, where they serve to maintain homogeneity of the composition while in process and then hold the composition together and bonded to the container during functioning. The binder also provides an initial reaction with the oxygen released from the sodium nitrate to provide a transition to burning of the magnesium. There can be some difference in performance as the binders change due to their stability under pyrolyzing environments (i.e., some binders are more stable and pyrolyze more slowly and reduce burn rates). Magnesium particle size and shape also play a role in the burning rate of the composition. Use of other metals has been shown to be less effective than magnesium in illuminants. This is mainly due to the low melting and boiling points of magnesium coupled with the very high heat of combustion. Other low melting and boiling metals do not have the high heat of combustion and are, therefore, not as effective in sodium excitation. Sodium nitrate particle size distribution affects the consolidation characteristics of formulations.

A typical illuminating composition consists of 50% (200 µ) magnesium powder, 43% (30–50 µ) sodium nitrate and 7% binder. Early binders included linseed oil and polyester resin. Army formulations currently use vinyl-alcohol acetate resin (VAAR) or polysulfide-epoxy resin binder systems. The VAAR binder is dissolved in a solvent and then mixed with the magnesium and sodium nitrate until the solvent is evaporated. This composition can then be stored and used whenever needed. No curing is required after consolidation. The polysulfide-epoxy combination is mixed with an amine cure agent and mixed with the magnesium and sodium nitrate. This mixture has a pot life and must be consolidated before the cure has progressed to the point that it will no longer flow under pressure. After consolidation, the candles are cured at an elevated temperature to complete the process. This binder gives a small amount of flexibility to the composition to prevent shrinkage and separation from the case.

Diameter Effect

It can also be shown that increasing the diameter of a candle does not produce a corresponding increase in output. This can be shown to be the effect of the entrainment of air into the plume along the plume axis. Diffusion of air into the plume can only occur at a certain rate. As the diameter increases, the central portion of the flare plume will begin to cool from radiative heat loss and there will be a corresponding loss of efficiency from the composition. The graph in Figure 6 shows a typical response of candela for a fixed composition as the diameter of the flare increases.

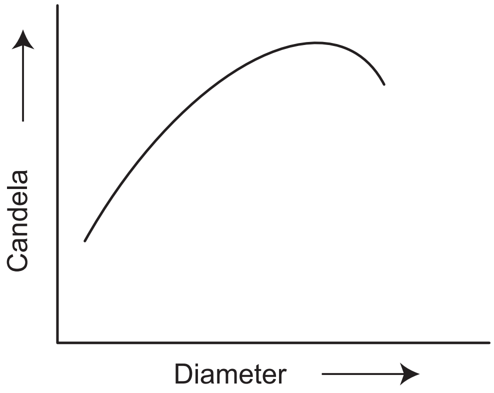


Figure 6. Typical response of candela for a fixed composition as flare diameter increases.

Spin Effect

A number of physical effects on flares were observed and their causes identified. For example, in military illuminants, many of the larger caliber illuminants are gun launched with high spin rates. Air brakes were frequently used to stop the spin on ejection of the payload. Field tests sometimes showed that the illuminants put out very low intensity light, followed by a large illuminant drop-out about half-way into the burn. Recovery of the rounds usually showed that the air brakes had failed and the illuminant in the canister had an unusual appearance. There were marked protrusions up from the center of the illuminant composition remaining in the canister. It appeared that the composition was burning faster around the periphery of the canister. It was assumed that the failure of the air brakes led to the flare spinning at a high rate, but the mechanism for reduced output was not obvious. The prevalent theory assumed that the sodium nitrate was melting and centrifugal force was carrying the reacting materials to the sidewall of the canister and choking the canister to cause a rise in pressure and shorten the burn time. The reduced opening for the plume explained the loss in light intensity. To test the theory, a spin test fixture was built to spin the illuminant canisters at controlled speeds while suspended upside down. A water jet was positioned to extinguish the burning composition at any point during the burn. The 105-mm candle was tested first. The graph in Figure 7 shows the results of the first set of spin tests.

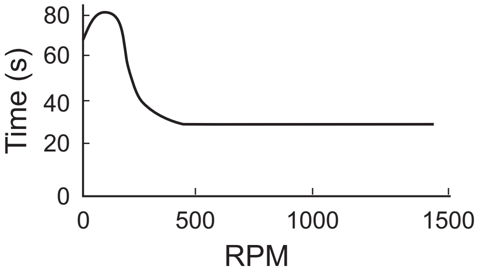


Figure 7. Results of the first set of spin tests.

The tests were repeated several times and the slight rise in burn time followed by a precipitous drop around 250 rpm was noted each time. This provided the proof that the effect was spin related. A series of tests were then run with extinguishment of the burning candle at various times into the burn. Examination of the surface provided an unexpected result. The illuminant was noted to regress faster at the edge producing a spiked appearance towards the end of the burn. This is shown in the Figure 8.

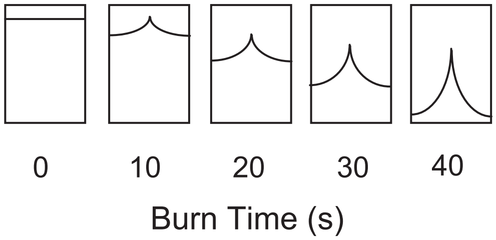


Figure 8. Diagrams showing the change in burn surface inside spinning candle over time.

The patterns observed did not agree with the original expectation of more rapid combustion down the center of the candle. A new theory was developed that involved the effect of decoupling of the gases from the illuminant surface. As the illuminant starts to spin, the gases evolved from the surface start to rotate with the surface. At a critical rpm, in this case 250 rpm, the gases start to lag behind the surface. The difference in rotation produces an increase in heat transfer. (This effect is well known and demonstrated by many physical phenomena, such as blowing on your hands to warm or cool them. The increased velocity of your breath either warms or cools the skin depending on which has the highest heat content.) As the spin velocity increases, the effect increases up to a maximum value determined by the thermal conductivity of the illuminant composition. Since the rotational velocity is greatest at the periphery, the heat transfer is greatest at that point. The slowest rotational velocity—in the middle—results in the slowest burn rate and leads to the formation of the spike. When the edge burning reaches the bottom of the canister, the center spike falls out, explaining the observed illuminant dropout. To test the theory, a set of candles was loaded with a “paddle-wheel” of metal plates inserted in the canister.

A split ram was used to press illuminant into each quadrant to load the candles. See Figure 9.

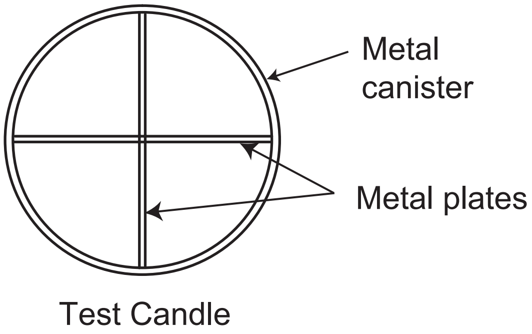


Figure 9. A cross-section of the "paddle wheel" of metal plates in a canister.

When these candles were burned in the spin fixture, there was no change in the burn time even at 1500 rpm. This is consistent with the paddles acting to keep the gases in sync with the burning surface thus preventing the differential spin rates and eliminating the increase in heat transfer. Once the principle was understood, other problems could be addressed.

The 60 mm illuminant was changed from a fin-stabilized round to a spin-stabilized round. The small size of the candle precluded the use of air brakes to stop the spin. The burn times were observed to change from 60 seconds in the static testing to 40 seconds in flight tests. The problem obviously resulted from the spinning of the illuminant, but there was no way to stop the spin, or even reduce it. The only control available seemed to be the thermal conductivity of the illuminant composition. The oxidizer was being ground from prilled sodium nitrate to a weight mean diameter (WMD) of about 50 µ; the magnesium was 30–50 mesh (about 200 µ WMD); and the binder content was about 6%. The formulation gave the needed candela and could not be readily changed. By grinding the sodium nitrate to a much finer particle size, it was possible to provide a more uniform distribution of the oxidizer to isolate the particles of magnesium, thereby reducing the thermal conductivity. This provided a reduced sensitivity to the heat transfer induced by the spin and the flight burn times were raised to about 55 seconds, which met the specification requirements. This is a prime example of the benefits of understanding both the chemistry and physics of the pyrotechnic reactions.

Liner Effect

Another example of applying analysis to the solution of problems involved the use of liners in illuminants. The 81-mm illuminants were changed from a cardboard tube to a metal canister. The canisters were lined with the binder solution and cured to provide a bonding surface for the illuminant composition. The liner thickness was not considered a serious problem and was allowed to vary during production. It soon became obvious that too little liner resulted in unbonded areas and high heat transfer down the canister wall resulting in short burn times. To avoid this, the liner amount was doubled. While this stopped the short burn times, it was noted that the candela of stationary flares had dropped to an unacceptable level. To determine the magnitude of the problem, a series of candles were loaded with carefully controlled liner thickness. It was found that a maximum thickness could be applied without loss of candela. Analysis revealed the cause. At low liner thickness, the heat transfer through the liner was absorbed by the metal canister, and this kept the liner from pyrolyzing from the heat of the flame. When a critical thickness was reached, the thick layer of liner could not transfer heat fast enough to keep the surface below the pyrolyzing temperature of the liner and the liner began to decompose and add carbonaceous residue to the flare plume. This acted just like an increase in inert binder, which reduced the thermochemical energy of the flare plume and lowered the candela. Again, the understanding of the chemistry and physics of the pyrotechnic reactions allowed a knowledgeable solution of the problem.

Shifting Spectral Output

The latest move in battlefield illumination is now directed towards "covert" illuminants. These illuminants are loaded with compositions that radiate most of their energy in the infrared part of the spectrum. The use of these illuminants with advanced night vision devices permits the observation of troops, equipment or areas without visibly showing illumination in the observed area. This covert illumination has definite advantages in operations that are close to the observers. They can light up an area with infrared light without showing themselves to an enemy that does not utilize the same night vision devices. The formulations used in the covert illuminants vary but generally do not use metal powders to avoid a broad continuum from hot particles producing visible light. The alkali metals cesium and rubidium have their D-line radiation in the near infrared with little overlap in the visible. Achieving higher burning rates without the use of metal powders has been one of the main challenges to their use.

Pyrotechnic illuminants continue to be a major battlefield item to permit identification and targeting of enemy positions. The shift in spectral output provides new challenges to the formulation developers to keep up with advancing technology.

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Propellant Chemistry

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ABSTRACT

Propellants used for pyrotechnics are composed of energetic materials that produce high-temperature and high-pressure gaseous products. The propellants are classified into three types by their physical structure and the ingredients used: (1) homogeneous propellants consisting of chemically bonded oxidizer and fuel components in the same molecule, (2) heterogeneous propellants consisting of physically mixed oxidizer and fuel components, and (3) granulated propellants consisting of energetic solid particles. While the energy content of a propellant is determined by the chemical properties of the ingredients, the physical properties and chemical processes of the ingredients determine the ballistic characteristics such as burn rate and pressure and temperature sensitivities.

Keywords: propellant chemistry, activation energy, burn rate

Nomenclature

a = burn rate constant defined in equation 18
c = specific heat, kJ/kgK
d = dark zone pressure exponent
E = activation energy, kJ/kmol
H_{exp} = heat of explosion, MJ/kg
I = radiative heat flux, kW/m^2
I_{sp} = specific impulse, s
k = reaction order
K_n = area ratio defined by A_b/A_t
m = mass flow rate, kg/m^{2}s or reaction order in the dark zone
M = molecular mass, kg/kmol
n = pressure exponent of burn rate
[OB] = oxygen balance
p = pressure, MPa
Q = heat release, kJ/kg
r = burn rate, m/s
R = gas constant, 8.315 kJ/kmolK
t = time, s
T = temperature, K
u = flow velocity, m/s
x = distance, m
Z = pre-exponential factor, (kg/m^{3}s)(MPa)$^{-K}$
α = thermal diffusivity, m^2/s
β = radiative heat flux factor defined in equation 8, kW/m^{2}K^4
γ = specific heat ratio
Γ = heat flux at the burning surface, kW/m^2
δ = reaction distance, mm
$\Delta H°_f$ = heat of formation, MJ/kg
λ = thermal conductivity, kW/mK
Λ = heat flux in the gas phase or in the condensed phase, kW/m^2
ξ = mass fraction
ρ = density, kg/m^3 or g/cm^3
φ = temperature gradient, K/m
ψ = temperature defined in equation 14, K
ω = reaction rate in the gas phase, kg/m^{3}s

Subscripts

c = combustion
d = decomposition or dark zone
f = flame or fizz zone
g = gas phase
m = melting point
p = propellant, condensed phase, or product
r = reactant
s = burning surface
0 = initial condition

1. Introduction

When a propellant is ignited and burned in a closed chamber, gaseous species at high temperature and pressure are formed. These energetic gaseous species generate propulsive forces used for rockets, guns, and pyrotechnics. The specific impulse (I_{sp}) is a parameter used to identify the energy content of propellants[1–3] and is represented by

$$I_{sp} \sim \left(\frac{T_c}{M_c} \right)^{1/2} \quad (1)$$

where T_c is combustion temperature and M_c is molecular mass of the combustion products. Though I_{sp} is also a function of the specific heat ratio (γ) of the combustion products, γ is relatively constant among propellants. It is evident from equation 1 that an energetic material that produces high T_c and high M_c combustion products may not be a useful propellant. For example, a pyrotechnic composition (pyrolant) containing metal powders is not used as a propellant because it generates metallic oxides with a high M_c even though a high T_c is generated by metal combustion. A propellant that generates low T_c can also be useful if the M_c is sufficiently low.[2–4]

Solid propellants may be classified into three types by their physical structures: (1) homogeneous propellant, (2) heterogeneous propellant, and (3) granulated propellant.

A homogeneous propellant consists of fuel and oxidizer components that are bonded chemically in the same molecule, and the physical structure appears to be homogeneous. A typical example of a homogeneous propellant is nitrocellulose (NC) that is composed of $–O–NO_2$ chemical bonds and a hydrocarbon structure. Breaking the $O–NO_2$ bond produces NO_2 gaseous species, which act as an oxidizer fragment, and the hydrocarbon structure acts as a fuel fragment. The physical structure of NC is homogeneous, and it is known as a single-base propellant. The mixture of NC with nitroglycerin (NG) forms a homogeneous gelled propellant known as a double-base propellant. The physical structure of a double-base propellant is also homogeneous.

A heterogeneous propellant is made as a mixture of fuel and oxidizer components, and the physical structure of the propellant is heterogeneous. A typical heterogeneous propellant is a mixture of crystalline oxidizer particles and a polymeric hydrocarbon, a so-called "composite propellant". The crystalline particles act as the oxidizer component, and the polymeric hydrocarbon acts as a fuel component when these are decomposed. The chemical reaction that produces heat and combustion products occurs on and above the burning surface of the propellant.

A granulated propellant consists of numerous granulated grains or powders that are composed of energetic materials. When a granulated propellant is used for a propulsion system, the propellant has a loosely packed shape. Black Powder is a typical example of this class of propellant. However, in some applications (model rocket motors, skyrockets, and signal rockets) Black Powder may be compressed into a single grain and performs as a heterogeneous propellant.[3]

These three types of propellants are fundamentally different from each other in various aspects: chemical ingredients, decomposition processes, burn rate characteristics, combustion products, etc. In this paper the chemical properties of propellants, their ingredients, and combustion characteristics are described in order to understand the ballistic properties of solid propellants.

2. Energetics of Propellants

2.1 Generation of Heat Energy

2.1.1 Heat of Explosion and Heat of Formation

When a propellant burns, heat and combustion products are produced. In general, the heat produced is evaluated by the "heat of explosion" H_{exp}. H_{exp} is defined as the difference between the heats of formation of the reactants ($\Sigma\Delta H^\circ_{f\,\text{(reactants)}}$) and the heats of formation of the products, ($\Sigma\Delta H^\circ_{f\,\text{(products)}}$) as represented by

$$H_{exp} = \Sigma\Delta H^\circ_{f\,\text{(reactants)}} - \Sigma\Delta H^\circ_{f\,\text{(products)}} \quad (2)$$

Each heat of formation (ΔH°_f) is dependent on the chemical structure and chemical bond energy of each molecule of propellant ingredient and the combustion products. Equation 2 indicates that a higher H_{exp} is obtained when a higher $\Sigma\Delta H^\circ_{f\,\text{(reactants)}}$ is used for the propellant and also when a lower $\Sigma\Delta H^\circ_f$(products) results from the combustion products.

Table 1 shows ΔH°_f for typical energetic propellant reactants, and Table 2 shows ΔH°_f for typical propellant combustion products. It is evident from the data in Table 1 that higher $\Delta H°_{f\ (\mathrm{reactants})}$ is generally obtained with oxidizers or materials containing nitrogen atoms.

Table 1. $\Delta H°_f$ for Propellant Reactant Ingredients.

Reactant	$\Delta H°_f$ (MJ/kg)
NG	–1.70
NC	–2.60
HMX	+0.25
NH_4ClO_4	–2.52
$KClO_4$	–3.12
NH_4NO_3	–4.56
KNO_3	–4.87
CTPB	–0.89
HTPB	–0.31
GAP	+0.96
BAMO	+2.46
Cubane	+5.47
Al	0
Mg	0
B	0

Table 2. $\Delta H°_f$ for Propellant Combustion Products.

Product	$\Delta H°_f$ (MJ/kg)
CO	–3.94
CO_2	–8.94
H_2	0
$H_2O_{(g)}$	–13.42
N_2	0
Al_2O_3	–16.40
B_2O_3	–18.30
MgO	–14.93

Table 3 shows percent nitrogen (N), density (ρ), H_{exp}, melting point temperature (T_m) and oxygen balance [OB] (see next section for more about oxygen balance) for typical energetic materials used as major components of propellants. To obtain higher H_{exp} of propellants, various types of chemicals are mixed to formulate propellants. The major chemicals are fuel and oxidizer. The oxidizer oxidizes the fuel to produce heat and gaseous products.

Table 3. Physicochemical Properties of Ingredients Used for Propellants.

Propellant Ingredient	Short-hand	Formula	N (%)	Density (ρ) (g/cm^3)	H_{exp} (MJ/kg)	T_m (°C)	[OB] (%)
Nitroglycerine	NG	$(ONO_2)_3(CH_2)_2CH$	18.50	1.59	6.322	13.2	+3.5
Nitrocellulose	NC	$C_{12}H_{14}N_6O_{22}$	14.14	1.67	4.13	D	–28.7
Ammonium perchlorate	AP	NH_4ClO_4	11.04	1.95	1.114	D	+34.04
Ammonium nitrate	AN	NH_4NO_3	35.0	1.72	1.601	169.6	+19.99
Nitroguanidine	NQ	$CH_4N_4O_2$	53.83	1.71	2.88	232	–30.7
Triaminoguanidine nitrate	TAGN	$CH_9N_7O_3$	58.68	1.5	3.67	216	–33.5
Cyclotetramethylene tetranitramine	HMX	$(NNO_2)_4(CH_2)_4$	37.83	1.90	5.36	275	–21.6
Cyclotrimethylene trinitramine	RDX	$(NNO_2)_3(CH_2)_3$	37.84	1.82	5.40	204	–21.6
Hexanitro-hexaazaisowurtzitane	CL-20	$(NNO_2)_6(CH)_6$	38.45	2.04	6.8	260	–10.95

D = decomposes instead of melting.

Note: H_{exp} is for H_2O as a gas.

2.1.2 Oxygen Balance

Even though $\Sigma\Delta H^\circ_f$ (reactants) of the fuel and oxidizer may be low, a higher H_{exp} is obtained if the oxidizer has the potential to oxidize the fuel completely. The complete oxidation reaction (i.e., complete combustion) produces lower $\Sigma\Delta H^\circ_f$ (products) as the combustion products. Thus, the concentration of oxygen atoms within the oxidizer represented by "oxygen balance:[OB]" is an important parameter to identify the potential of oxidizers. Oxygen balance is the amount of oxygen remaining after oxidizing hydrogen, carbon, magnesium, aluminum, etc. to produce H_2O, CO_2, MgO, Al_2O_3, etc. If excess oxygen molecules remain after the oxidation reaction, the oxidizer is termed to have a "positive" oxygen balance. If the oxygen molecules are completely consumed and excess fuel molecules remain, the oxidizer is termed to have a "negative" oxygen balance.[3]

Since the reaction of an oxidizer composed of a $C_aH_bN_cO_dCl_eS_f$ oxidizer is represented by

$$C_aH_bN_cO_dCl_eS_f \rightarrow a\,CO_2 + 1/2\,(b-e)\,H_2O + c/2\,N_2 + e\,HCl + f\,SO_2 - \{(a+f) + 1/4(b-e) - d/2\}\,O_2$$

The oxygen balance, expressed as mass percent, is given by

$$[\mathrm{OB}] = -\{(a+f)+1/4(b-e)-d/2\}\times \frac{32}{\text{molecular mass of oxidizer}}\times 100$$

For example, NG produces excess oxygen molecules during its combustion as given by

$$C_3H_5N_3O_9 \rightarrow 3\,CO_2 + 5/2\,H_2O + 3/2\,N_2 + 1/4\,O_2$$

The oxygen balance of NG is given by

$$[\mathrm{OB}]_{NG} = 1/4\times\frac{32}{227}\times 100 = +3.52\%$$

The oxygen balance for any type of oxidizer can be obtained by assuming the oxidized products as shown above. Table 3 shows the oxygen balance for some ingredients used in propellants.

2.2 Characterization of Energetic Materials

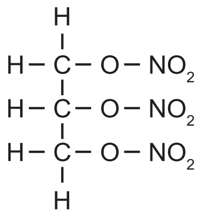
Typical materials containing oxygen and nitrogen atoms are known as nitrate esters and include nitrocellulose (NC) and nitroglycerin (NG). Nitrate esters consist of $-O-NO_2$ chemical bonds in their structures. The oxidizer component is oxygen, and the fuel components are carbon and hydrogen. The oxidized combustion products are CO_2 and $H_2O_{(g)}$ for which ΔH°_f are –8.94 and –13.42 MJ/kg, respectively as shown in Table 2. The nitrogen atoms in the reactants produce nitrogen gas for which ΔH°_f is zero (Table 2). Also materials containing a $-C-NO_2$ bond such as trinitrotoluene [TNT : $C_7H_5N_3O_6$] and tetryl ($C_7H_5N_5O_8$), those containing a $-N-NO_2$ bond such as RDX ($C_3H_6N_6O_6$) and HMX ($C_4H_8N_8O_8$), and those containing a $-N{=}N^{-}{=}N^{+}$ bond such as lead azide ($Pb(N_3)_2$) and glycidyl azide polymer [GAP : $C_3H_5N_3O$] are high-energy materials useful for propellants.[5,6] These materials act to produce CO_2 and N_2 through the following chemical bonds that are attached to the oxidizers:

$$\begin{array}{lll} -C-NO_2 & & \\ -O-NO_2 & \rightarrow & O{=}C{=}O \\ -N-NO_2 & & N{\equiv}N \\ -N{=}N^{-}{=}N^{+} & & \end{array}$$

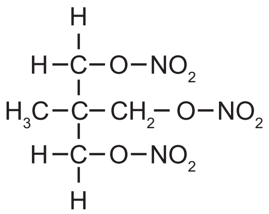
Thus, a high H_{exp} as shown in equation 2 is obtained by the combustion of materials containing these chemical bonds. Molecular structures of typical energetic materials are shown in Figure 1. All these materials contain $-O-NO_2$ or $-N-NO_2$ bonds.

Crystalline materials such as KNO_3, NH_4NO_3, and NH_4ClO_4 are used as oxidizers due to the high concentration of oxygen atoms in their molecules. These materials generate oxidizing fragments when thermally decomposed. On the other hand, hydrocarbon polymers such as polyurethane and polybutadiene generate gaseous fuel fragments when thermally decomposed. Thus, the mixture of an oxidizer and a hydrocarbon polymer forms a composite propellant. Accordingly, a composite propellant generates high temperature gases during combustion.

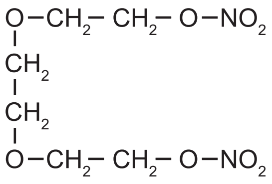
The mechanical properties of propellants are important to produce desirable propellant grains.



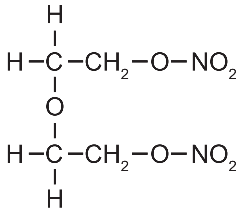
Nitroglycerine (NG)



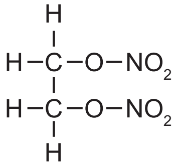
Trimethylolethane trinitrate (TMETN)



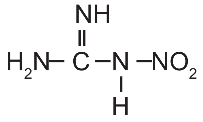
Triethyleneglycol dinitrate (TEGDN)



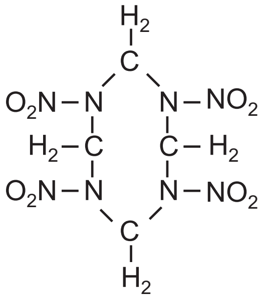
Diethyleneglycol dinitrate (DEGDN)



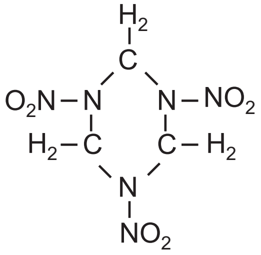
Nitroglycol (NGC)



Nitroguanidine (NQ)



Cyclotetramethylene tetranitramine (HMX)



Cyclotetramethylene trinitramine RDX

Figure 1. Molecular structures of energetic materials used for propellants.

The mass burn rate of propellant is dependent not only on the linear burn rate of the propellant but also on the burning surface area of the propellant grain. During pressure transient processes, such as ignition and oscillatory burning in a rocket motor, very high mechanical stresses are produced in the propellant grain. If the internal grain shape is complicated, these stresses may damage the propellant grain. The increased burning surface area caused by unexpected damage to the grain, such as cracks, increases pressure in the combustion chamber. Furthermore, the elongation property (elasticity) decreases as the temperature decreases. This may cause damage to the grain when mechanical shock is applied to the grain at low temperature. On the other hand, mechanical strength decreases as temperature increases. This may allow deformation of the grain due to its mass. Accordingly, the propellant grain geometry should be maintained by adequate elongation and strength properties of the propellant.

3. Propellant Ingredients

3.1 Homogeneous Propellants

Nitrocellulose (NC) is a major energetic ingredient used for single-base and double-base propellants. As shown in Table 3, NC is a nitrate ester composed of carbon, hydrogen, nitrogen, and oxygen atoms. The oxygen atoms are attached as $–O–NO_2$ with a nitrogen atom. When NC is thermally heated, NO_2 is formed because the O–N bond is the weakest of the NC chemical bonds. The remaining oxygen then forms aldehydes such as HCHO and CH_3CHO. The reaction between NO_2 and aldehydes produces heat and the combustion gases that are used for propulsive forces in rockets, guns, and pyrotechnics.

In general, NC is produced from cellulose, $\{C_6H_7O_2(OH)_3\}_n$, of cotton or wood, which is nitrated using nitric acid (HNO_3) to gain $–O–NO_2$ bonds in its structure as

$$\{C_6H_7O_2(OH)_3\}_n + x\,HNO_3 \rightarrow (C_6H_7O_2)_n(OH)_{3n-x}(ONO_2)_x + x\,H_2O$$

Through this nitration the –OH contained within the cellulose is replaced with $–O–NO_2$; the degree of nitration determines the energy available to form high temperature combustion gases. The maximum nitration is obtained when the nitrogen mass becomes 14.14% within NC.

The major ingredient of single-base propellant is NC. Diphenylamine, $(C_6H_5)_2NH$, is also added as a chemical stabilizer. In some cases, a small amount of K_2SO_4 or KNO_3 is mixed as a flame suppressor. Ethyl alcohol (C_2H_5OH) or diethylether ($C_2H_5OC_2H_5$) is mixed within the NC to soften it and to gain an adequate size and shape of the propellant grain. The grain surface is coated with carbon black to keep the surface smooth.

Table 4. Physicochemical Properties of Nitrate Esters Used for Double-Base Propellants.

Nitrate Ester	N (%)	Density (ρ) (g/cm^3)	ΔH°_f(r) (MJ/kg)	H_{exp} (MJ/kg)	T_m (°C)	[OB] (%)
diethyleneglycol dinitrate [DEGDN : $(CH_2)_4O(ONO_2)_2$]	14.29	1.38	–2.208	4.852	2	–40.8
triethyleneglycol dinitrate [TEGDN : $(CH_2)_6O_2(ONO_2)_2$]	11.67	1.34	–2.526	3.140	–19	–66.7
trimethylolethane trinitrate [TMETN : $CH_3C(CH_2)_3(ONO_2)_3$]	16.46	1.47	–1.610	5.527	–3	–34.5

Table 5. Plasticizers and Stabilizers Used for Double-base Propellants.

Plasticizers and Stabilizers	N (%)	Density (ρ) (g/cm^3)	ΔH°_f(r) (MJ/kg)	[OB] (%)
dibutylphthalate [DBP : $C_{16}H_{22}O_4$]	0	1.045	–3.027	–224.2
triacetin [TA : $C_9H_{14}O_6$]	0	1.15	–5.606	–139.4

A double-base propellant is also known as smokeless powder (propellant) when used for guns and rockets. Two major ingredients are used to formulate double-base propellant grains: NC and nitroglycerin (NG). NG, $C_3H_5(ONO_2)_3$, is also a nitrate ester characterized with the $–O–NO_2$ structure and is a high explosive. Since NG is liquid at room temperature, NG is absorbed by the NC and acts to gelatinize NC to form double-base propellant grains. Nitroglycol (NGC) has similar physicochemical properties to NG and is used as an additive to reduce the freezing point of NG.

Since NG is highly shock sensitive, other types of nitrate esters can be used to formulate non-NG double-base propellants. Diethyleneglycol dinitrate [DEGDN : $(CH_2)_4O(ONO_2)_2$], triethyleneglycol dinitrate [TEGDN : $(CH_2)_6O_2(ONO_2)_2$], and trimethylolethane trinitrate [TMETN : $CH_3C(CH_2)_3(ONO_2)_3$] are typical examples of energetic nitrate esters that are mixed with NC. Though these nitrate esters are less energetic than NG, the mass fraction of desensitizers is less than that of NC/NG double-base propellants. The physicochemical properties of these nitrate esters are shown in Table 4.

Two production methods are used to produce double-base propellant grains: (1) extrusion using an external mechanical press and (2) casting using finely divided NC powders or NC/NG powders. The extrusion method is used for grains less than 0.1 kg, typically used in guns and pyrotechnics. The casting method is used for grains larger than 1 kg such as rockets. Since NG is a detonative explosive, the concentration of NG is kept less than approximately ξ(0.5) for double-base propellants. Furthermore, various chemicals such as plasticizers, stabilizers, and burn rate modifiers are added to NC/NG mixtures to improve the physicochemical properties of double-base propellants.

The mechanical properties and shock sensitivities of double-base propellants are highly dependent on the mixture ratio of NC and NG. Though the specific impulse of double-base propellants increases with the concentration of NG, the strength of the propellant decreases. It becomes difficult to maintain grain shape when the concentration of NG is as high as ξ(0.5). For example, dynamites contain more than ξ(0.8) NG, and their grains are very soft and have high shock sensitivity. When the concentration of NC becomes higher than ξ(0.6), the elongation properties become poor. Thus, double-base propellants need to contain desensitizers, stabilizers, and chemicals to improve mechanical properties. In order to obtain superior mechanical properties, plasticizers such as dibutylphthalate [DBP : $C_{16}H_{22}O_4$]; diethylphthalate [DEP : $C_{12}H_{14}O_4$]; triacetin [TA : $C_9H_{14}O_6$]; and stabilizers such as ethyl centralite [EC : $CO\{N(C_6H_5)(C_2H_5)\}_2$] are added. Table 5 shows the physicochemical properties of the plasticizers and stabilizers used for double-base propellants. These chemicals are used to obtain superior grain formation and to improve mechanical properties, shock sensitiveness and chemical stability.[5,6]

The I_{sp} and T_f (the adiabatic flame temperature) of double-base propellants are dependent on the mass fraction of NG, ξ(NG), mixed within the NC and other chemicals. When a double-base propellant is composed of NG and NC, the maximum I_{sp} and T_f are obtained at ξ(NG) = 0.80 as shown in Figure 2. However, some plasticizers and stabilizers such as DEP or TA are needed for practical use of double-base propellants as shown in Table 6. In general, the mass fraction of ξ(DEP) = 0.10 is needed to gain superior mechanical properties. Thus the I_{sp} and T_f are reduced approximately 5% by the addition of DEP.

Table 6 *[next page]* shows materials used to formulate double-base propellants. Typical examples of chemical compositions and energetics of double-base propellants are shown in Table 7.

Table 7. Chemical Compositions and Energetics of Typical Double-Base Propellants.

NC	NG	DEP	2NDPA	T_f (K)	H_{exp} (MJ/kg)
53.0	40.5	4.0	2.5	2800	4.62
48.0	36.7	13.0	2.3	2200	3.78

3.2 Heterogeneous Propellants

3.2.1 Composite Propellants

When crystalline oxidizer particles are mixed with a hydrocarbon polymer, a heterogeneous propellant, or "composite propellant", is formed. Unlike double-base propellants, the physical structure of composite propellants is heterogeneous due to the dispersed crystalline particles within the polymer. As described previously, at the burning surface of the propellant, the oxidizer particles generate gaseous oxidizing fragments, and the polymer generates gaseous fuel fragments. Both gaseous fragments diffuse with each other and react to generate heat and combustion products. Accordingly, ballistic properties, such as burn rate and pressure sensitivity, are dependent not only on the chemical properties of oxidizers and binders but also are dependent on the shape and size of the oxidizer particles.

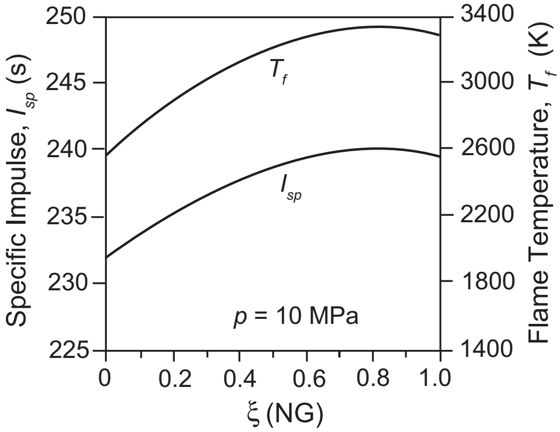


Figure 2. Combustion performance of double-base propellant as a function of the mass fraction of NG.

The major oxidizer used for composite propellants is ammonium perchlorate [AP : NH_4ClO_4]. When AP is heated, it decomposes as

$$NH_4ClO_4 \rightarrow NH_3 + HClO_4$$

$$HClO_4 \rightarrow HCl + 2\ O_2$$

The oxidizing fragments react with fuel fragments when these crystalline materials are mixed with fuel components, for example,

$$NH_4ClO_4 + C_mH_n \text{ (hydrocarbon polymer)} \rightarrow CO_2 + H_2O + N_2 + HCl$$

This reaction produces significant heat and gaseous molecules, which yields a high I_{sp} as defined in equation 1.

Ammonium nitrate [AN : NH_4NO_3], is a halogen-free oxidizer that produces nontoxic combustion products. However, disadvantages of AN compared with AP are hygroscopicity and crystal structure transitions at 125.2, 84.2, 32.3, and –16.9 °C. These transitions produce internal mechanical stresses in the propellant grain, which sometimes damages the grain. Though potassium nitrate [KN : KNO_3], and potassium perchlorate [KP : $KClO_4$], produce high temperature combustion products, the combustion products contain potassium oxide

Table 6. Ingredients Used for Double-Base Propellants.

Plasticizer (Oxidizer and Fuel)	
NG	Nitroglycerin
TMETN	Trimethylol ethane trinitrate
TEGDN	Triethylene glycol dinitrate
DEGDN	Diethylene glycol dinitrate
DNT	Dinitrotoluene

Plasticizer (Fuel)	
DEP	Diethylphthalate
DBP	Dibutylphthalate
TA	Triacetine
PU	Polyurethane

Burn Rate Catalyst	
PbSa	Lead salicylate
PbSt	Lead stearate
Pb2EH	Lead 2-ethylhexanoate
CuSa	Copper salicylate
CuSt	Copper stearate
LiF	Lithium fluoride

High Energy Additive (CMDB Propellant)	
RDX	Cyclotrimethylene trinitramine
NQ	Nitroguanidine
HMX	Cyclotetramethylene tetranitramine
CL-20	Hexanitrohexaazaisowurtzitane
ADN	Ammonium dinitramide

Coolant (Fuel)	
OXM	Oxamide
TAGN	Triaminoguanidine nitrate

Plasticizer (Energetic Fuel)	
GAP	Glycidyl azido polymer
BAMO	bis-azide methyl oxetane
AMMO	3-azidomethyl-3-methyl oxetane

Binder (Fuel and Oxidizer)	
NC	Nitrocellulose

Stabilizer	
EC	Ethyl centralite
2NDPA	2-nitrodiphenylamine
DPA	Diphenylamine

Burn Rate Catalyst Modifier	
C	Carbon black (used with lead or copper salts)

Oxidizer (CMDB Propellant)	
AP	Ammonium perchlorate
HNF	Hydrazinium nitroformate

Combustion Instability Suppressant	
Al	Aluminum
Zr	Zirconium
ZrC	Zirconium carbide

Opacifier	
C	Carbon black

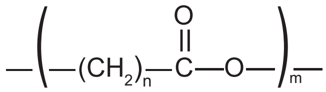
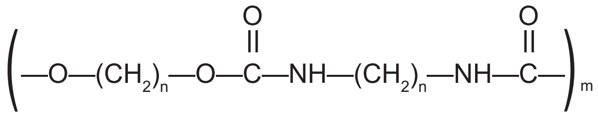
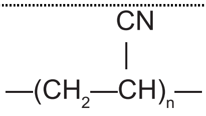
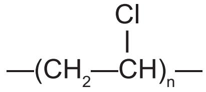
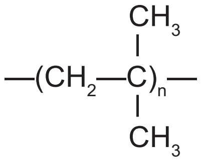
Metal Fuel	
Al	Aluminum

(K_2O), which has high M_c and significantly reduced I_{sp}. KN is a well-known oxidizer used as the oxidizer in Black Powder. KP is also used as an oxidizer in pyrotechnic compositions (pyrolants).

The binders, used to adhere oxidizer particles to form propellant grains, are also fuel ingredients. Table 8-1 shows typical polymers and their basic polymer unit that are used for composite propellants.

The binders are based on hydrocarbon polymers that have a relatively low viscosity during the process of mixing the oxidizer particles and the polymer before the curing process. Two types of polymers are commonly used for modern propellants: (1) polyurethane copolymer and (2) polybutadiene copolymer. (Polyether and polyester types of polyurethane copolymers are used.) The molecular concentration of hydrogen contained within polybutadiene copolymers is relatively high, and the heat of formation is also high. Also, the viscosity of the copolymer is low enough to allow mixing with oxidizer particles before curing.

Table 8-1. Types of Polymers Used for Composite Propellants.

Polymeric Binder	Basic Polymer Unit
Polyester	 $-\left(-(CH_2)_n-\overset{\overset{O}{\parallel}}{C}-O-\right)_m-$
Polyethylene	$\left(-(CH_2)-(CH_2)-\right)_n$
Polyurethane	 $\left(-O-(CH_2)_n-O-\overset{\overset{O}{\parallel}}{C}-NH-(CH_2)_n-NH-\overset{\overset{O}{\parallel}}{C}-\right)_m$
Polybutadiene	$-(CH_2-CH=CH-CH_2)_n-$
Polyacrylonitrile	 $-(CH_2-\overset{\overset{CN}{\vert}}{CH})_n-$
Polyvinyl chloride	 $-(CH_2-\overset{\overset{Cl}{\vert}}{CH})_n-$
Polyisobutylene	 $-(CH_2-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}})_n-$

Since composite propellants consist of crystalline particles and a polymeric binder, the mechanical properties of propellant grains are dependent on the physical and chemical properties of these ingredients and also on the additives such as bonding agents, surfactants, crosslinkers, and curing agents. The binder, as well as the mass fraction and particle size of the oxidizer, determine the characteristics of mechanical strength and elongation.

The polymers chosen for composite propellants are dependent on application conditions. Low viscosity is needed to allow high concentrations of AP particles, aluminum powders, and metallic powders used for burn rate modifiers to achieve high I_{sp}. Hydroxy-terminated polybutadiene (HTPB) is considered to be the best binder to obtain both high combustion performance and superior elongation properties at low temperatures and is widely used for modern composite propellants. HTPB is characterized with a terminal –OH on a butadiene polymer. The functionality of the HTPB prepolymer is also an important chemical parameter during the process of curing and crosslinking to achieve superior mechanical properties of the HTPB binder. Another useful butadiene polymer is carboxy-terminated polybutadiene (CTPB) that is characterized with a terminal –COOH on a butadiene polymer. HTPB and CTPB form regularly distributed matrices of polymers through crosslinking reactions.

Table 8-2 [at the end of the chapter] shows chemical processes and molecular structures of typical binders used for composite propellants. Polysulfide binder is formed with LP-3 polymer and PQD curative whose process produces H_2O. Polyurethane binder is formed with either NPGA polyester or D-2000 polyether and TDI curative. CTPB binder is formed with HC-434 polymer and MAPO imin-type curative or ERLA-0510 epoxy-type curative. HTPB binder is formed with R-45M polymer and IPDI curative. Polybuthadine-acrylonitrile (PBAN) is used as the binder in the booster propellant of the Space Shuttle.

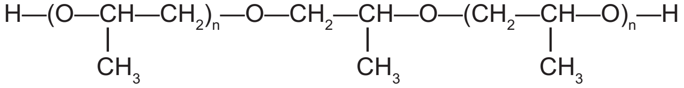
Table 8-3. Chemical Properties of HTPE and HTPS Binders.

Binder	Chemical Formula	$\xi(O)^{(a)}$	$\Delta H_f^{o(b)}$
HTPE	$C_{5.194}H_{9.840}O_{1.608}N_{0.194}$	25.7	–302
HTPS	$C_{4.763}H_{7.505}O_{2.131}N_{0.088}$	34.1	–550

a) Oxygen concentration, % by weight

b) Heat of formation (298 K), kJ/mol

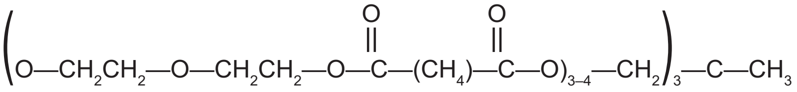
Polyether pre-polymer



$$H—(O—\underset{CH_3}{CH}—CH_2)_n—O—CH_2—\underset{CH_3}{CH}—O—(CH_2—\underset{CH_3}{CH}—O)_n—H$$

Where n = 17

Polyester pre-polymer



$$\left(O—CH_2CH_2—O—CH_2CH_2—O—\overset{\overset{\displaystyle O}{\|}}{C}—(CH_4)—\overset{\overset{\displaystyle O}{\|}}{C}—O)_{3–4}—CH_2\right)_3—C—CH_3$$

Since the concentration of oxygen within a binder is dependent on the molecular structure of the binder, high oxygen concentration binders are used to formulate HMX- or RDX-based composite propellants because these nitramines produce no excess oxygen fragments when decomposed. The binders are used to generate gaseous fragments without oxidation when mixed with these nitramines. Table 8-3 shows the chemical properties of HTPE and HTPS that contain a relatively high concentration of oxygen. Using these binders it is possible to formulate high-energy nitramine based composite propellants.

To gain superior mechanical properties, a small amount of bonding agent is added to adhere each oxidizer particle to the binder. As shown in Figure 3a, the maximum I_{sp}, 259 s (p = 10 MPa), is obtained when the mass fraction of AP, ξ(AP), is 0.89 mixed with the mass fraction of HTPB binder of 0.11.

To gain higher I_{sp} with AP-based composite propellants, aluminum particles are added as a fuel component. Though the addition of aluminum particles increases the M_c, the increase of T_f is the larger effect resulting in higher I_{sp}. The effect of aluminum addition on the adiabatic flame temperature is shown in Figure 3b. However, it should be noted that the maximum solid fraction within composite propellants is limited to approximately 0.85 due to mixing difficulties.

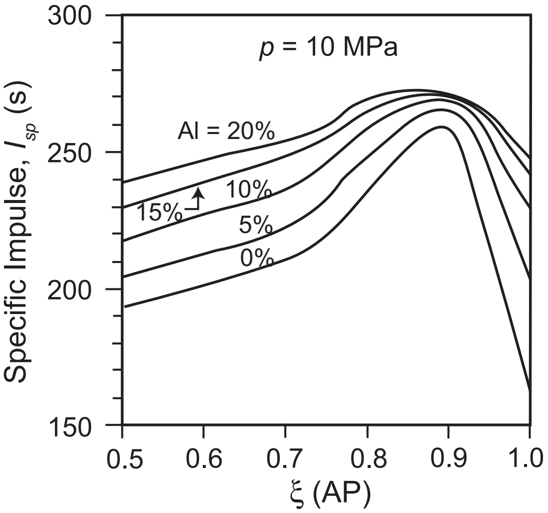


Figure 3a. Specific impulse of AP/HTPB/Al propellant as a function of the mass fraction of AP.

3.2.2 Smoke, Smokeless and Low IR Propellants

When aluminum particles are added to composite propellants, white smoke is generated due to the combustion product, aluminum oxide. If the smoke is not desirable because of military requirements or use in a fireworks display, aluminum cannot be used. Furthermore, if the atmosphere is very humid, white smoke is

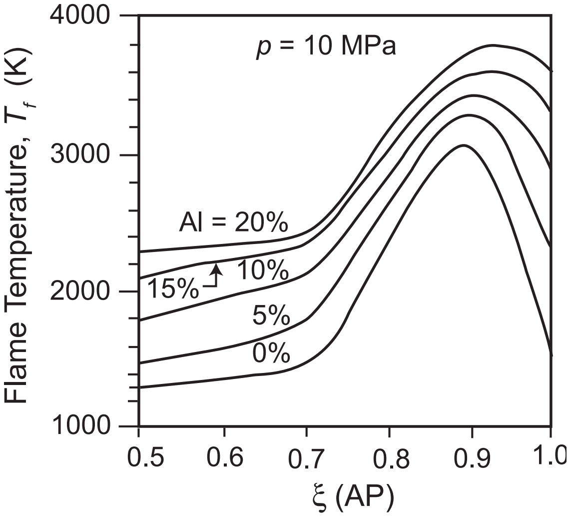


Figure 3b. Adiabatic flame temperature of AP/HTPB/Al as a function of the mass fraction of AP.

also generated due to the HCl produced as a combustion product. This is because the HCl molecule acts as a nucleus for moisture from the atmosphere, and relatively large-sized water drops are formed producing a fog or a mist. This occurs only when the humidity in the atmosphere is high or the temperature is low (below –10 °C). Double-base propellants are classified as smokeless propellants, and composite propellants, using AN as an oxidizer without halogen molecules, are also known as smokeless propellants. Figure 4 shows the nature of smoke exhausted from a rocket nozzle composed of (a) an AP/HTPB/Al composite propellant and (b) an NC/NG double-base propellant.

When HMX or RDX particles are mixed with a polymeric binder, nitramine-based composite propellants are formed. Though these nitramine particles contain excess oxidizer fragments to burn the binder, the binder is gasified by the heat generated by the combustion of these nitramines. The major combustion products are N_2, H_2, and CO; however, no CO_2, H_2O, or solid carbon (C) are formed when these propellants burn. This implies that infrared emission from the combustion products is reduced significantly. Nitramine composite propellants are useful for military rockets to gain stealth characteristics for launching sites and flight trajectories.

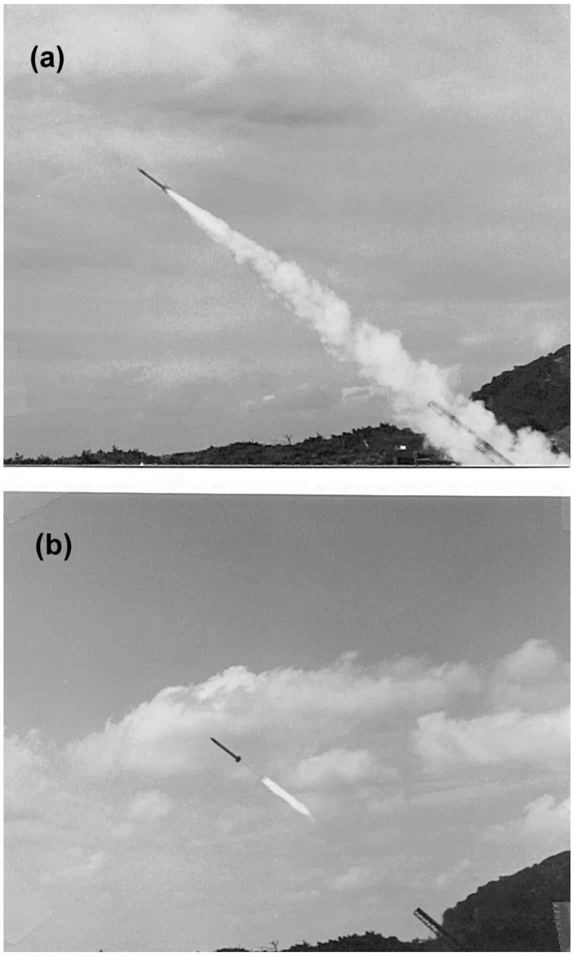


Figure 4. Rocket flight trajectories assisted by (a) an AP / HTPB / Al propellant and (b) an NC / NG double-base propellant.

3.2.3 Composite Modified Double-Base Propellants

The propellant composed of AP particles with NC/NG used as a binder is the so-called “ammonium perchlorate-based composite modified double-base propellant (AP-CMDB propellant)”. AP-CMDB propellant is called a composite propellant because of its physical structure. However, the binder of NC/NG burns by itself and produces numerous diffusional flamelets around each AP particle at the burning surface. The AP particles act as an oxidizer to increase T_f and I_{sp}. Figure 5 shows the T_f and I_{sp} of AP-CMDB propellants at p = 10 MPa as a function of ξ(AP). The base matrix used as a binder is composed of NC/NG = 1/1. The maximum T_f and I_{sp} are obtained at ξ(AP) = 0.5.

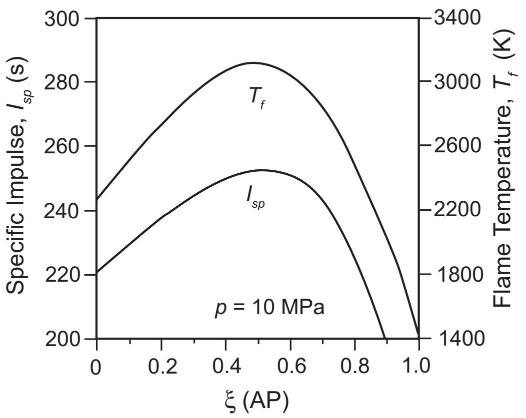


Figure 5. Combustion performance of AP-CMDB propellant as a function of the mass fraction of AP.

The propellant composed of nitramine particles and NC/NG is the so called "nitramine-based composite modified double-base propellant (nitramine-CMDB propellant)". HMX and RDX are typical nitramines used to formulate high energy CMDB propellants. Since HMX and RDX are stoichiometrically balanced energetic materials, they do not react with NC/NG used as a base matrix. These nitramines act as energetic additives to increase T_f and I_{sp} without chemical reactions. Thus, the T_f and I_{sp} of a nitramine-CMDB propellant appear to be mass averaged T_f and I_{sp} of the nitramines and the NC/NG base matrix.

Since the combustion products of nitramine-CMDB propellants are fundamentally smokeless, these propellants are used for military application. Furthermore, when these propellants burn, no acids are formed because nitramines are halogen-free materials.

Table 9 shows the materials used to formulate composite propellants. An example of the chemical composition of a composite propellant is shown in Table 10.

Table 9. Chemical Ingredients Used for Composite Propellants.

Oxidizer	
AP	ammonium perchlorate
AN	ammonium nitrate
HNF	hydrazinium nitroformate
Curing and/or Crosslinking Agent	
IPDI	isophorone diisocyanate
TDI	toluene-2,4-diisocyanate
PQD	paraquinone dioxime
HMDI	hexamethylene diisocyanate
MAPO	tris(1-(2-methyl)aziridinyl) phosphine oxide
Metal Fuel	
Al	aluminum
Plasticizer	
DOA	dioctyl adipate
IDP	isodecyl pelargonate
DOP	dioctylphthalate
High Energy Additive	
RDX	cyclotrimethylenetrinitramine
HMX	cyclotetramethylenetetranitramine
NQ	nitroguanidine
CL-20	hexanitrohexaazaisowurtzitane
ADN	ammonium dinitramide
Combustion Instability Suppressant	
Al	aluminum
Zr	zirconium
ZrC	zirconium carbide
Binder (Fuel)	
HTPB	hydroxy-terminated polybutadiene
CTPB	carboxy-terminated polybutadiene
PU	polyurethane
PS	polysulfide
PVC	polyvinyl chloride
Binder (Energetic Fuel)	
GAP	glycidylazido polymer
BAMO	bis-azidemethyloxetane
AMMO	3-azidomethyl-3-methyloxetane
Bonding Agent	
MAPO	tris(1-(2-methyl)aziridinyl) phosphine oxide
TEA	triethanolamine
MT-4	adduct of 2.0 moles MAPO, 0.7 mole adipic acid, and 0.3 mole tartaric acid

Table 9. Chemical Ingredients Used for Composite Propellants (Continued).

Burn Rate Catalyst	
Fe_2O_3	ferric oxide
FeO(OH)	hydrated ferric oxide
NBF	n-butyl ferrocene
LiF	lithium fluoride

HCl Suppressant	
Mg	magnesium
MgAl	magnalium
$NaNO_3$	sodium nitrate

Table 10. Chemical Composition and Combustion Products of a Typical Composite Propellant.

Ingredients (weight %)		
AP	HTPB	T_f, K
80.0	20.0	2358

Products (mole fractions)					
CO	CO_2	HCl	H_2O	N_2	H_2
0.251	0.055	0.143	0.244	0.075	0.213

3.3 Granulated Propellants

3.3.1 Black Powder

Granulated propellants are used in a loosely packed shape containing numerous individual grains or powders. Though single-base propellants normally are classified as homogeneous propellants, some propulsion applications use a packed shape consisting of granulated single-base propellant.

Black Powder is a typical granulated propellant used for propulsion and is used as a propellant for small-sized rockets, guns, and pyrotechnics. Though the theoretical I_{sp} of Black Powder is less than that of single-base, double-base, and AP-based composite propellants, Black Powder is useful for short-duration operations of simplified propulsive systems. The advantages of Black Powder are low cost, very low aging effect, and simple adjustment of propulsive forces by the amount used.

Black Powder is a mechanically mixed material of KN powder (60–80%), charcoal (10–25%), and sulfur (8–25%) that is pressed, granulated, and formed as a packed shape for use. When Black Powder is ignited, combustion occurs over all granulated surfaces. Thus, the rate of gas production becomes much higher than that of conventional propellants used for rockets. However, this combustion phenomenon is deflagration, not detonation. The burn rate of Black Powder is not defined as that of rocket propellants because of the nature of the granulated combustion, except when pressed in some applications. The overall gas production rate is an important combustion parameter, and it is dependent on the granulation size of the powder as well as the density of the packed shape. The specific impulse, I_{sp}, ranges from 60 to 150 s, and the combustion temperature ranges from 1400 to 3200 K. These values are determined by the mixture ratio of the ingredients. Table 11 shows the chemical composition and properties of typical Black Powder.

Table 11. Chemical Composition and Properties of Typical Black Powders.

Ingredient	Percentage
Potassium nitrate	60 – 80
Charcoal	10 – 25
Sulfur	8 – 25

Property	Range of Values
I_{sp}, s	60 – 150
Density, g/cm^3	1.2 – 2.0
Flame temperature, K	1400 – 3200

3.2.2 Gun Propellants

In general, powdered grains made of single-base, double-base, and triple-base propellants are classified as granulated propellants. These are used as gun propellants, and the burn time is on the order of 10 to 100 ms. The mass burn rate of these grains is very high because the web thickness (the length or thickness of the propellant grain) is very thin compared to rocket propellants, and the burning pressure is on the order of 100 to 1000 MPa. Though the physical structures of single-base and double-base granulated grains are essentially homogeneous, these grains burn independently in combustion chambers. Thus, the flame structures appear to be heterogeneous in nature. The shape of each grain is designed to obtain the desired pressure versus time relationship during burning. The reaction products of granulated propellants are essentially the same as single-base gun propellant and double-base rocket propellant. Table 12 shows the chemical composition of a typical single-base propellant.

Table 12 Chemical Composition and Energetics of a Typical Granulated Single-base Propellant.

Ingredients (mass %)				
NC	DNT	DBP	DPA	T_f, K
85.0	10.0	5.0	1.0	1598

Products (mol/kg)				
CO_2	CO	H_2O	H_2	N_2
2.32	22.84	5.81	9.55	4.39

4. Reaction of Propellants

4.1 Thermal Decomposition Process

There have been numerous studies on the decomposition of propellants and their ingredients to elucidate the aging mechanisms and burn rate characteristics. Various types of experimental techniques are used: (1) differential thermal analysis (DTA), (2) thermogravimetric analysis (TG), (3) Fourier transform infrared analysis (FTIR), (4) Raman spectrum (RS), (5) gas chromatography (GC), and (6) scanning electron microscopy (SEM). Since the chemical process of aging is very slow and the decomposition process for combustion is very fast, the experimental techniques shown above are applied at accelerated conditions for aging analysis and at decelerated conditions for combustion process analysis.

Typical examples of the thermal decomposition process of AP as obtained by DTA and TG are shown in Figure 6. These experiments are conducted to determine the endothermicity and/or exothermicity of AP decomposition. The AP sample size is 5 mg in a quartz cell under an argon atmosphere. The heating rate of the cell is varied from test to test and ranges from 0.08 to 0.33 K/s. An endothermic peak is seen at 520 K, and an exothermic peak is seen at 720 K using a heating rate 0.33 K/s.

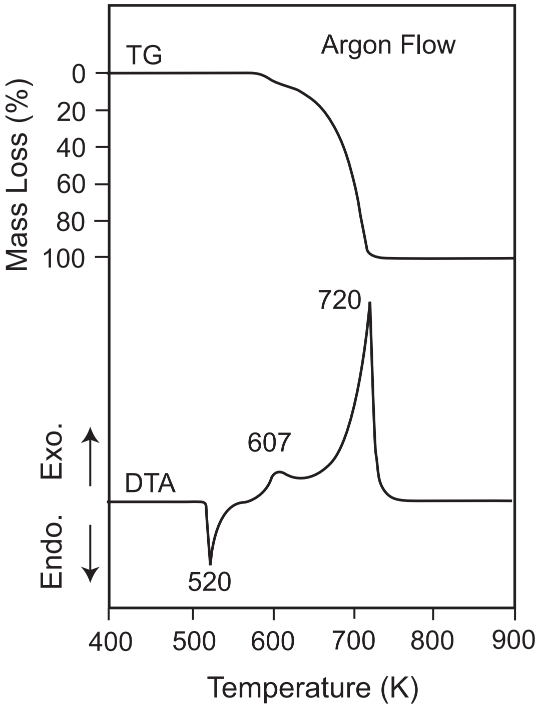


Figure 6. Thermochemical data of AP obtained by DTA and TG showing an endothermic peak at 520 K and an exothermic peak at 720 K.

When the heating rate is increased, these peaks shift toward higher temperatures. As shown in Figure 7, the plot of reciprocal temperature versus heating rate produces a straight line that determines the activation energy of the observed phenomenon. Based on data at different heating rates, the activation energy E_a for the decomposition is determined to be 134 kJ/mol. The activation energy of the burning surface decomposition is used to determine burn rate characteristics at high-pressure conditions.

4.2 Characteristics of Thermal Decomposition

The thermal decomposition process is different for each material. For example, the exothermicity of NG is different from that of NC even though both are nitrate esters. Also, the exothermicity of a double-base propellant that

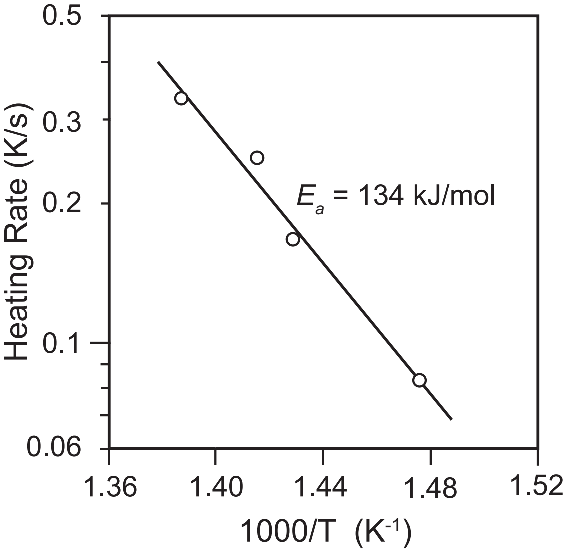


Figure 7. Arrhenius plot of reciprocal exothermic peak temperature as a function of heating rate obtained by DTA.

is a mixture of NG and NC appears to be different from that of either NG or NC and is also different from an averaged value for NG and NC. This indicates that the thermal decomposition property of propellant is not an averaged value of each propellant ingredient. Furthermore, the exothermicity of an AP-based composite propellant is much higher than the sum of the exothermicity of each ingredient because an exothermic oxidation reaction occurs between AP and the binder.

Though the aging chemistry of propellants is complicated, the surface chemistry between oxidizer particles and binder plays a dominant role in determining the aging period. No definite methods are available to quantify such a very slow reaction mechanism, however, one can estimate it through theoretical analysis based on the data from DTA, TG, and other thermal measurement equipment.

The thermal decomposition at the burning surface of a propellant is more than ten thousand times higher than that of DTA and TG heating rates. Though the data obtained by DTA and TG cannot be applied to determine ballistic characteristics, these are used to determine the thermal properties of propellant burning.

5. Combustion of Propellant

5.1 Combustion Wave Structure of Propellants

5.1.1 Combustion Zone

The burn rate of solid propellant is dependent on various physicochemical parameters such as propellant chemical ingredients, particle size of crystalline oxidizers, chamber pressure, initial propellant temperature, and burn rate catalysts. A schematic representation of the combustion wave of a solid propellant is shown in Figure 8a. In the condensed phase (zone I), no chemical reactions occur, and the temperature increases from the initial temperature (T_0) to the decomposition temperature (T_d). In the solid phase reaction (zone II), the temperature increases from T_d to the burning surface temperature (T_s), where a phase change from solid to liquid and/or to gas occurs, and reactive gaseous species are formed. In the gas phase reaction (zone III), the temperature increases rapidly from T_s to the flame temperature (T_f), where an exothermic gas phase reaction takes place in the luminous flame (zone IV).

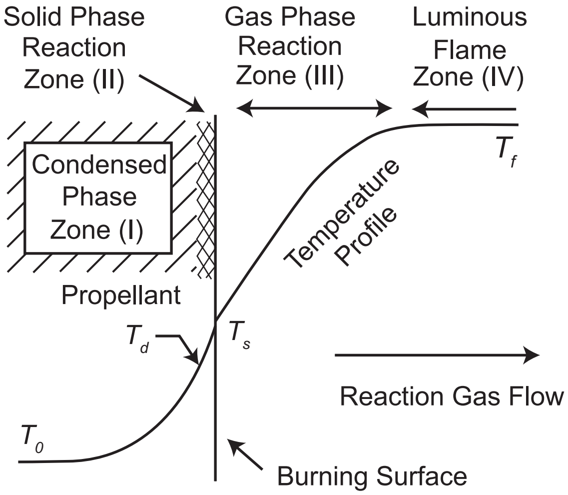


Figure 8a. Thermochemical structure of combustion wave of a solid propellant.

5.1.2 Heat Transfer Process

During the steady state burning of a propellant, the heat transfer in the combustion wave occurs as illustrated in Figure 8b. If one assumes that physical properties λ_g and c_g are constant in the gas phase, the energy conservation equation in the gas phase reaction (zone III) in the combustion wave is represented by

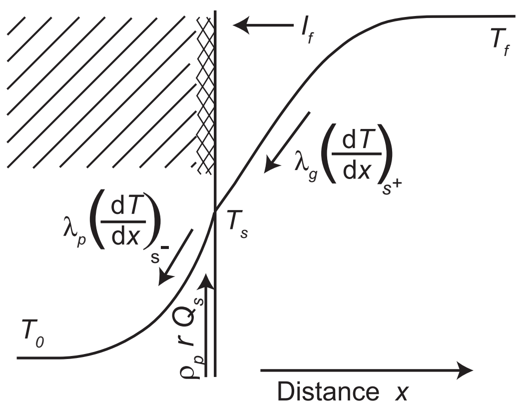


Figure 8b. Heat balance in combustion wave of a solid propellant.

$$\lambda_g\, d\varphi/dx - \rho_p r c_g \varphi + Q_g \omega_g(x) + I_f = 0 \qquad (3)$$

where the mass conservation-equation is represented by

$$m = \rho_g u_g = \rho_p r \qquad (4)$$

The overall reaction rate in the gas phase can be represented by

$$\omega_g \delta = \int \omega_g(x)\,dx = m \qquad (5)$$

At the burning surface, the heat flux feedback from the gas phase reaction (zone III) to the burning surface (zone II) by conductive heat transfer is given by

$$\Lambda_g = \lambda_g \phi \qquad (6)$$

where ϕ is the temperature gradient in zone III at the burning surface represented by

$$\phi = \left(\frac{dT}{dx}\right)_{s,III} \qquad (7)$$

The heat flux feedback from zone III to zone II by radiative heat transfer is given by

$$I_f = \beta T^4 \qquad (8)$$

The heat flux produced in zone II is given by

$$\Gamma_s = \rho_p r Q_s \qquad (9)$$

The heat flux feedback from the burning surface to the condensed phase (zone I) is given by

$$\Lambda_p = r \rho_p c_p (T_s - T_0) \qquad (10)$$

The overall heat balance at the gas/condensed phase interface is represented by

$$\Lambda_p = \Lambda_g + I_f + \Gamma_s \qquad (11)$$

The determination of the magnitude of each term of equation 11 is the center of research on the combustion study of solid propellants.

If one assumes that the radiative heat flux feedback from zone III to zone II is much smaller than the other terms, the burn rate is obtained by substituting equations 6, 9 and 10 into equation 11 and then solving for *r*

$$r = \alpha_s \frac{\phi}{\psi} \qquad (12)$$

where

$$\alpha_s = \frac{\lambda_g}{\rho_p} c_p \qquad (13)$$

$$\psi = T_s - T_0 - Q_s / c_p \qquad (14)$$

Equation 12 indicates that the burn rate of solid propellants is determined by two parameters: the gas phase parameter ϕ, which is determined by the physical and chemical properties in the gas phase, and the condensed phase parameter ψ, which is determined by the physical and chemical properties in the condensed phase.[3,17]

It is known that the burning rate is dependent on the initial propellant temperature T_0, the so-called temperature sensitivity of burning rate. For example, the heat required to raise the condensed phase temperature from T_0 to the burning surface temperature T_s decreases as T_0 increases. Accordingly, the burning rated increases as T_0 increases at constant pressure.[9–12]

5.2 Combustion of Homogeneous Propellant

5.2.1 Combustion Wave Structure

The combustion wave of a homogeneous propellant is known to consist of successive one-dimensional, homogeneous reaction zones. Figure 9 shows a typical example of the combustion wave of double-base propellants. There exist four reaction zones: surface, fizz, dark, and flame zones. The temperature increases smoothly from the initial propellant temperature T_0 to the burning surface temperature T_s, to the dark zone temperature T_d, to the flame zone temperature T_g.[7–9]

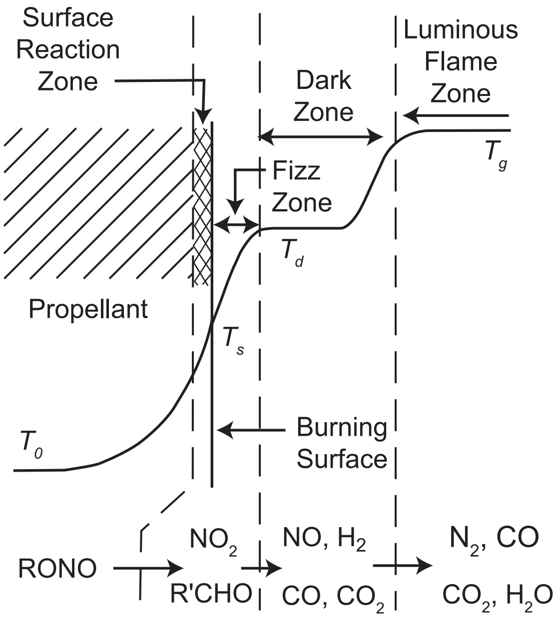


Figure 9. Combustion wave structure of a double-base propellant.

At the surface reaction zone (including subsurface reaction), NO_2 is formed due to the breaking of O–NO_2 bonds in the nitro groups of NC and NG. The decomposition of the remaining fragments follows, producing fuel components such as aldehydes. These combustible gaseous species react rapidly in the fizz zone and produce large amounts of heat. Thus, a steep temperature rise is observed in the fizz zone. In the succeeding dark zone, the NO produced by the reduction of NO_2 in the fizz zone reacts slowly, and the temperature also rises slowly. The NO and the rest of the fuel products react more rapidly after some elevated temperature is achieved at some distance from the burning surface and form the luminous flame zone. In this flame zone, the final combustion products, such as N_2, CO_2, H_2O, etc., are produced, and the temperature reaches its maximum. These reaction processes are largely dependent on pressure.

5.2.2 Burn Rate Characteristics

The burn rate of a double-base propellant is approximately a straight line in a log *p* versus log *r* plot. The pressure exponent, *n*, of the burn rate is determined to be 0.60. Table 13 shows the chemical compositions of double-base propellants—A, B, and C. As shown in Figure 10, the pressure exponent is unchanged even when the mass fraction of DEP is increased (H_{exp} is decreased by the increase of the mass fraction of DEP). The mixture ratio of NC/NG is kept at 1.31 for Propellants A, B, and C. It is evident that the burning rate increases as H_{exp} increases, also the burning rate increases as the energy contained in the unit mass of propellant increases.

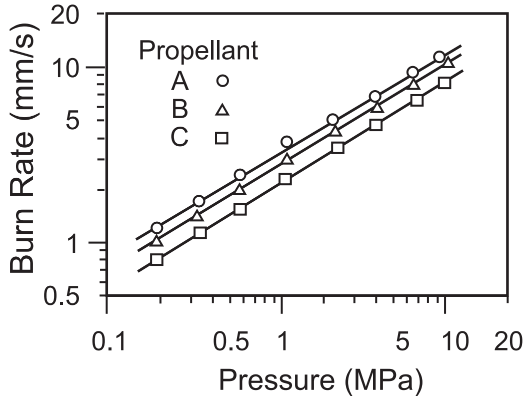


Figure 10. Burn rate of double-base propellants as a function of pressure showing that the pressure exponent remains unchanged when the mixture ratio of NC/NG is changed.

5.2.3 Dark Zone Reaction

The photographic observation of the flame structure shows that the luminous flame zone approaches the burning surface as the pressure increases. The dark zone length, which is approximately equal to the luminous flame standoff distance, L_d, (the fizz zone length is much

Table 13. Chemical Compositions of Propellants—A, B, and C Showing Increasing Mass Fraction of DEP.

Propellant	NC	N (%)	NG	DEP	2NDPA	H_{exp} (MJ/kg)	NC/CG
A	53.0	12.20	40.5	4.0	2.5	4.59	1.31
B	51.3	12.20	39.3	7.0	2.4	4.21	1.31
C	48.0	12.20	36.7	13.0	2.3	3.47	1.31

shorter than that of the dark zone), is represented by

$$L_d = ap^d \tag{15}$$

where d is the dark-zone pressure exponent. The reaction time to produce the luminous flame, t_d, is defined in

$$t_d = L_d / u_d \tag{16}$$

where u_d is the gas flow velocity in the dark zone. Applying the mass conservation equation given by equation 4 to the dark zone, one gets

$$r\rho_p = u_d \rho_d \tag{17}$$

The gas density in the dark zone, ρ_d, is proportional to pressure and the reaction time is proportional to p^{m-1} where m is the overall order of the reaction in the dark zone. In general, the burn rate is represented by

$$r = ap^n \tag{18}$$

where n is the pressure exponent of burning rate and a is constant that is dependent on the chemical composition and the initial temperature. Substituting equations 16 to 18 into equation 15, one gets

$$L_d = cp^{m-n} \tag{19}$$

where c is constant. As shown in Figure 11, d is determined to be –2.0. The overall reaction order in the dark zone, m, is determined to be approximately 2.6. This reaction order indicates that the reaction in the dark zone is more pressure sensitive than other gas-phase reactions of which reaction orders are approximately 2.0. It has been reported that the reaction involving NO as an oxidizer is a termolecular (or trimolecular) reaction (i.e., larger than 2.0). Thus, the reaction in the dark zone is responsible for the NO reduction to produce the final combustion product.

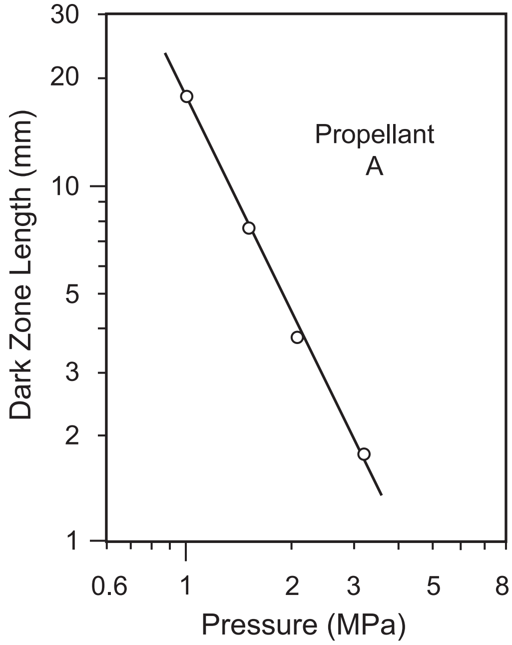


Figure 11. Dark zone length versus pressure for a double-base propellant A.

5.2.4 *Fizz Zone Reaction*

The temperature gradient in the fizz zone, $(\mathrm{d}T/\mathrm{d}x)_{s,f}$, is represented by

$$(\mathrm{d}T/\mathrm{d}x)_{s,f} = \frac{\omega_f Q_f}{\rho_p c_p r} \tag{20}$$

where Q_f is the heat of reaction in the fizz zone. The reaction rate in the gas phase is given by

$$\omega_f = p^k Z_f exp\left(\frac{-E_f}{RT_f}\right) \tag{21}$$

Substituting equation 21 into equation 20, one obtains the relationship between $(\mathrm{d}T/\mathrm{d}x)_{s,f}$ and pressure as

$$(\mathrm{d}T/\mathrm{d}x)_{s,f} \sim p^{k-m} \tag{22}$$

The results of the measurement of $(\mathrm{d}T/\mathrm{d}x)_{s,f}$ as a function of pressure show that $k - m$ appears to be constant for double-base propellants and is determined to be 0.85. Thus, the reaction order in the fizz zone is determined to be $k = 1.7$.

5.2.5 Burn Rate Characteristics

The burn rate of double-base propellants is determined by the heat flux transferred back from the gas phase to the burning surface as given by equation 12. The reaction rate in the fizz zone and the dark-zone temperature play a dominant role in burn rate. Since the mixture ratio of NC and NG alters the temperature profile in the gas phase, the heat flux is also altered.

Figure 12 shows that the burn rate of double-base propellants increases with increasing the energy contained within the unit mass of propellant that is represented by H_{exp} However, it must be noted that the burning rate is not determined by the temperature in the flame zone, T_g, but is determined by the increased reaction rate in the fizz zone. The reaction rate in the fizz zone increases as H_{exp} increases.

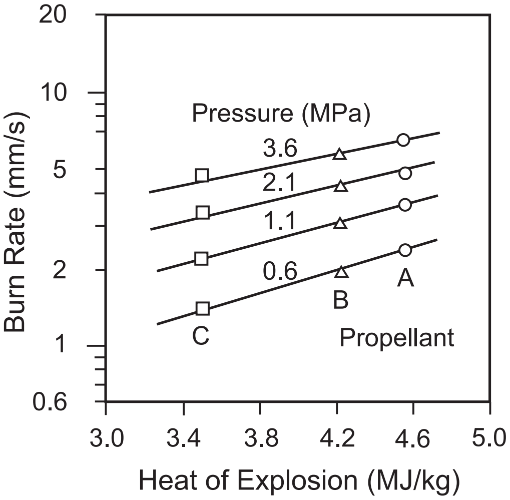


Figure 12. The burn rate of double-base propellant increases as the heat of explosion increases.

5.3 Combustion of Heterogeneous Propellant

5.3.1 Combustion Wave Structure

Heterogeneous propellants consist of crystalline oxidizer particles and a polymeric fuel binder. The decomposition process of these materials occurs on and above the burning surface of the propellant. The gaseous oxidizer and the fuel fragments generated at the burning surface diffuse and mix together above the burning surface. This binary diffusion process produces a reactive gaseous fragment that reacts to produce heat and a combustion product.

Figure 13 shows the combustion wave structure of an AP/HTPB composite propellant. Unlike those of a double-base propellant, the surface and gas phase reaction zones are heterogeneous because the AP particles decompose to produce an oxidizer fragment through the reaction process described in Section 3.2, and the HTPB binder decomposes to produce gaseous hydrocarbon fragments at the burning surface. These gaseous fragments diffuse with each other to produce reactive gases that combine to produce its final reaction product. Since the thermochemical properties of AP and HTPB are different, the temperatures of decomposition are different. In addition, the rates of decomposition of AP and HTPB are also different. Thus, not only the physical structure but also the thermal structure of the burning surface of the propellant becomes heterogeneous. As shown in Figure 13, the time-averaged temperature increases from the initial propellant temperature T_0 to the burning surface temperature T_s, and then to the flame temperature T_g.

5.3.2 Burn Rate Characteristics

The heat feedback from the gas phase to the burning surface is not only dependent on the reaction rate of the reactive gases above the burning surface, but also on the diffusion rate between the oxidizer and fuel fragments. Accordingly, the particle size of the oxidizer plays an important role in the determination of the heat flux feedback from the gas phase to the burning surface. The diffusion rate increases as the AP particle size decreases. As shown in equation 12, the burn rate is dependent on the heat flux feedback to the burning surface. Thus, one can conclude that the burn rate increases as the AP particle size decreases. Figure 14 shows

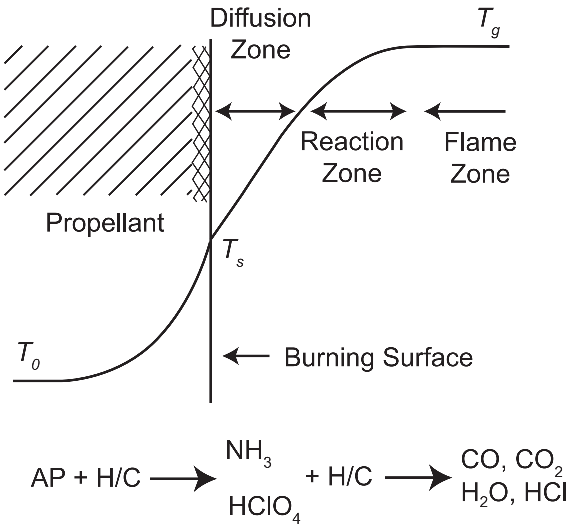


Figure 13. Combustion wave structure of an AP composite propellant. Note that "H/C" in the figure means hydrocarbon.

a typical example of burning rate versus pressure relationship of AP/HTPB composite propellants as a function of AP particle size.

The flame temperature T_f is dependent on the mass fraction of AP, ξ(AP), as shown in Figure 3b. It is shown that T_f increases as ξ(AP) increases at constant AP particle size. However, T_f reaches a maximum at ξ(0.87) and thereafter decreases as ξ(AP) increases. Since the burn rate is dependent on T_f as shown in equation 12, the burn rate becomes a function of ξ(AP). Thus the burn rate increases as ξ(AP) increases up to ξ(0.87) at constant AP particle size. Figure 14 shows the results of the effect of AP particle size on the burn rate of AP/HTPB propellants. It is evident that the burn rate increases as the particle size of AP particles decreases at constant ξ(AP). In addition, the burn rate increases as ξ(AP) decreases when the same size of AP particles is used.[2,3,8,9]

5.3.3 Combustion of CMDB Propellant

The AP particles mixed with an NC/NG matrix of an AP-CMDB propellant act as an oxidizer on and above the burning surface. The luminous flame streams are formed by diffusion of the AP oxidizer-rich gas and the NC/NG fuel-rich gas in the dark zone of the NC/NG matrix. As the mass fraction of the AP particles increases, the number of luminous flame streams increases until the dark zone is completely eliminated. The flame temperature in the dark zone is increased, and then the heat flux feedback from the gas phase of the propellant is increased by the addition of AP particles. Thus, the burn rate of AP-CMDB propellants depends largely on the mass fraction and the AP particle size mix.

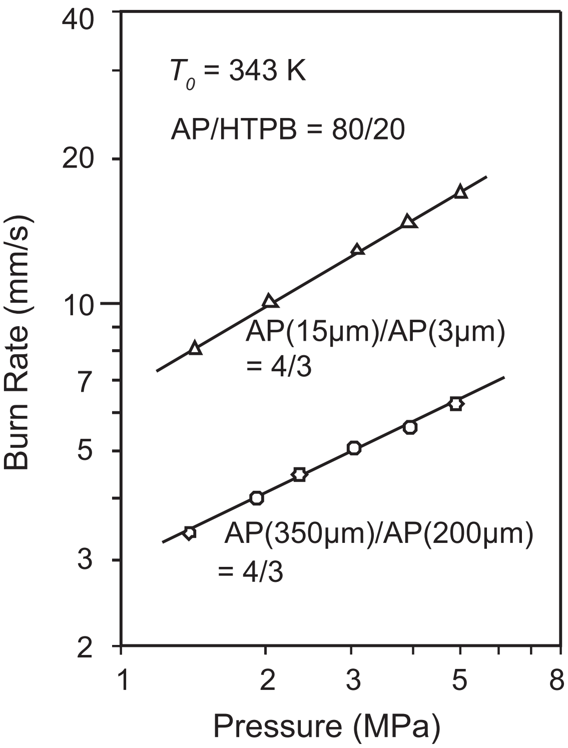


Figure 14. Burn rate of AP composite propellant showing that the burn rate increased with the mixing of fine AP particles.

On the other hand, nitramines such as HMX and RDX are stoichiometrically balanced energetic materials, and they produce high temperature combustion products without excess oxidizer fragments. Furthermore, the nitramine particles melt and diffuse on the NC/NG matrix and form homogeneously mixed gases above the burning surface. Thus, the gas phase structure appears to be similar to that of a double-base propellant. A luminous flame stands some distance above the burning surface, and a dark zone is formed between the luminous flame and the burning surface. The luminous flame approaches the burning surface as pressure increases.

As shown in Figure 15, the burn rate of HMX-CMDB propellant increases as pressure increases when ξ(HMX) remains constant. However, the burn rate decreases as ξ(HMX) increases at constant pressure. This indicates that the burn rate decreases as the energy contained within the unit mass of HMX-CMDB propellant increases. However, the burn rate appears to be less dependent on the HMX particle size mixed.

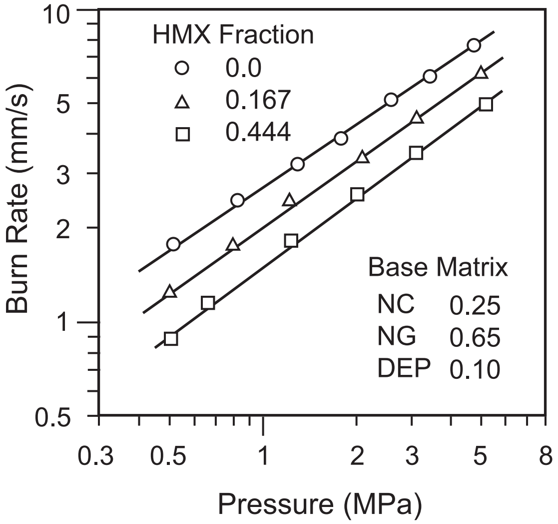


Figure 15. Burn rate of HMX-CMDB propellant as a function of the mass fraction of HMX.

TAGN is a unique energetic material that produces a high I_{sp} defined in equation 1. Table 14 shows the thermochemical properties of TAGN and HMX. Though the heat of formation of TAGN is much lower than that of HMX, the energetics defined in $(T_f / M_c)^{1/2}$ appears to be approximately equal for both materials. This is because the molecular mass (M_c) of the combustion products is low even though the flame temperature (T_f) is low due to the high mass fraction of hydrogen atoms contained within TAGN. In addition, the burn rate of TAGN is about double that of HMX at the same burn pressure. This occurs due to the ionic chemical bond of the HNO_3 molecule attached to the TAGN molecular structure. The pressure exponent (n) is 0.78 for TAGN and 0.66 for HMX. Since TAGN is a crystalline material similar to HMX, it is used to formulate a TAGN-CMDB propellant. When TAGN particles are mixed with a polymeric binder such as HTPE or HTPB, a TAGN-based composite propellant is formed as a cool propellant or a cool gas-generating material.

5.4 Combustion of Granulated Propellant

Each grain within a granulated propellant burns independently. When the grains are composed of a double-base propellant used for rockets, the linear burn rate of each grain appears to be the same as the burn rate of the double-base propellant in a rocket motor. Accordingly, the combustion wave structure of the granulated propellant made of a double-base propellant is the same as that of the double-base propellant. However, the difference between a granulated propellant and a rocket propellant is evident. The mass burn rate of the granulated grains is much faster than that of rocket grains because the burning surface area of the granulated grains is much larger than that of rocket grains.

When Black Powder is used as a propellant, the mass burn rate is much greater than granulated single-base and double-base propellants. This is due to the high porosity and small size of each grain of Black Powder. The burn rate is also dependent on the type of charcoal. Various charcoals are made from different types of trees. The porosity of charcoal is dependent on the type of tree used.

Table 14. Thermochemical Properties of TAGN and HMX.

	Symbol (Units)	TAGN	HMX
Chemical Formula →		$CH_9N_7O_3$	$C_4H_8N_8O_8$
Flame Temperature	T_f (K)	2055	3255
Molecular Mass	M_c (kg/kmol)	18.76	24.24
Heat of Formation	ΔH°_f (MJ/kg)	–0.28	+0.25
Energy Content	$[(T_f/M_c)^{1/2}]$ $(\text{K-kmol/kg})^{1/2}$	10.47	11.59

In general, granulated propellants are used to eject projectiles from launch tubes such as gun projectiles and to burst fireworks shells because they produce high pressure almost instantaneously. The ejection velocity of a projectile is determined by various parameters: projectile mass, launch tube length, pressure versus time in the launch tube. Detailed examination of the ejection process is accomplished by the analysis of interior ballistics.

Summary

The chemical ingredients mixed within propellants are used to gain various properties such as to increase specific impulse, to gain smokeless combustion products, to gain high or low burning rate, and to suppress combustion instability in a rocket motor, and so on. This chapter presents an overview of propellant chemistry to give information on the fundamentals of propellant combustion.

Since propellants are composed of energetic chemicals of oxidizer and fuel components, the reactivity and combustion are dependent on the physicochemical properties of the chemicals. When a propellant is ignited by an external heat source, the temperature of the propellant increases from the initial temperature of the propellant to the decomposition temperature without chemical reaction. When the temperature reaches the gasification temperature at the burning surface, reactive gases are formed on and above the surface.

In the gas phase, an exothermic reaction occurs, the final combustion products are formed, and the temperature reaches the maximum. The heat flux transferred back from the high temperature gas to the burning surface increases the propellant temperature to gain a successive burning.

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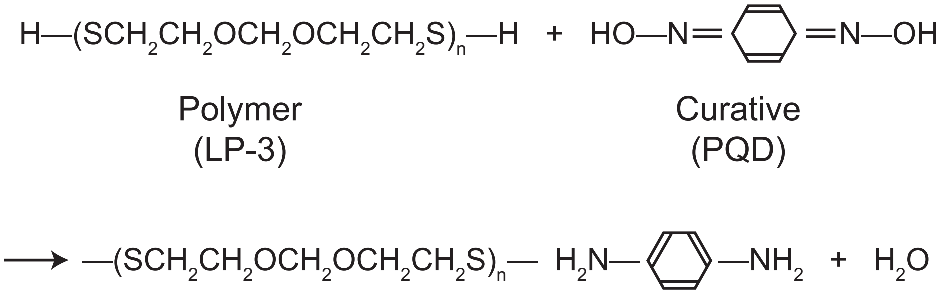
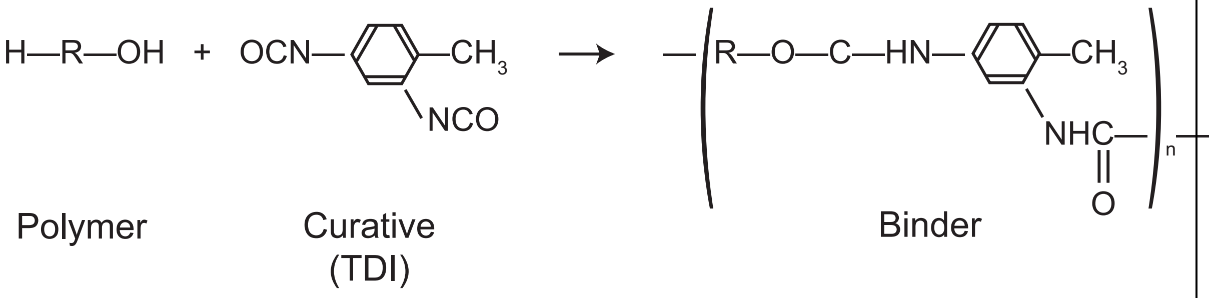
Table 8-2. Chemical Processes and Molecular Structures of Typical Binders Used for Composite Propellants.

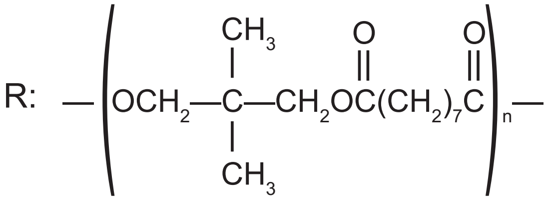
Polysulfide



Polyurethane

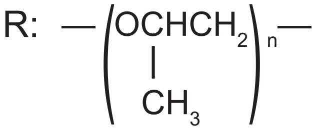


Polyester-type (NPGA)



$$R:\ -\left(OCH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2O\overset{\overset{O}{\|}}{C}(CH_2)_7\overset{\overset{O}{\|}}{C}\right)_n-$$

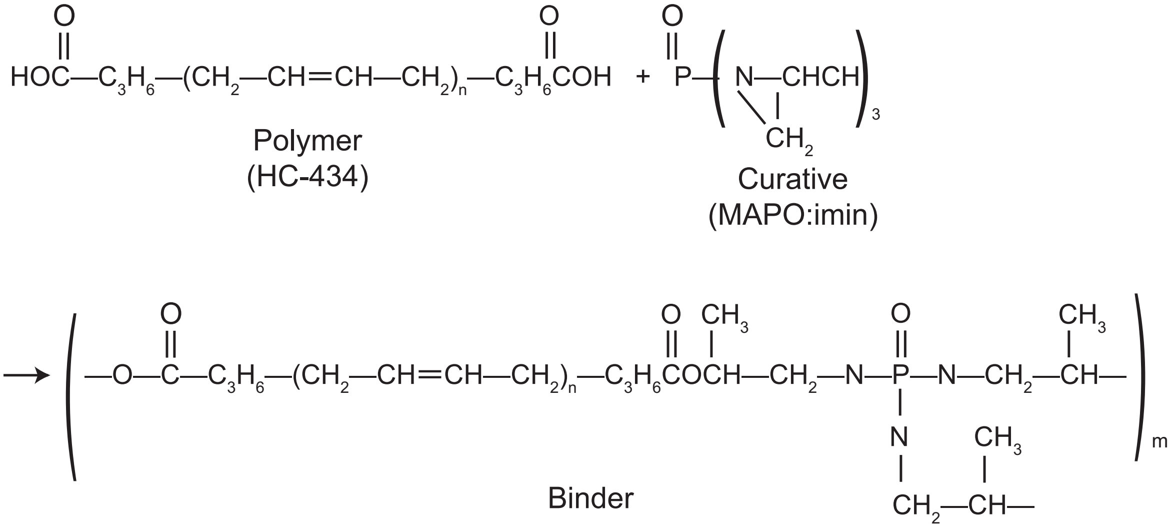
Polyether-type (D-2000)



$$R:\ -\left(O\underset{\underset{CH_3}{|}}{C}HCH_2\right)_n-$$

Table 8-2. Chemical Processes and Molecular Structures of Typical Binders Used for Composite Propellants. (Continued)

Carboxyl terminated polybutadiene (CTPB)
Imin-type curative



Carboxyl terminated polybutadiene (CTPB)
epoxy-type curative

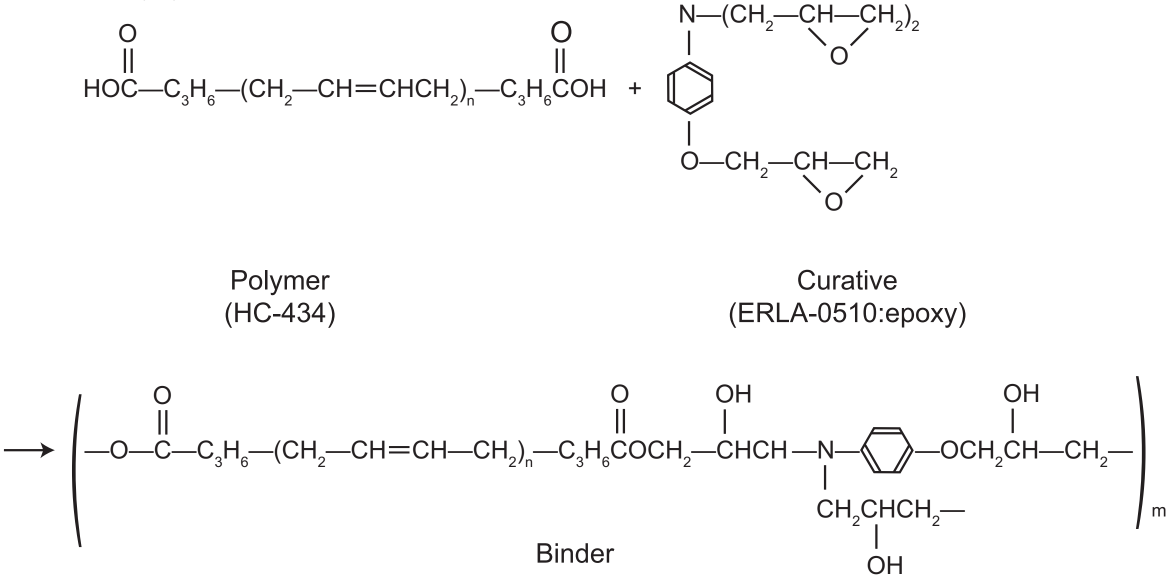
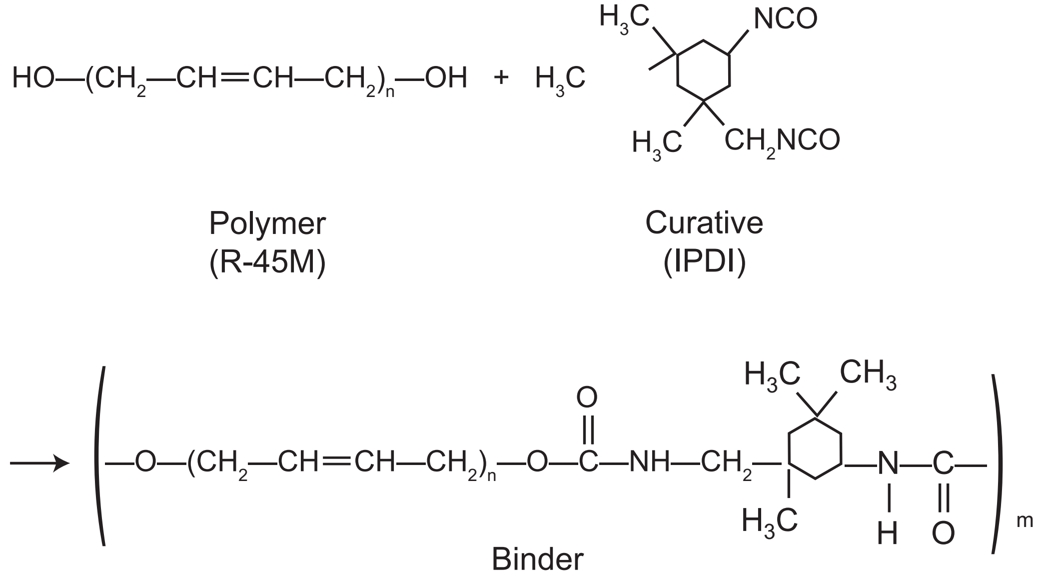


Table 8-2. Chemical Processes and Molecular Structures of Typical Binders Used for Composite Propellants. (Continued)

Hydroxyl terminated polybutadiene (HTPB)



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Notes

Principles of Solid Rocket Motor Design

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ABSTRACT

A number of parameters are needed to design a rocket motor to satisfy the specified flight trajectory of its payload. The major components of a rocket motor are propellant grain, motor case and its insulation, nozzle, and igniter. One of the key parameters is the burn rate characteristic of the propellant grain that is set in a rocket chamber either by cast method or by free-stand. The combustion phenomena in the motor are highly dependent on the design of the perforated propellant grains in which transient burning, erosive burning, oscillatory burning, and unstable burning occur. As a special rocket motor design, a two stage motor with two propellant grains in a single chamber, is described and compared with practical firing test results.

Keywords: flight dynamics, rocket motor, propellant combustion, two-stage motor, igniter, propellant grain, nozzle

1. Introduction

Rocket projectiles are used to carry a payload from a launch site to a specified location or altitude within a specified time. Rocket motors are used to generate propulsive forces for the projectile flight of which velocity is either subsonic or supersonic, or even hypersonic. The size, mass, and thrust of solid rocket motors vary widely from the space shuttle booster (3.77 m in diameter, 45.45 m in length, 502.12×10^3 kg of mass, and 11.79 MN thrust at sea level) to a micro-rocket motor (smaller than 0.01 m in diameter, 0.05 m in length, 0.1 kg of mass, and 1.0 N thrust). However, the fundamental concepts of rocket motor design are independent of the size, mass, and thrust.

The thrust generated by the combustion of a solid propellant is determined not only by the chemical energy of the propellant but also the thermodynamic processes in a rocket motor. In this chapter, the physicochemical properties of propellants and the energy conversion processes in rocket motors are presented in light of the design of various types of rocket motors.

2. Flight Dynamics of Rocket Projectiles

2.1 Momentum Change of Exhaust Gas

The design of a rocket projectile assisted by a solid rocket motor is determined by the requirement of flight trajectory. Once its flight trajectory and payload are given, an optimized total mass of the projectile and the thrust versus time of flight are determined.[1] The flight path of the projectile is dependent on various external parameters such as gravitational force, air density, wind velocity, and so on.

Although the physical structure of solid rocket motors is a very simplified one when compared with that of liquid rocket motors, once the propellant is ignited, the thrust generated by the propellant combustion cannot be changed. Thus, the chosen design parameters are not flexible. The mass and the size of the propellant grain are evaluated through the required thrust versus burning time relationship. In general, as the mass of the payload increases, the mass of the propellant grain in the motor increases, and the size of the motor also increases.

The momentum change of the projectile during rocket motor operation is represented by

$$(M - \Delta m)(V + \Delta V) - MV = M\Delta V - V\Delta m \quad (1)$$

where M is the mass of the projectile at time t, V is the flight velocity, ΔV is the velocity change during the time interval Δt, Δm is the exhaust mass from the projectile during the time interval Δt. In equation 1, it is assumed that the $\Delta V \Delta m$ term is such a small value that it can be ignored. The momentum change of the exhaust gas is represented by

$$\left(V - u_e\right)\Delta m = V\Delta m - u_e \Delta m \tag{2}$$

where u_e is the exhaust gas velocity from the projectile. Thus, the overall momentum change is given as

$$M\Delta V - u_e \Delta m \tag{3}$$

The thrust F is given by the momentum changes of the projectile and the exhaust gas per unit time as

$$F = \frac{M\Delta V - u_e \Delta m}{\Delta t} \tag{4}$$

2.2 Aerodynamic Drag and Flight Trajectory

As shown in Figure 1, the force balance acting on the rocket projectile is represented by

$$F = -D - Mg\cos\theta \tag{5}$$

where D is the aerodynamic drag and g is the gravitational acceleration. Since the mass of the projectile decreases (ΔM during the time interval Δt), the relationship of $\Delta m/\Delta t = -\ (\Delta M/\Delta t)$ is obtained. Using equations 4 and 5, one gets the force balance of

$$M\Delta V + u_e \Delta M = \left(-D - Mg\cos\theta\right)\Delta t \tag{6}$$

Thus, the velocity increase of the projectile is obtained as

$$\Delta V = -\frac{u_e \Delta M}{M} - \frac{D\Delta t}{M} - g\cos\theta\Delta t \tag{7}$$

Assume horizontal flight ($\theta = 90°$), for example, without aerodynamic drag ($D = 0$), the flight velocity increases from V_0 to V and the mass decreases from M_0 to M. Thus, one gets

$$V - V_0 = u_e \ln\varphi \tag{8}$$

where φ is the mass ratio defined by $\varphi = M_0/M$. The maximum flight velocity V_{max} is obtained

$$V_{max} = V_0 + u_e \ln\varphi_0 \tag{9}$$

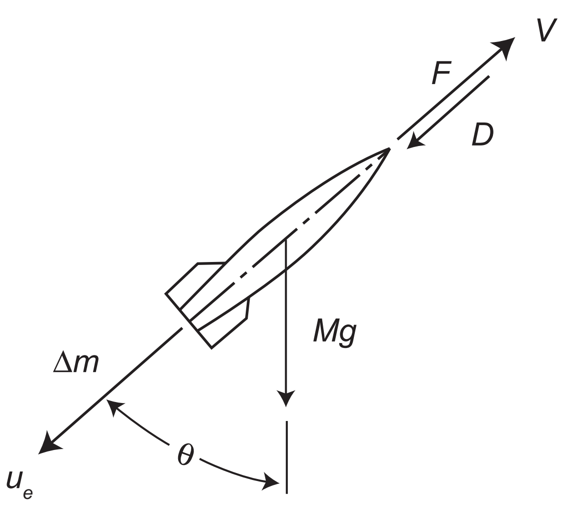


Figure 1. Force balance during flight of a rocket projectile.

where φ_0 is the mass ratio of the initial mass M_0 and the burnout mass M_b of the projectile.

In the case of vertical flight ($\theta = 0°$) from the ground without aerodynamic drag ($D = 0$), the flight velocity at time t is also obtained by the integration of equation 7 as

$$V = u_e \ln\varphi - gt \tag{10}$$

The altitude h_b at the burnout time t_b is obtained by the integration of equation 10 as

$$h_b = u_e t_b \left\{\frac{1 - \ln\varphi_0}{\varphi_0 - 1}\right\} - \frac{g t_b^2}{2} \tag{11}$$

It can be seen from equation 11 that the flight altitude increases as φ_0 increases and/or u_e increases. The maximum flight altitude h_f of the projectile is obtained by the conservation of the kinetic energy and the potential energy of the projectile as

$$M_b \frac{V_b^2}{2} = M_b g\left(h_f - h_b\right) \tag{12}$$

Since the burnout velocity V_b at time t_b is obtained by $V_b = u_e \ln \varphi_0 - g\, t_b$, h_f is obtained as

$$h_f = u_e^2 \frac{\left(\ln\varphi_0\right)^2}{2g} - u_e t_b \left(\frac{\varphi_0 \ln\varphi_0}{\varphi_0 - 1} - 1\right) \tag{13}$$

The thrust required for flight in the atmosphere is determined by the aerodynamic drag for deceleration shown in equation 5. The aerodynamic drag is represented by

$$D = \frac{1}{2} \rho_a V^2 A C_d \tag{14}$$

where V is flight velocity, A is the maximum cross sectional area of the projectile, ρ_a is air density, and C_d is the drag coefficient. Since C_d is dependent on the flight velocity and the physical shape of the projectile, C_d must be determined by either wind tunnel tests, mathematical computations using computational fluid dynamics (CFD), or physical simulations. Figure 2 shows a typical drag coefficient of a rocket projectile as a function of Mach number. Mach number is defined as the ratio of the flight velocity and the speed of sound in the flight atmosphere.

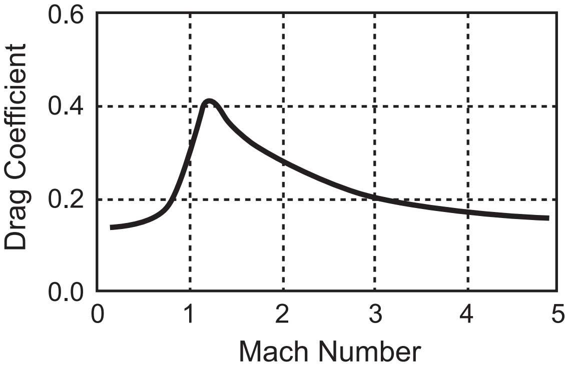


Figure 2. Drag coefficient of a typical rocket projectile as a function of Mach number.

The deceleration of the projectile after burnout (a) due to the aerodynamic drag and gravitational force is obtained by

$$a = \frac{F}{M} = -\frac{1}{2} C_d \rho_a A \frac{V^2}{M} - g \cos\theta \tag{15}$$

In the case of θ = constant, the velocity at time t is obtained by the integration of equation 15 as

$$V = V_b - \int \left(\frac{1}{2} C_d \rho_a A \frac{V^2}{M} \right) \mathrm{dt} - gt \cos\theta \tag{16}$$

The flight altitude at time t is obtained by the integration of equation 16. It must be noted that C_d is a function of velocity when equations 15 and 16 are integrated.

If one assumes that the flight is vertical and C_d remains constant during free flight, the altitude h_f is obtained by the integration of equation 16 as

$$h_f = \int V \, dt \tag{17}$$

Using equations 16 and 17, the relationship between V and h_f as a function of t is obtained.

3. Thermodynamics for Thrust Generation

3.1 Structure and Combustion of a Rocket Motor

The chemical energy of a solid propellant is converted to thrust that is generated by a rocket motor through combustion phenomena. When a solid propellant burns in a rocket motor, high temperature combustion products are formed and high pressure is created in the motor. Then the thrust is generated by the high pressure based on the momentum change through a thermodynamic nozzle attached at the aft end of the combustion chamber. Figure 3 shows the fundamental structure of a solid rocket motor. The motor consists of combustion chamber, nozzle, and propellant. The propellant grain is set in the combustion chamber and the nozzle is attached at the aft end of the combustion chamber. The nozzle is used as an accelerator of the combustion gas from subsonic flow to supersonic flow, and the combustion gas is exhausted to the atmosphere through the nozzle. The nozzle consists of a convergent part, a throat, and a divergent part. The convergent part accelerates the subsonic flow to sonic speed and then the divergent part accelerates the gas flow from sonic speed to supersonic speed. The maximum speed is obtained at the exit plane of the divergent part. The convergent part and the divergent part (A_e) are connected at the nozzle throat where the cross-sectional area is the minimum of the nozzle A_t.[1–3]

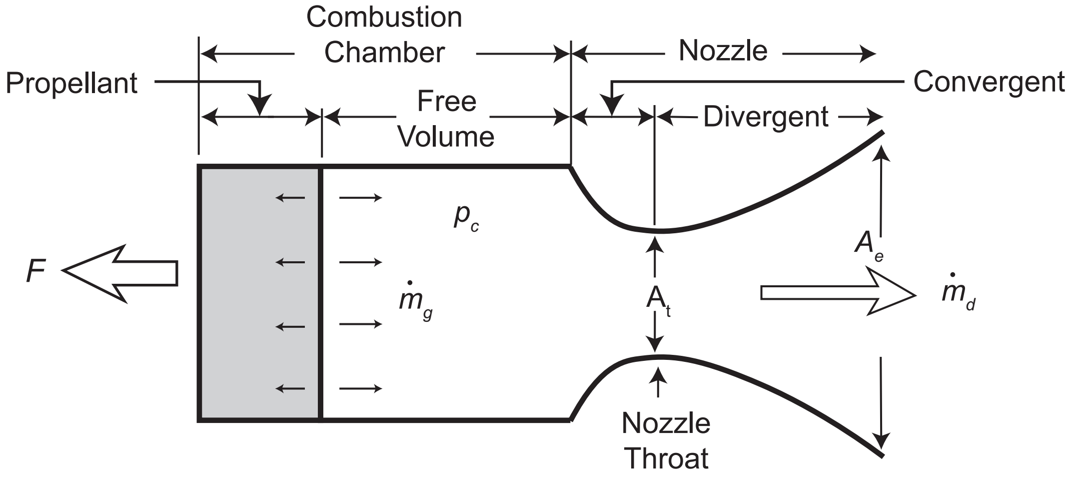


Figure 3. Structure of a rocket motor and burning of a propellant grain.

Since the propellant grain is set in the combustion chamber, the free volume in the chamber increases as the propellant grain is consumed. The internal surface of the chamber maybe covered by an insulating material to protect the chamber wall from the high temperature combustion products. Thermally resistant material is used for the nozzle to prevent thermal erosion from the high temperature and high velocity gas flow. An igniter is attached to the chamber wall to ignite the initial surface of the propellant grain.

3.2 Mass Balance in a Rocket Motor

As shown in Figure 4, a rocket motor is a high pressure vessel in which high pressure is formed by the combustion of a propellant grain in the vessel. The high pressure decreases in the nozzle as the gas flow velocity increases. Since the pressure acts perpendicular to the internal surface of the combustion chamber and the nozzle, the thrust, acting on the rocket motor, yields as the resultant pressure. Thus, the pressure in the chamber and in the nozzle is an important parameter in determining the thrust characteristics of the rocket motor.

When a propellant grain set in a combustion chamber burns, combustion gas is generated and is discharged from the nozzle as shown in Figure 3. The mass generation rate in the combustion chamber, $\dot{m}_g$, is given by

$$\dot{m}_g = \rho_p A_b r \qquad (18)$$

where r is burning rate of the propellant, A_b is the burning surface area of propellant, and ρ_p is the density of propellant. The mass discharge

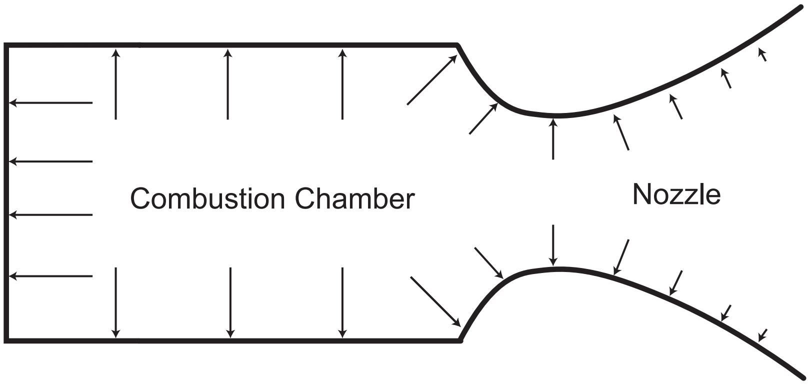


Figure 4. Pressure distribution in the combustion chamber and the nozzle of a rocket motor.

rate from the nozzle, $\dot{m}_d$, is given by

$$\dot{m}_d = c_D A_t p_c \tag{19}$$

where A_t is the cross-sectional area of the throat, p_c is the chamber pressure, and c_D is the nozzle discharge coefficient given by

$$c_D = \left(\frac{M_g}{RT_g} \frac{2}{\gamma+1} \right)^{\frac{\gamma+1}{\gamma-1}} \tag{20}$$

Equation 20 shows that c_D is dependent on the combustion properties of propellant such as combustion temperature T_g, molecular mass M_g, and γ the ratio of specific heats at constant temperature and pressure of the combustion product. The universal gas constant R is defined by $R = R_g M_g$, where R_g is the gas constant of the combustion product.

The mass balance of the rocket motor at steady state is given by

$$\dot{m}_g = \dot{m}_d \tag{21}$$

Using equations 18, 19 and 21, the chamber pressure is determined to be

$$p_c = \frac{\rho_p K_n r}{c_D} \tag{22}$$

where $K_n = A_b / A_t$, which is determined by the physical dimension of the rocket motor design. In general, the burn rate of propellant increases linearly as pressure increases in a ln p versus ln r plot at constant initial temperature T_0, where r is burn rate and p is pressure. Thus, the burn rate is represented by the experimental law, Vieille's law or Saint Robert's law as

$$r = ap^n \tag{23}$$

where n is the pressure exponent of burn rate and a is a constant based on the initial propellant temperature T_0. Substituting equation 23 into equation 22, one gets

$$p_c = \left(\frac{a \rho_p K_n}{c_D} \right)^{\frac{1}{1-n}} \tag{24}$$

The mass balance of a rocket motor is illustrated in Figure 5. The chamber pressure p_c is at the intersection of the straight line $\dot{m}_d$ and the curved line of $\dot{m}_g$. It is evident that the intersection point is a stable point only when the pressure exponent n is less than unity. When $n > 1$, $\dot{m}_g$ becomes larger than $\dot{m}_d$ and the chamber pressure increases slightly. As a result, the rate of gas generation becomes greater than the rate of mass discharge, and the chamber pressure increases to an even higher pressure. When the chamber pressure decreases slightly, $\dot{m}_d$ becomes larger than $\dot{m}_g$. As a result, the chamber pressure decreases to atmospheric pressure—usually resulting in an explosion.

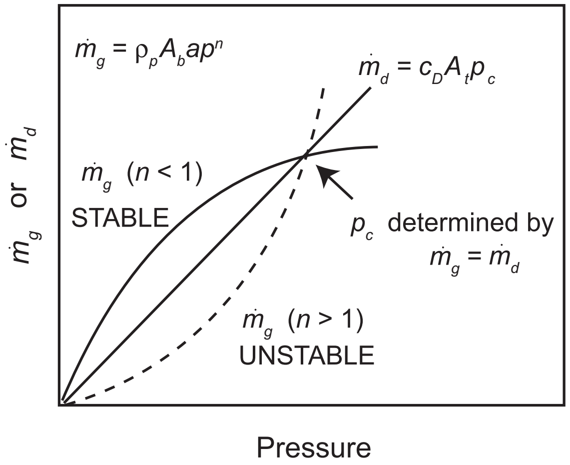


Figure 5. Mass balance of the mass generation in the chamber and the mass discharge from the nozzle showing the conditions of stable and unstable burning.

3.3 Thrust and Specific Impulse

Once the thrust required is determined, the mass generation rate $(\dot{m}_g)$ of the propellant grain in the rocket motor is determined by the following relationship:

$$F = \dot{m}_g I_{sp} \tag{25}$$

where I_{sp}, the specific impulse, is determined by[1–4]

$$I_{sp} = \frac{1}{g}\sqrt{\frac{2\gamma}{\gamma-1}\frac{RT_g}{M_g}\left\{1-\left(\frac{p_e}{p_c}\right)^{\frac{\gamma-1}{\gamma}}\right\}} + \frac{1}{g}\left(\frac{\gamma+1}{2}\right)^{\frac{\gamma+1}{2(\gamma-1)}}\sqrt{\frac{RT_g}{\gamma M_g}}\left(\frac{p_e-p_a}{p_c}\right)\frac{A_e}{A_t} \tag{26}$$

where T_g is the combustion temperature, M_g is the molecular mass of the combustion products, γ is the specific heat ratio, R is the universal gas constant, A_e is the cross-sectional area of the nozzle exit, p_e is the pressure at the nozzle exit, p_a is atmospheric pressure, and g is the gravitational acceleration. This shows that I_{sp} is a function of not only the energetics of the propellant but also the expansion ratio of the nozzle, which is determined by ratio of the nozzle exit area to the throat area and the ambient atmospheric pressure. The maximum specific impulse ($I_{sp,max}$) is obtained when the nozzle exit pressure is equal to atmospheric pressure (i.e., $p_e = p_a$) as

$$I_{sp,max} = \frac{1}{g}\sqrt{\frac{2\gamma}{\gamma-1}\frac{RT_g}{M_g}\left\{1-\left(\frac{p_e}{p_c}\right)^{\frac{\gamma-1}{\gamma}}\right\}} \tag{27}$$

This condition is obtained when the expansion ratio is chosen to be an optimum expansion ratio as described in Reference 2.

The thrust of a rocket motor is expressed by[1–3]

$$F = c_F A_t p_c \tag{28}$$

where F is thrust, p_c is pressure in the combustion chamber, and c_F is the so-called "thrust coefficient", which is determined by the nozzle expansion ratio of the rocket motor as given by

$$c_F = \sqrt{\frac{2\gamma^2}{\gamma-1}\left(\frac{2}{\gamma-1}\right)^{\frac{\gamma+1}{\gamma-1}}\left\{1-\left(\frac{p_e}{p_c}\right)^{\frac{\gamma-1}{\gamma}}\right\}} + \left(\frac{p_e-p_a}{p_c}\right)\frac{A_e}{A_t} \tag{29}$$

This shows that c_F is only dependent on the expansion ratio of the divergent part of the nozzle and is independent of the combustion performance of the propellant in the combustion chamber. The maximum thrust coefficient ($c_{F,max}$) is obtained when the pressure at the nozzle exit (p_e) is equal to the atmospheric pressure (p_a). Thus, $c_{F,max}$ is given by

$$c_{F,max} = \sqrt{\frac{2\gamma^2}{\gamma-1}\left(\frac{2}{\gamma-1}\right)^{\frac{\gamma+1}{\gamma-1}}\left\{1-\left(\frac{p_e}{p_c}\right)^{\frac{\gamma-1}{\gamma}}\right\}} \tag{30}$$

In general, c_F is approximately 1.4–1.5 for low altitude operation and 1.5–1.6 for high altitude operation when the nozzle is designed to gain an optimized expansion ratio. The overall performance of a rocket motor is given by I_{sp}, which consists of two parameters:[1–3] the performance of combustion in the rocket motor represented by T_g / M_g and the performance of the nozzle represented by c_F.

3.4 Pressure Sensitivity of Burn Rate

The pressure sensitivity of burn rate is expressed as[1–5]

$$n = \frac{\mathrm{d}\ln r}{\mathrm{d}\ln p} \quad \text{at constant } T_0 \tag{31}$$

The burn rate also increases as T_0 increases at constant pressure. A typical example of the results obtained by a strand burner at $T_0 = 233$ and 333 K is shown in Figure 6. The temperature sensitivity of burn rate, σ_p, is defined as the fraction of burn rate increase when the initial propellant temperature of 273 K is increased at constant pressure as

$$\sigma_p = \frac{\dfrac{r_1 - r_0}{r}}{T_1 - T_0} \tag{32}$$

where r_0 and r_1 are the burn rates at temperatures T_0 and T_1, respectively. The differential form of σ_p is

$$\sigma_p = \frac{\mathrm{d}\ln r}{\mathrm{d}T_0} \quad \text{at constant } p \tag{33}$$

Substituting equation 23 into equation 33, one gets

$$\sigma_p = \frac{\mathrm{d}\ \ln\left(ap^n\right)}{\mathrm{d}T_0}$$

at constant p, and then

$$\sigma_p = \frac{\frac{\mathrm{d}a}{\mathrm{d}T_0}}{a} \quad \text{at constant } p \tag{34}$$

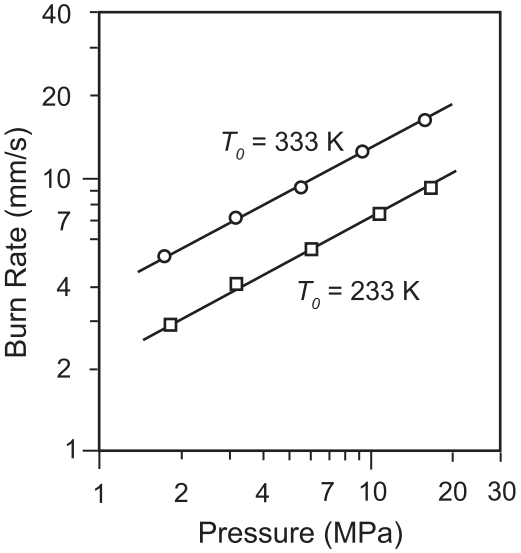


Figure 6. Burn rate versus pressure at different initial propellant temperatures.

3.5 Pressure Sensitivity of Rocket Motor

When T_0 of the propellant in the combustion chamber is changed, p_c is changed according to the relationship of equation 24. The pressure sensitivity of a rocket motor, π_k, is defined as[1–5]

$$\pi_k = \frac{\frac{p_{c_1} - p_{c_0}}{p_c}}{T_1 - T_0} \quad \text{at constant } K_n \tag{35}$$

where p_{c_1} and p_{c_0} are the chamber pressures at T_1 and T_0, respectively. The differential form of equation 35 is given by

$$\pi_k = \frac{\mathrm{d}\ln p_c}{\mathrm{d}T_0} \quad \text{at constant } K_n \tag{36}$$

Substituting equation 24 into equation 36, one gets

$$\pi_k = \frac{\frac{\mathrm{d}a}{\mathrm{d}T_0}}{a(1-n)} = \frac{\sigma_p}{1-n} \tag{37}$$

Thus, it should be noted that the temperature sensitivity of burn rate σ_p and the pressure exponent of burning rate n are the two important parameters to determine the chamber pressure p_c (i.e., the thrust of the rocket motor as shown by equation 28 at different initial propellant temperatures).

Figure 7 shows a typical result of rocket motor firing tests at $T_0 = 233$ and 333 K (constant K_n). The propellant used is hydroxyl-terminated polybutadiene (HTPB) / ammonium perchlorate (AP) composite propellant composed of $\xi(\text{AP}) = 0.84$ with $\sigma_p = 0.003$/K and $n = 0.5$ ($\pi_k = 0.006$/K). It is important to note that the chamber pressure increased from 4.9 MPa ($T_0 = 233$ K) to 8.0 MPa ($T_0 = 333$ K).

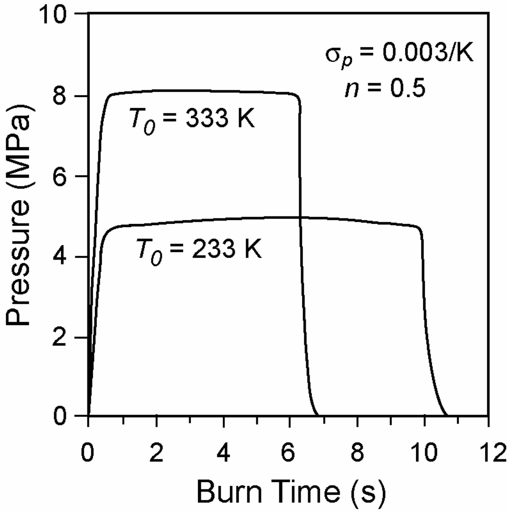


Figure 7. Firing test results of a rocket motor at different temperatures.

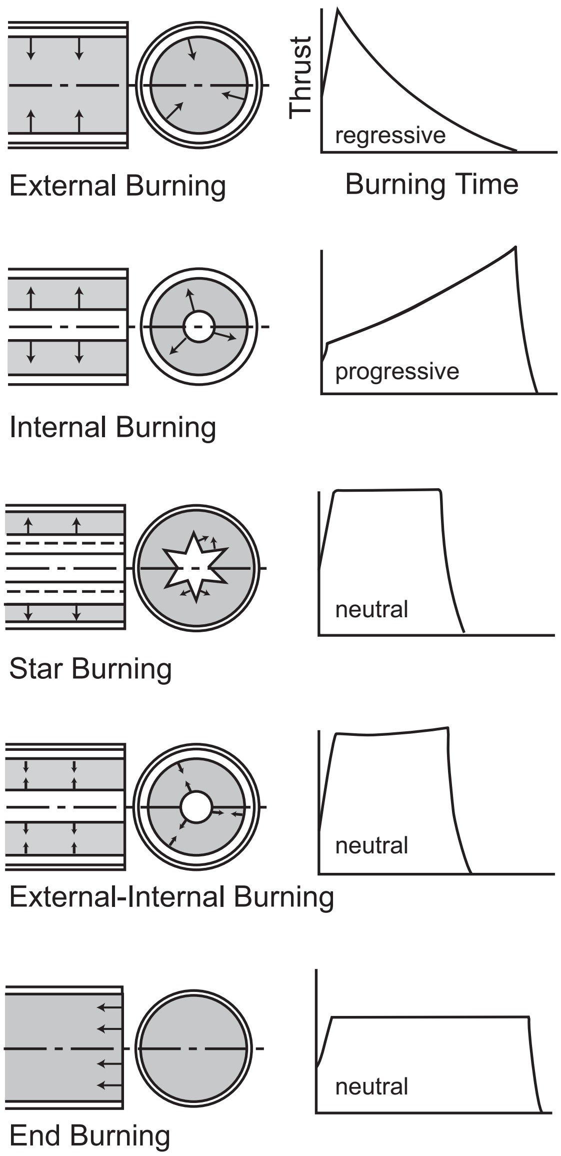


Figure 8. Propellant grains and their thrust (pressure) versus burning time.

4. Propellant Grain Design

4.1 Thrust Versus Burning Time

The thrust generated by the burning of a propellant grain is determined by the mass burn rate and the mass discharge from the nozzle. The mass burn rate is dependent on the linear burn rate, burning surface area, and propellant density. The burning time t_b is given by

$$t_b = \frac{L_b}{r} \tag{38}$$

where L_b is the length or thickness of the propellant grain and is termed "web thickness". The burning surface area A_b is dependent on the grain geometry.

Figure 8 shows typical propellant grain shapes to gain various types of thrust versus burning time relationships.[1] The external burning—from the outside of a cylindrical grain—generates a regressive thrust as the burn time increases. On the other hand, an internal burning grain from the internal surface of a hole in a cylindrical grain generates a progressive thrust as burning time increases. A star-shaped internal burning generates a neutral burning (i.e., the area remains relatively unchanged during burning). The external-internal burning cylindrical grain generates a neutral burning. An end burning cylindrical grain also generates a neutral burning.

Figure 9 shows various types of granulated propellant grains used for guns and pyrotechnics. Since a large number of the granulated grains burn simultaneously in a combustion chamber, the burning surface area A_b is significantly higher than the propellant grains shown in Figure 8; also the mass burning rate of the granulated grains is high. The chamber pressure becomes high due to high K_n based on equation 22, and the thrust becomes high. On the other hand, the burning time t_b becomes very short, based on equation 38, since the web thickness of the granulated grains is very thin.

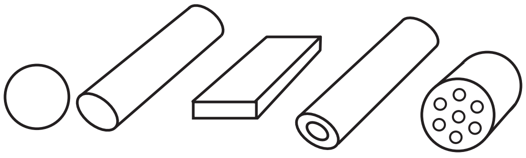


Figure 9. Various types of granulated propellant grains.

Internal burning grains are commonly used for solid rocket motors to protect the chamber wall from the high temperature gas generated by the propellant combustion. The side chamber wall is exposed only when the burning of the grain is complete. Thus, the heat insulation of the chamber wall is not a major issue for the motor design. Figure 10 shows typical cross

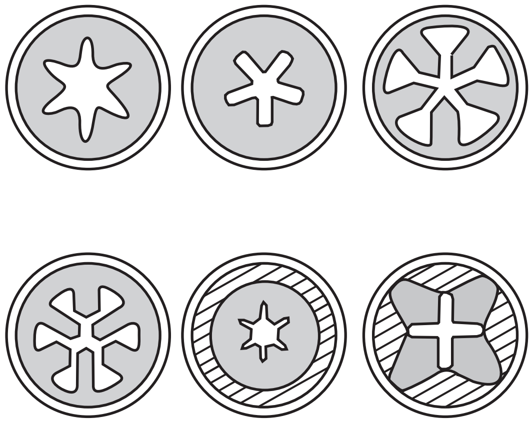


Figure 10. Cross-sections of perforated internal-burning propellant grains.

sections of perforated propellant grains, such as star-shaped, wagon-wheel-shaped, and dendrite-shaped. Two or more different propellant layered grains are also used to gain various types of thrust versus burning time.[1]

Since rocket projectiles are generally launched from the ground or from low speed carriers, and the initial speed of the projectile is low, a high thrust is required to gain stabilized flight of the initial stage to protect the rocket motor from side wind effects and/or to avoid tip-off from launchers. Thus, the thrust of a rocket motor often consists of two phases, booster phase and sustainer phase. When the thrust ratio of the booster and sustainer phases is not high, the required thrust versus burning time curve is attained. However, when the ratio is high, two propellant grains are needed: a high burn-rate grain for the booster phase and a low burn-rate grain for the sustainer phase. Figure 11 shows typical combinations of two grains and internal and/or end burning type of grains to obtain high thrust ratios of booster and sustainer phases.

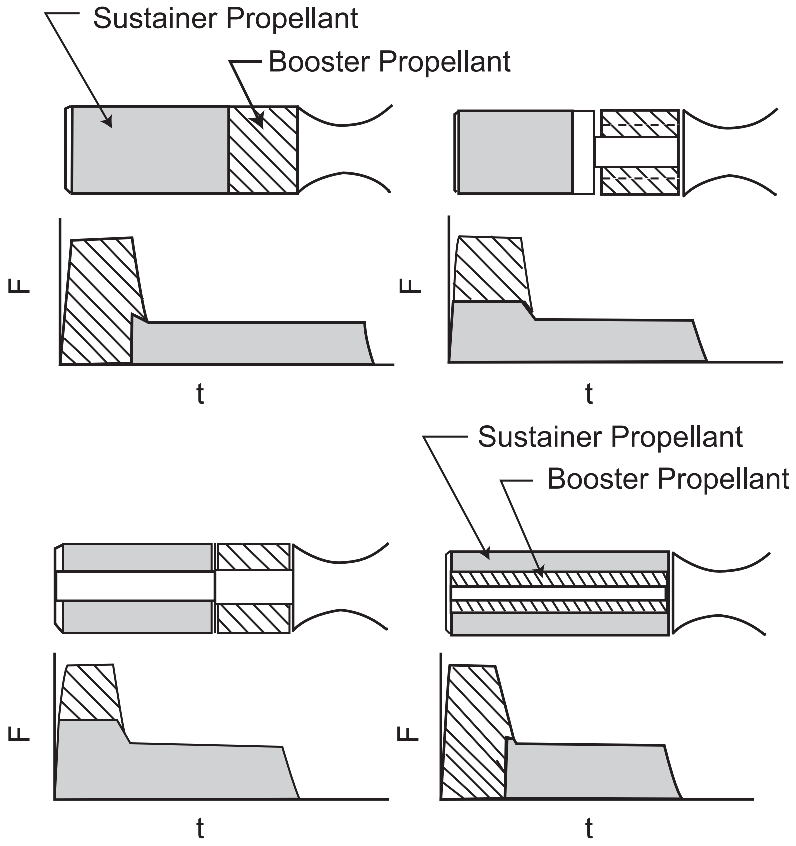


Figure 11. Some typical combinations of two propellant grains in a rocket motor.

4.2 Grain Design Concept

The selection of propellant for a specific requirement for a practical rocket motor design is based on the specific impulse, combustion temperature, exhaust products and the relationship of burn rate and pressure. This includes the value of the pressure exponent and temperature sensitivity of burn rate. The burn rate is increased by the cross-flow in the port of the internal burning grain, the so-called erosive burning. In the case of aluminized propellants, the local burning rate of the burning surface of an internal burning grain is increased under a centrifugal acceleration. Furthermore, an oscillatory burning occurs in a rocket chamber when the burn rate response of the propellant is matched to the acoustic mode of the free volume of the chamber. These combustion phenomena must be examined prior to the practical grain design.[6–10]

Once a propellant is chosen, the following three parameters are taken into account for the propellant grain design:

1) Burning area versus burning distance (also referred to as "web thickness")
2) Mechanical stress analysis
3) Anti-aging analysis

The thrust versus burning time requirement is obtained by the selection of the propellant grain combinations or the perforation of the grain shape.[6–8] Since the propellant grain in a rocket chamber encounters various mechanical stresses from the high axial and/or radial acceleration or by the temperature change of the grain, a mechanical stress analysis is required. If the rocket motor is used even after a decade, an anti-aging analysis is required to maintain its design performance.

4.3 Selection of Propellants

A propellant composed of ammonium perchlorate (AP) as the oxidizer and hydrocarbon polymer as the fuel component is the so-called "AP composite propellant" and is commonly used. Hydroxyl-terminated polybutadiene (HTPB) or carboxyl-terminated polybutadiene (CTPB) is used as a fuel component and as a binder to adhere to the AP particles to form a propellant grain. AP composite propellants are widely used for space launch rockets and missile rockets because of their wide range of burning rate characteristics, relatively safe production, low sensitivities to friction and mechanical shock, and low production cost. The mechanical properties such as stress strength, elongation, and elasticity are chosen based on the required ballistic characteristics. The burning rate characteristics expressed by equation 23 are managed by the choice of AP particle sizes, solids loading and burn rate catalysts. When a high burning rate is needed, small AP particles are used. Furthermore, the burning rate is increased by the addition of a small amount of iron oxide (e.g., 1% Fe_2O_3) and is decreased by the addition of lithium fluoride (e.g., 1% LiF).

The specific impulse defined in equation 26 is increased by the addition of fine aluminum powder to AP composite propellants, for example, I_{sp} is increased about 7 % by the addition of 15% Al. However, large amounts of white smoke are formed as combustion products from the formation of aluminum oxide (Al_2O_3) particles. Though the exhausted white smoke does not interfere with any application of space launch rockets, it must be eliminated from tactical rockets to avoid detection of the launch sites or ballistic trajectories. When no aluminum particles are added to AP composite propellants, no generation of solid particle white smoke occurs. This class of AP composite propellants is called "reduced smoke propellants" and is used for air-to-air missiles and surface-to-air missiles. However, when the humidity in the atmosphere is much above 70% or the temperature in the atmosphere is much below 250 K (–23 °C), white smoke is generated by the hydrogen chloride (HCl) produced by the AP particles used as the oxidizer. The hydrogen chloride exhausted from rocket nozzles into the atmosphere acts as nuclei to form water mists with the high humidity of the atmosphere or reacts with water from the combustion products after exhausted to a low temperature atmosphere.

If one requires smokeless exhaust gas—even under high humidity conditions—double-base propellants or ammonium nitrate (AN) based composite propellants are used. Since these propellants are composed of halogen-free ingredients, no visible smoke is formed even when the humidity in the atmosphere is high. Since double-base propellants are composed of nitrate esters such as nitroglycerin and nitrocellulose, the cost of production is relatively high and the mechanical properties are inferior to AP composite propellants. The disadvantage of using AN as an oxidizer is that the specific impulse is low and strict humidity control is needed during the production process because of the hygroscopic nature of AN.

5. Design of Rocket Motor Case and Thermal Protection

5.1 Size and Shape of Rocket Motor Case

The chamber of a rocket motor case is used as the container for a propellant grain and is also used to burn the propellant grain under conditions of high pressure and high temperature. The size of the chamber is determined by the volume of the propellant grain required to generate the total impulse. The chamber pressure in the motor is given by the required thrust and the nozzle throat area as

$$p_c = \frac{F}{c_F A_t}$$

The thickness of the chamber wall is determined by the size and the mechanical properties of the material used for the motor case. Although the combustion pressure changes during burning due to the changing burning surface area of the propellant grain, the wall thickness must be determined by the maximum chamber pressure $p_{c,max}$ during burning. In addition, a safety margin of the wall thickness must be taken into account, for example, $1.2 \times p_{c,max}$.

In general, rocket motor cases are cylindrical and slender in shape. This is because of the reduction of aerodynamic drag during flight and the cost reduction of the machining process of the case materials. The ratio of the diameter to the length is determined by the flight dynamics of the rocket projectile.

In the case of outer atmospheric flight aerodynamics, drag is not considered. Spherical shaped motor cases are used for the upper stage of space rockets to gain advantage of the minimized wall thickness at a given combustion pressure. However, the cost of production is much higher as compared to cylindrical motor cases.

5.2 Materials Used for Motor Cases

Many types of materials are used for the rocket motor cases.[3,7,8] Modern rocket motors are made of carbon composite materials whose mechanical properties are superior to those of metals. However, the cost of these materials is relatively high unless there is mass production as for small motors and very large motors such as space rocket boosters and ICBM rocket motors. Medium-sized motors such as air-to-air missiles and anti-tank missiles are made of steel or titanium alloy because of the effectiveness of the ratio of mechanical strength to density. This is evident from the mechanical strength and elongation characteristics of the materials.

For commercial use of rocket motors such as the launch of hobby rockets, shell bursts for fireworks, life-saving signal rockets, and lightning-earth rockets, the motor cases are made of paper or plastic. The advantages of these materials are greater safety when the empty motor case falls to the ground after burnout and low production cost. However, a high safety margin for wall strength must be taken into account to avoid any unexpected manufacturing or material irregularities from the hand-made motor cases.

5.3 Thermal Protection

Since the combustion temperature in rocket motors is typically greater than 2000 K, the chamber wall should be protected from heat. The temperature of the interior of the propellant grain remains at the initial temperature of the grain in an operating motor until the burning surface approaches. Thus, the chamber wall is isolated from the combustion zone temperatures as long as the wall is covered by the propellant grain.

However, when a part of the propellant grain is burned completely, the interior wall surface is exposed to the high temperature combustion gas. Then, the wall is thermally eroded and can be burst by the combustion pressure. To protect the casing from the combustion gas, a heat insulating material is added to the interior surface of the chamber wall. The heat insulting material typically consists of rubber sheets that are adhered to the chamber wall. The propellant is then cast into the chamber (direct cast method) or the propellant grain is inserted into the chamber (freestanding method). An important parameter for the direct case method is to assure the complete adhesion between the insulation and the propellant after curing of the propellant.

The thickness of the insulation depends on the duration of exposure to the combustion gas and on the location within the chamber. When the propellant grain is of an end-burning geometry, the aft (nozzle) end of the insulation is exposed from ignition to burnout. Thus, a thicker sheet of insulation is needed at the nozzle (aft) end.

6. Design of Nozzle

6.1 Size and Shape of Nozzle

Rocket nozzles are used to convert the low-velocity combustion gases in the chamber to high velocity exhaust through thermodynamic processes. In other words, conversion is through expansion. Once the chamber pressure p_c and the nozzle throat area A_t are determined, the expansion ratio ε defined by the area ratio of the nozzle exit area A_e and A_t is determined thermodynamically. The thrust coefficient c_F, defined by equation 29, indicates the efficiency of the nozzle. The maximum thrust coefficient $c_{F,max}$ is determined by the chamber pressure p_c and the atmospheric pressure p_a. The optimum expansion ratio ε_{max} increases because p_a decreases with altitude. Chamber pressure p_c is unaffected by anything past the throat of the rocket motor.

During the process of nozzle design the nozzle throat area (A_t) is determined first based on the thrust requirement, and then the nozzle exit area (A_e) is determined to gain an optimum expansion ratio. It is evident that the shorter the length of the nozzle, the lower the nozzle mass. The convergent nozzle angle is larger than the divergent nozzle angle because of the subsonic flow and the decreasing pressure along the nozzle wall towards the throat of the nozzle. Thus, no flow separation in the boundary layer occurs from the convergent nozzle wall.

On the other hand, the divergent nozzle angle is important to gain a smooth pressure gradient and to minimize the friction loss caused by the nozzle wall and the supersonic exhaust gas flow. In general, the expansion angle is limited to approximately 30° to gain smoothly expanded gas flow, to minimize the friction loss of the supersonic flow, and to limit vector losses in the nozzle. The convergent and divergent parts of the nozzle are connected at the nozzle throat. (See Figure 3.)

When the pressure at the nozzle exit (p_e) is higher than the local atmospheric pressure (p_a), the nozzle is considered to be under-expanded, and when p_e is smaller than p_a, the nozzle is considered to be over-expanded. The specific impulse (I_{sp}) is less for both cases when compared to the optimum expansion ratio as shown in equation 26. When the trajectory of a rocket projectile varies from a low altitude to a high altitude, the atmospheric pressure decreases as the altitude increases. As a result, the nozzle expansion ratio must be altered to gain an optimum expansion ratio as long as the combustion pressure remains constant. Since the geometry of a conventional nozzle is fixed, the optimum expansion is set for a specific altitude and chamber pressure.

6.2 Materials Used for Nozzle

Since rocket nozzles are exposed to high temperature and high velocity combustion gas during propellant burning, the heat flux from the gas to the nozzle wall is significantly higher than in the combustion chamber. The maximum heat flux is at the nozzle throat (approximately 2 MW/m^2 for conventional AP composite propellants). In addition, the mechanical stress acting on the interior surface of the nozzle is approximately 10 MPa for a typical ground launched rocket motor.

As shown in equation 28, the nozzle throat (A_t) is an important parameter to attain an expected performance of thrust versus time for operation. A change of A_t (throat erosion) changes p_c and then c_F, which changes F significantly. To avoid the change in A_t, high temperature resistant materials are used not only for the nozzle throat but also in the convergent and divergent parts of the nozzle. Typical and conventional materials used for nozzles are graphite and carbon because the combustion products of solid propellants are generally fuel rich gases and graphite and carbon are not oxidized by the gas flow. High-density graphite is commonly used for modern rocket motors to resist not only these high temperatures but also erosion by sonic or supersonic flow. The density of a graphite nozzle for practical applications is approximately 1.9×10^3 kg/m^3. The high-density graphite also protects the casing from mechanical damage from the thermal shock during the ignition stage. When the heat flux is much higher, the nozzle surface is damaged and A_t increases. Also, ceramics such as aluminum oxide or zirconium oxide can be coated on the interior surface of the nozzle by a plasma torch. [Note: Aluminized propellants form an aluminum oxide coating on the throat, especially at and just after ignition, which reduces A_t.]

When the size of a motor case is small (less than about 50 mm in diameter), the size of the nozzle is also small. In this instance, the convergent and divergent parts of the nozzle, including the throat, are made of graphite. The mechanical stress acting on the interior surface of the nozzle is not high because the interior diameter is small. However, the mechanical stress increases as the diameter of the throat increases, and graphite becomes insufficient to protect the nozzle from damage. In general, a larger nozzle is separated into three parts (i.e., convergent, throat, and divergent). Since the heat flux and the flow velocity at the convergent and divergent parts are relatively small when compared to the throat, glass fiber reinforced plastics (GFRP) with phenolic or epoxy resin are commonly used for the other parts. An ablative process due to the melting and gasification of the glass fibers and plastic resins of GFRP effectively act to protect the nozzle from high heat flux.

Carbon fiber reinforced plastics (CFRP) with various types of plastic resins are also used for the convergent and divergent parts. Though no ablative effect is expected for the carbon fibers of CFRP, the superior heat resistant properties of the carbon fibers protect the parts from heat and gas flow. In addition, the mechanical properties of CFRP, such as stress strength and density, are superior to those of GFRP. When reduction of the nozzle mass is an important parameter to obtain high performance of rockets such as a third of a four-stage motor used at high altitude, carbon-carbon (C/C) is used for the nozzle system including convergent, throat, and divergent parts. Though C/C is the best material for rocket nozzles, at present time, the cost of C/C is extremely high and the application is highly limited.

7. Design of Igniter

7.1 Ignition Transient

An igniter is used to ignite the surface of the propellant grain set in a combustion chamber. When an igniter is operated, hot gas and/or particles are applied to the surface of the propellant grain in the combustion chamber. The ignited surface generates high temperature combustion gases and the chamber pressure increases. The ignited surface area increases along the grain surface. During this ignition process, the burn rate is not given by equation 23, which is only effective for steady state burning.

The ignition process of the propellant grain includes the temperature rise of the grain surface, heat conduction into the grain, gasification at the surface, and production of sufficient gases to raise the chamber pressure. When the igniter charge, the so-called “pyrolant” (pyrogen) —which is an energetic material—burns, this causes a spike in the pressure. This results in a rapid onset and decay that can “shock” the system, possibly causing failures. In addition, the heat flux generated by the pyrolant must be enough to ignite the grain surface, enabling the pressure of steady-state combustion to be reached within a required short duration.

The ignition transient depends on the type of pyrolants and propellants. Two types of pyrolants are used for igniters: high volume gas producing and high temperature particle producing. Black Powder produces more gaseous products than pyrolants composed of metallic particles and crystalline oxides. Since the chamber pressure of a double-base propellant rocket motor requires more than 4 MPa to reach steady-state combustion, Black Powder is often used as a pyrolant for this class of rocket motors.

On the other hand, composite propellants, such as ammonium perchlorate or ammonium nitrate-based composite propellants, require high heat flux to raise the burning surface temperature and to gasify the grain surface. High temperature hot spots are made on the grain surface when metal particles are used as a component of pyrolants. The metal particles are oxidized by the other components, crystalline oxidizers, generating high temperature hot spots dispersed on the grain surface. The grain surface at each hot spot is ignited by the heat conduction from the hot spot and the burning area spreads along the entire grain surface.

The heat flux that must be applied to a propellant grain surface for ignition is dependent on the chemical ingredients, the physical shape of the grain and the type of igniter ingredients. In general, high pressure is needed for the ignition of double-base propellant grains in a rocket motor. The minimum pressure is approximately 4 MPa to reach a steady state burning to satisfy the mass balance relationship given by equation 21 since the combustion temperature of double-base propellants decreases rapidly below 4 MPa. The mass discharge rate $\dot{m}_d$ given by equation 19 increases more than expected if one assumes c_D given by equation 20 is constant. The mass discharge coefficient c_D increases as pressure decreases.

Since AP composite propellants burn stably even below 0.1 MPa and the temperature of the combustion products is relatively independent of pressure, c_D remains constant throughout ignition pressure to the steady-state pressure. When even a part of the grain surface is ignited, the burning surface increases due to the flame spreading phenomena along the grain surface, and the chamber pressure increases until the pressure reaches the steady-state pressure given by equation 24.

Since AN particles mixed within an AN composite propellant decompose endothermically, a high heat flux is needed to gasify the AN particles. Furthermore, the AN particles melt and form a molten layer on the burning surface of the propellant and absorb much energy to generate combustible gas for ignition. Accordingly, the ignitability of AN composite propellants appears to be inferior to that of AP composite propellants.

7.2 Pyrolants Used for Igniter

The typical materials used for the pyrolants of igniters are the physically mixed particles of boron and potassium nitrate (B-KN), zirconium and ammonium perchlorate (Zr-AP), and magnesium and polytetrafluoroethylene (Mg-TF). The particles of boron (B), zirconium (Zr), or magnesium (Mg) are oxidized to produce their oxides, and they generate high temperature particles. These particles are showered onto the igniting surface of the propellant grains.

Although boron particles are not metal particles, they act like metal particles similar to aluminum, zirconium, or magnesium. When boron particles are oxidized by the gaseous nitrogen oxides produced by the thermal decomposition of crystalline potassium nitrate (KNO_3) particles, high temperature (greater than 4000 K) boron oxides are formed. Similar to boron particles, zirconium particles are oxidized by the gaseous perchloric acid produced by the thermal decomposition of crystalline ammonium perchlorate (NH_4ClO_4) particles.

Polytetrafluoroethylene (TF) is a polymeric material that produces fluorine (F_2) gas when it thermally decomposes. The fluorine gas oxidizes the magnesium particles to produce magnesium fluoride (MgF_2) particles that are agglomerated during the process of the oxidation reaction. High-temperature (greater than 3500 K) particles are showered onto the propellant grain surface. The hot particles of boron oxide, zirconium oxide, or magnesium fluoride act as hot spots to transfer heat to the grain surface and gasify the propellant ingredients. Once thermal gasification occurs on the propellant grain surface, an exothermic reaction proceeds to ignite the gases and the pressure in the rocket chamber rises.

The pyrolants are ignited indirectly by very thin wires that are electrically heated. These wires are made of platinum or other electrically resistive metals of about 30 μm in diameter. When an electric current is applied to the wires, heat is generated due to the electric resistance of about 400 Ω/m. Generally, the platinum wires are coated with mixtures of nitrocellulose, potassium perchlorate ($KClO_4$), and fine metallic particles whose mixture is first ignited, and then the heat produced by the combustion of the mixture ignites the pyrolants successively.

The pyrolant and hot wires are set an igniter case that is made of a metal or plastic material. A number of holes are made on the side of the case wall to shower the burning hot gas and particles on the surface of the propellant grain. For large rocket motors, such as the space shuttle booster or an ICBM rocket motor, ignition is accomplished by using a small rocket motor that is attached at the top end of the inside of the motor. Once the small motor is ignited, the exhaust gas from the nozzle ignites the large interior surface of the propellant grain.

8. Combustion Phenomena in a Rocket Motor

Combustion in a rocket motor includes various phenomena such as ignition transient, flame spread, erosive burning, oscillatory burning, unstable burning, and burning interruption.[1,8] These phenomena are highly dependent on the physicochemical properties of propellant grains.

8.1 Erosive Burning

Erosive burning occurs at an early stage in the burning of a propellant grain when the cross-sectional area of the gas flow channel inside the grain, the so-called “port area”, is a value close to that of the nozzle throat area. When the port area is equal to the nozzle throat area, the flow velocity at the aft end of the grain reaches sonic velocity (i.e., 300 m/s at normal temperatures, which varies with flame temperature, pressure and composition). Since the heat flux transferred back from the gas flow to the burning grain-surface increases when the cross-flow velocity is high, the burn rate of the grain increases compared with that of no gas flow. The burn rate expressed by equation 23 is no longer valid. As the port area increases, the cross-flow velocity decreases and the erosive burning effect diminishes.[1,2]

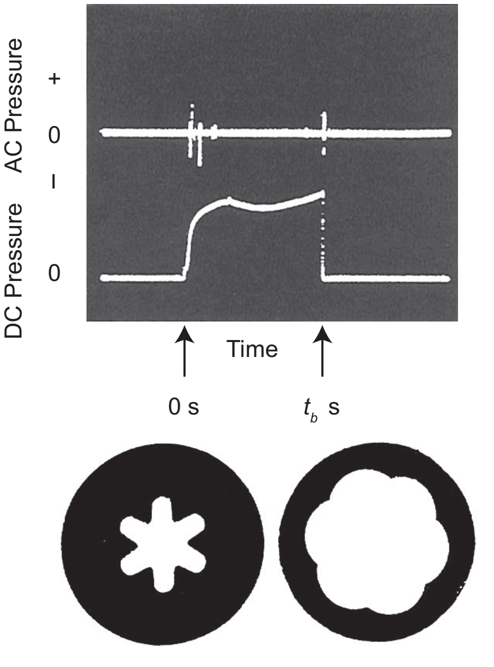
When erosive burning occurs, the pressure in the combustion chamber increases. The increased pressure increases the burn rate that is given by equation 23. It is important to take in to account the increased pressure of erosive burning to obtain a required thrust versus burning time relationship.

8.2 Stable and Unstable Combustion

An oscillatory burning occurs in the chamber when a standing wave is established between the facing grain-surfaces or between the fore-end and aft-end of the chamber. The standing pressure wave in the chamber enhances the burn rate of the propellant grain. The oscillatory frequency is dependent on the size of the internal port of the grain or the length of the motor. No oscillatory burning is observed when an end-burning-type grain is used. When the oscillatory mode is resonated to the burn-rate mode of the propellant grain, the overall mass-burn-rate is increased, and then the pressure in the chamber is increased drastically.[1,2]

Figure 12 shows the cross-section of an extinguished propellant grain obtained from a nozzle separation.[1,2] The nozzle separation was caused by the increased pressure that was the result of an irregular burning. The grain was a six-pointed star shaped composition of AP/HTPB propellant. Immediately after the grain was ignited, at 0 seconds, the chamber pressure increased as expected as shown in the measured DC pressure curve. However, a strong peak of AC pressure was generated at t_b seconds after ignition. The extinguishing of the propellant occurred due to the rapid pressure decay. The cross-section of the grain after being extinguished at time t_b seconds was the same shape as expected at the steady state burning. The results indicate that the resonant burning occurs with a specific grain shape.

When a small quantity of solid particles such as aluminum or zirconium was added to the propellant grain, no pressure peaks were generated and a steady state burning was conducted until the propellant grain was completely consumed. The solid particles absorb the energy of oscillation and damp the observed oscillatory combustion when the generated oscillation is in the range of acoustic mode, approximately 500 Hz.



Before Combustion at Time 0 s

After Extinguishment at Time t_b s

Figure 12. DC and AC pressures in a rocket combustion chamber and cross-sections of the propellant grain before combustion and after being extinguished.

When a high-pressure oscillation is induced along the radial axis of the chamber, a rod can be set in the center axis of the port of the grain to alter the resonance acoustic mode of the radially directed oscillation. The rod is made of a ceramic-coated metal to protect against the high temperature combustion gas in the chamber.

When a low-frequency oscillation is induced along the axis of the chamber, physical separation of propellant grain by some insulation acts effectively to change the oscillatory mode.

When a non-acoustic mode of oscillation occurs, no oscillatory damping effect is accomplished by the addition of metal particles because the size of the particles is much smaller than the traveling oscillatory wavelength. However, the burning grain acts as a damping material if the shape of the grain is chosen to absorb the traveling pressure wave adequately.

8.3 Combustion under Centrifugal Acceleration

A spinning motion along the axis of a rocket projectile is provided to stabilize the vehicle and improve the flight trajectory. The spinning motion is created aerodynamically either by the fins attached to the projectile or by the nozzle fins attached to the interior surface of the nozzle, similar to thrust vector control fins. The centrifugal acceleration caused by the spinning motion affects the burn rate of the propellant grain, and then the thrust versus burning time is varied as compared to the case of no centrifugal acceleration.[9,10]

The combustion gas in the port of an internal burning grain flows along the burning surface towards the nozzle when no centrifugal acceleration is given. When a centrifugal acceleration is given, a pressure gradient towards the radial direction in the port is created and then the burn rate is increased by the increased pressure at the port surface of the grain. However, the effect of the centrifugal acceleration is trivial when the combustion products are only gaseous species.

When aluminum particles are added to a propellant grain, molten aluminum agglomerates are formed on the burning surface under the centrifugal force.[9,10] This agglomeration process occurs due to the higher density of the molten metal particles than that of gaseous products. The size of the molten agglomerates increases as the burning of the propellant grain proceeds. Since the temperature of the molten agglomerates is high, the heat flux transferred from the agglomerates to the burning propellant surface increases. Accordingly, the local burn rate of the propellant increases and then a number of pits are formed on the burning surface.

Combustion tests of an AP/CTPB composite propellant-grain were conducted using a spinning rocket motor.[9] The propellant consisted of 76.8% AP, 15.0% CTPB and 8.2% aluminum particles. The aluminum particles were 48 µm in diameter. The burning tests were conducted at 4 MPa under the centrifugal acceleration of 60 g. Burning interruption tests were done by nozzle separation during burning. When a tubular shaped grain was extinguished, pits were formed non-uniformly on the whole surface.

However, when a 6-pointed star-shaped grain was burned, pits were formed along the six points of the star as shown Figure 13. In addition, the burning surface area increased due to the formation of the pits. As a result, the pressure in the rocket motor was further increased corresponding to the relationship given by equation 24.

9. Design of Two-Stage Motors with Two Propellant Grains in One Chamber

9.1 Mass Balance of Booster Phase

To attain high thrust ratio of the booster and sustainer stages, two different propellant grains are combined in a single combustion chamber and burned simultaneously. Figure 14 shows a typical thrust or pressure versus burn time of a two-stage motor with two propellant grains (Propellant D and Propellant C) that burn in a single chamber. Propellants D and C burn simultaneously to create the booster phase with Propellant D being completely consumed in the booster phase. Then Propellant C, which remains after the booster phase, burns continuously to create the sustainer phase.

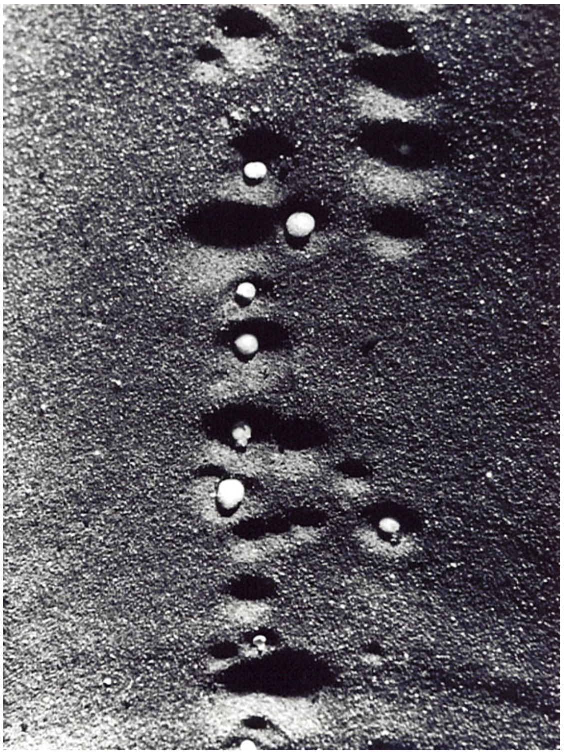


Figure 13. An extinguished burning surface of a six-pointed star-shaped aluminized AP/CTPB propellant grain.[9] Many pits are formed along each point of the star.

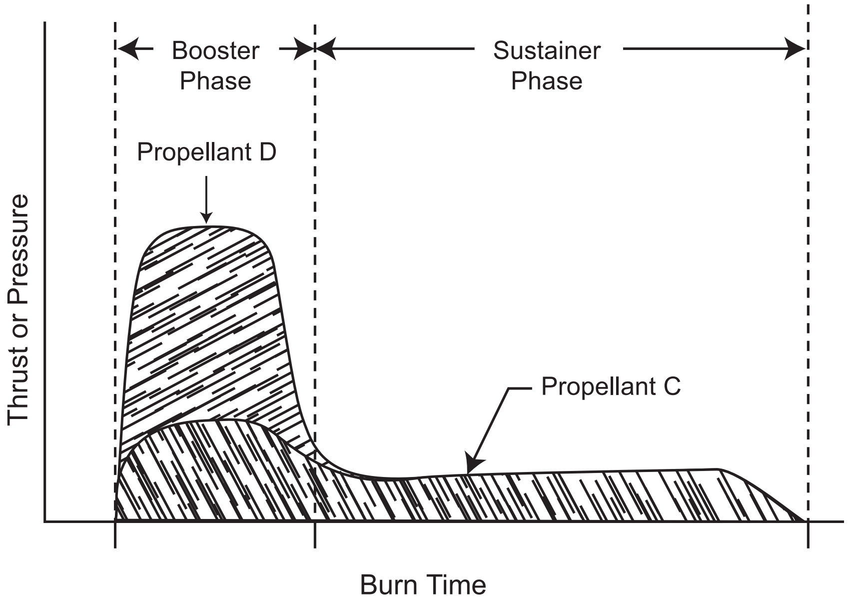


Figure 14. A two stage motor with two propellant grains in a single motor to create booster and sustainer phases.

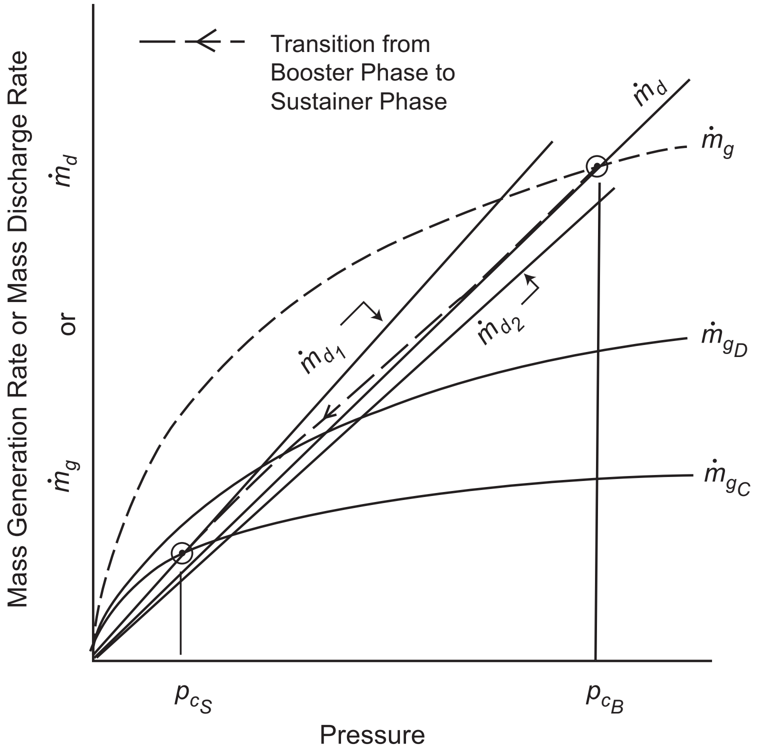


Figure 15. Mass balance in a rocket motor in which two propellant grains burn simultaneously to create the booster phase and one of propellant grain continues to burns to create the sustainer phase.

Figure 15 shows the mass balance in a rocket motor in which two propellant grains burn simultaneously during the booster phase and the one-grain that continues burning during the sustainer phase. If one assumes that the linear burning rates of Propellants D and C are given by

$$r_D = a_D p^{n_D} \quad \text{for Propellant D} \tag{39}$$

$$r_C = a_C p^{n_C} \quad \text{for Propellant C} \tag{40}$$

then the mass generation rates ($\dot{m}_{g_D}$ for Propellant D and $\dot{m}_{g_C}$ for Propellant C) at pressure p are given by

$$\dot{m}_{g_D} = a_D \rho_{p_D} p^{n_D} A_{b_D} \quad \text{for Propellant D} \tag{41}$$

$$\dot{m}_{g_C} = a_C \rho_{p_C} p^{n_C} A_{b_C} \quad \text{for Propellant C} \tag{42}$$

where the subscripts D and C denote Propellants D and C, respectively. The mass discharge rate $\dot{m}_d$ during the booster phase is given by

$$\dot{m}_{d_B} = c_{D_B} A_t p \tag{43}$$

As shown in Figure 15, the mass balance at the booster phase is expressed by the use of equation 21 as

$$\dot{m}_{d_B} = \dot{m}_{g_D} + \dot{m}_{g_C} \tag{44}$$

Substituting equations 39 to 43 into equation 44, one can determine the nozzle throat area A_t as

$$A_t = \frac{1}{c_{D_B}}\left(a_D \rho_{p_D} p^{n_D-1} A_{b_D} + a_C \rho_{p_C} p^{n_C-1} A_{b_C}\right) \tag{45}$$

As shown in equation 20, c_{D_B} is determined by the combustion temperature T_g, molecular mass M_g, and specific heat ratio γ of the combustion product. Since two different types of propellants burn simultaneously in a single chamber, the physical properties of the combustion products are not the mass averaged values of Propellants D and C. Both combustion products react with each other to produce an equilibrium combustion product as long as the reaction time in the chamber is sufficient. These physical values can be determined theoretically by the use of NASA SP-273 computer code[13] if one can provide the mass fractions and the chemical compositions of both Propellant D and Propellant C.

9.2 Mass Balance of Sustainer Phase

After burnout of the Propellant D grain in the booster phase, the remaining Propellant C grain continues to burn to create the sustainer phase. Since the nozzle throat area is the same as in the booster phase, A_t, determined by equation 45, the ratio of $A_b / A_t = K_n$ decreases rapidly and the pressure in the chamber decreases. As shown in Figure 15, the mass generation rate of Propellant C at the sustainer phase is given by

$$\dot{m}_{g_C} = a_C \rho_{p_C} p^{n_C} A_{b_C} \quad \text{for Propellant C} \qquad (42)$$

On the other hand, the mass discharge rate at the sustainer phase ($\dot{m}_{d_S}$) is given by

$$\dot{m}_{d_S} = c_{D_S} A_t p \qquad (46)$$

where c_{D_S} is determined using equation 20 adapted to the physical values of Propellant C. The mass balance is given by $\dot{m}_{d_s} = \dot{m}_{g_C}$ at the sustainer phase and is given by combining equations 42 and 46 as

$$c_{D_S} A_t p = a_C \rho_{p_C} p^{n_C} A_{b_C} \qquad (47)$$

The equilibrium chamber pressure at the sustainer phase (p_{c_S}) is determined by the use of equation 24 as

$$p_{c_S} = \left(\frac{a_c \rho_{p_c} K_{n_S}}{c_{D_S}} \right)^{\frac{1}{1-n_c}} \qquad (48)$$

where K_{n_S} is given by

$$K_{n_S} = \frac{A_{b_S}}{A_t} \qquad (49)$$

The burning surface area at the sustainer phase $\left(A_{b_s}\right)$ becomes equivalent to the burning surface area of A_{b_C} after burnout of the booster phase.

9.3 Design of Propellant Grains

An example of a practical design requirement of thrust versus burn time is shown in Figure 16 for a two-stage motor composed of two grains in a single combustion chamber. The booster phase thrust (F_B) is 800 N and the burning time (t_{b_B}) is 1.0 s; the sustainer phase thrust (F_S) is 85 N and the burning time (t_{b_B}) is 27 s. The transient time of 0.3 s from the booster phase to the sustainer phase is included in the booster phase. Since the maximum chamber pressure is in the booster phase, the chamber pressure at the booster phase $\left(p_{c_B}\right)$ is chosen to be 11.0 MPa for the design booster pressure. This booster chamber pressure is assigned by the choice of the chamber wall thickness and the strength of the material.

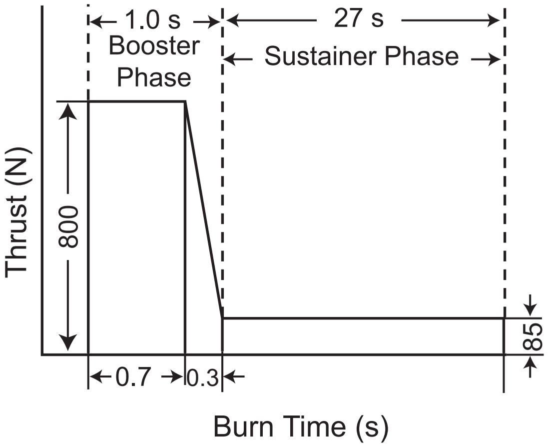


Figure 16. Thrust versus burning time requirement of a two-stage motor.

It is assumed that the convergent-divergent nozzle is designed to obtain an under expansion from p_{C_B} to atmospheric pressure p_a equal to 0.1 MPa. This is because the nozzle is used not only for the booster phase but also for the sustainer phase. Thus, the thrust coefficient c_{F_B} at the booster phase is determined to be 1.52 based on equation 29.

Using equation 28 one can get the nozzle throat area as

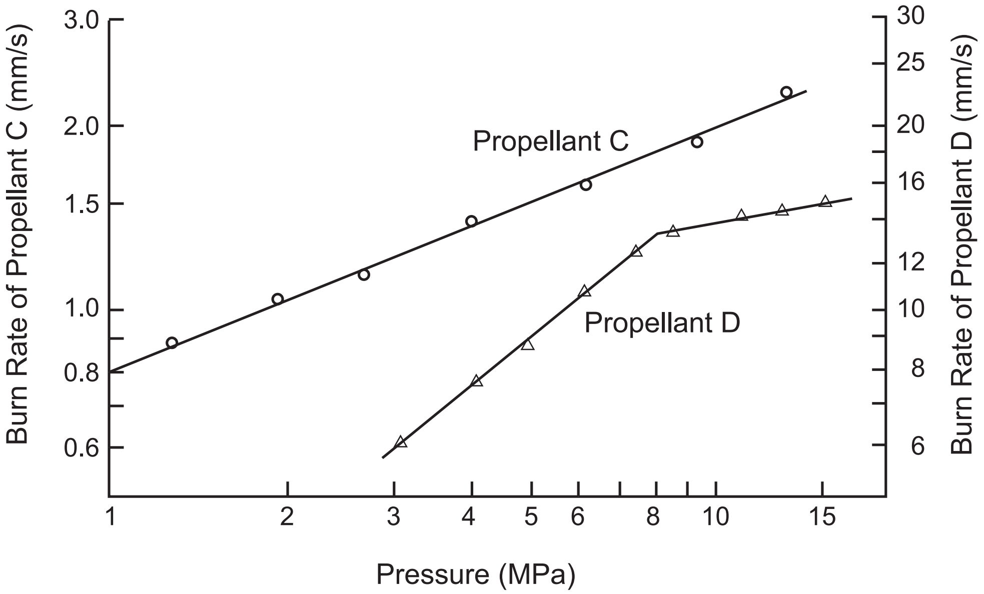


Figure 17. Burning rates of Propellant D and Propellant C as a function of pressure.

$$A_t = \frac{F}{c_{F_B} p_{c_B}} = \frac{800}{1.52 \times 11.0} = 47.8 \text{ mm}^2$$

The chamber pressure at the sustainer phase $\left(p_{c_S}\right)$ is also determined by the use of equation 28 as

$$p_{c_s} = \frac{F}{c_{F_s} A_t} = \frac{85}{1.30 \times 47.8} = 1.37 \text{ MPa}$$

where c_{F_S} is determined to be 1.30 because the nozzle expansion ratio is considered to be a close value of an optimum expansion of the nozzle.[11,12]

Accordingly, the design of the propellant grains used for the booster and sustainer phases is conducted at

p_{c_B} =11.0 MPa

p_{c_S} =1.37 MPa

A_t = 47.8 mm^2

The burn rate characteristics of Propellants D and C are shown in Figure 17. The physicochemical properties of the propellants are shown in Table 1.[11,12] The pressure exponent (n) of Propellant D changes from 0.81 below 8.0 MPa to 0.18 above 8.0 MPa. The burn rate

Table 1. Physicochemical Properties of Propellant D and Propellant C.

Property, Symbol (Units)	Propellant D		Propellant C
Density, ρ_p (kg/m^3)	1.57 x 10^{-3}		1.57 x 10^{-3}
Pressure exponent, n	$p \le 8.0$	0.81	0.40
	$p > 8.0$	0.18	
Burn rate constant, a	$p \le 8.0$	0.038	0.032
	$p > 8.0$	0.620	
Combustion temperature, T_g (K)	2470		1500
Gas constant, R_g (kg·m/kg·K)	36.9		33.9
Specific heat ratio, γ	1.25		1.24
Nozzle discharge coefficient, c_D (s^{-1})	7.38 x 10^{-3}		9.10 x 10^{-3}

(r) of Propellant C is extremely low to attain a low pressure burning and a long burning time (t_b). In addition, the combustion temperature (T_g) of Propellant C is low enough to protect against nozzle-throat erosion.

The burning area of the grain of Propellant C is determined by using equation 47 as

$$\begin{aligned} A_{b_C} &= \frac{c_{D_S} A_t}{a_C \rho_{p_C} p^{n_C - 1}} \\ &= \frac{9.10\times10^{-3}\times47.8}{0.032\times1.57\times10^{-3}\times1.37^{0.40-1}} \\ &= 4.20\times10^{4}\ \text{mm}^2 \end{aligned} \tag{50}$$

Using equations 41 to 45 plus combustion temperature, T_g, radius of curbature, R_g, and specific heat ratio, γ, obtained by NASA SP-273,[11] c_{D_B} and A_{b_D} are determined to be

$$c_{D_B} = 7.44\times10^{-3}\ \text{s}^{-1}$$

and the burning area of Propellant D is determined to be

$$A_{b_D} = 1.15\times10^{4}\ \text{mm}^2$$

Based on the required thrust versus burning time, the geometrical grain shapes are those shown in Figure 18 for Propellant D and in Figure 19 for Propellant C. The shape of the Propellant D grain is a wagon-wheel type, internal-burning shape, and the side and both ends are insulated with rubber sheets. The shape of the Propellant C grain is a star-type, internal and one-end burning shape, and the other end and the perimeter are insulated with rubber sheets. The relationship between the burning area and the regressing grain from the initial

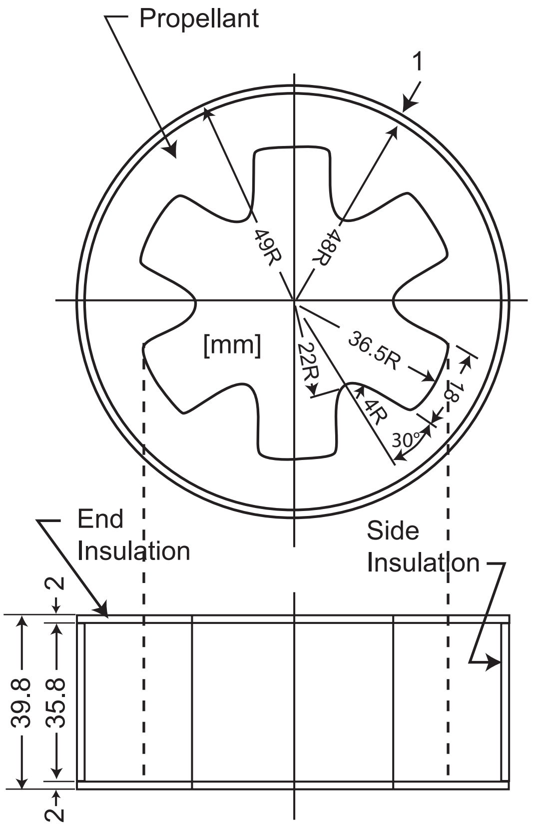


Figure 18. Geometrical propellant-grain shape of Propellant D. Note "R" refers to the radius of curvature.

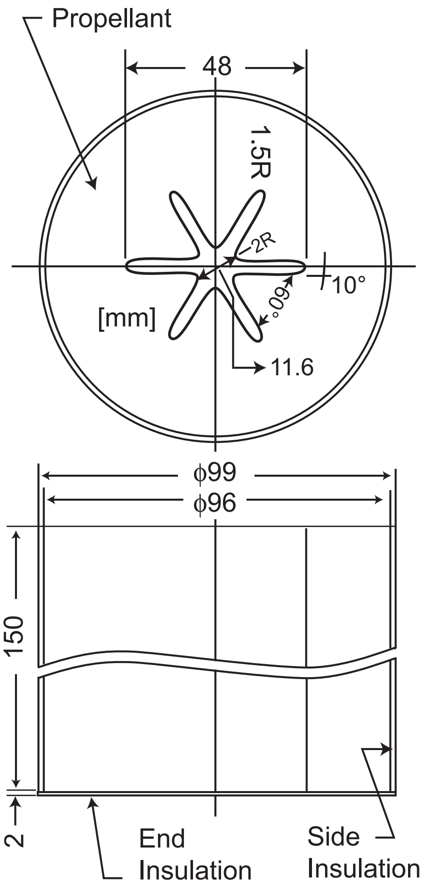


Figure 19. Geometrical propellant-grain shape of Propellant C. Note "R" means the radius of curvature.

surface is shown in Figure 20 for both Propellant D and Propellant C grains.

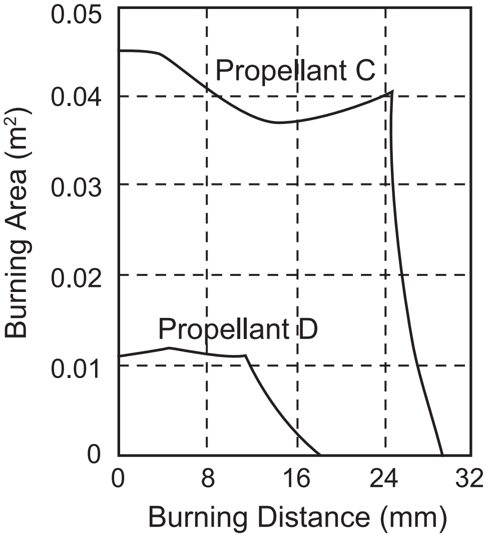


Figure 20. Relationship of burning area and regressing grain distance (web thickness consumed) of Propellant D and Propellant C.

9.4 Firing Test Results

Both grains, Propellants D and C, are set in a heavy weight rocket motor for static firing tests as shown in Figure 21. A pyrotechnic igniter, which is ignited electrically, is attached at the head end of the rocket motor, and a convergent-divergent nozzle is attached at the rear end of the motor. Pressure in the motor is measured with a pressure transducer gauge attached to the head end of the motor. Thrust is measured with a load-cell set in the thrust bench on which the rocket motor is set.

Figure 22 shows a pressure versus burning time curve of the rocket motor shown in Figure 21. The experimental curve agrees with the theoretical curve except for the increased pressure of 1.8 MPa at the booster phase. The burning time of the sustainer phase decreased about 0.6 s due to the excess burning of Propellant C during the booster phase. This observed excess burning of Propellant C during the booster phase is considered to be an effect of erosive burning, which occurs during high cross flow along the burning surface of Propellant C.

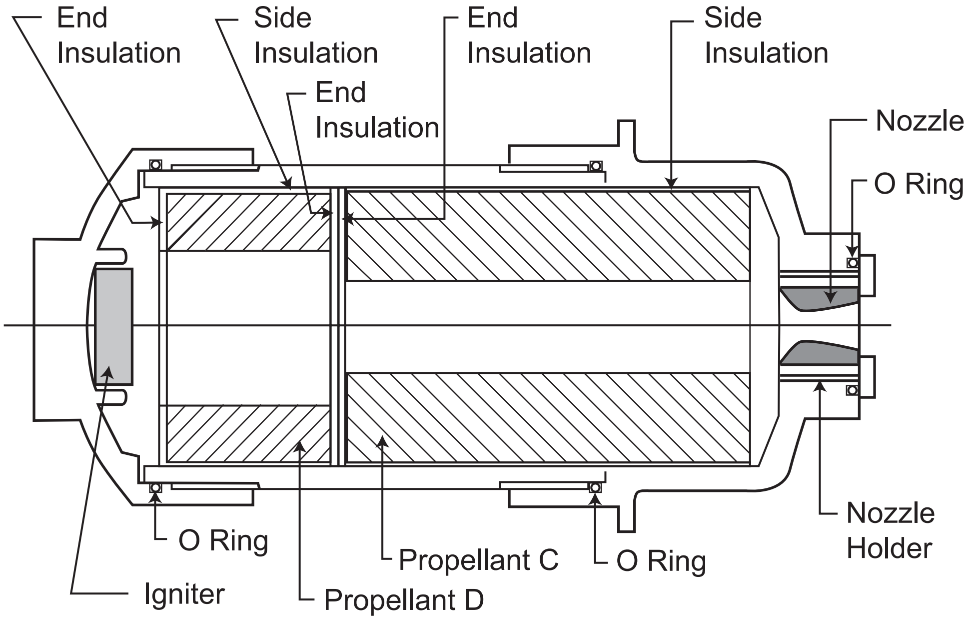


Figure 21. A structure of the two-stage heavy-weight motor with Propellant D and Propellant C grains in a single chamber.

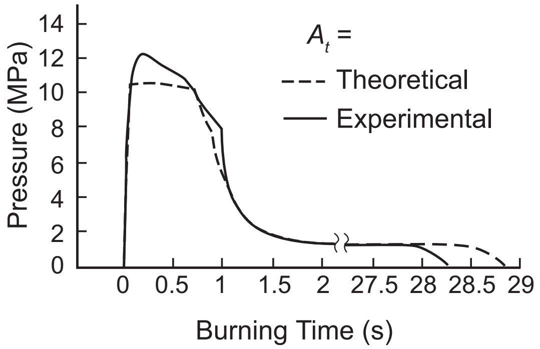


Figure 22. Theoretical and experimental results of pressure versus burning time of the two-stage motor with two propellant grains in one single chamber shown in Figure 21.

To examine the erosive burning effect on the burning rate of Propellant C, a burning interruption experiment was performed. One second after ignition of the rocket motor, the nozzle attached at the end of the rocket motor was separated. The chamber pressure decreased rapidly to atmospheric pressure (0.1 MPa). The Propellant D grain was completely consumed, but Propellant C grain remained. Figure 23 shows the cross-sectional star shaped Propellant C grain before combustion (a) and after it was extinguished (b) at the time of the Propellant D burnout. These results indicate that the burning rate of Propellant C increased about 7 % due to the erosive burning effect. This is confirmed by the pressure versus time plot shown in Figure 22.

Summary

The performance of a rocket motor is dependent on the physicochemical parameters of propellants such as burning rate, pressure exponent, temperature sensitivity, and the physical shape of the propellant grain. The thrust required for the rocket motor is determined by the required flight trajectory and by the aerodynamic drag that acts on the rocket projectile.

The thrust is dependent on the combustion pressure and the nozzle throat area that are determined by the mass generation rate and the mass discharge rate. A two-stage- rocket motor is attained by the combination of two different types of propellant grains in the combustion chamber.

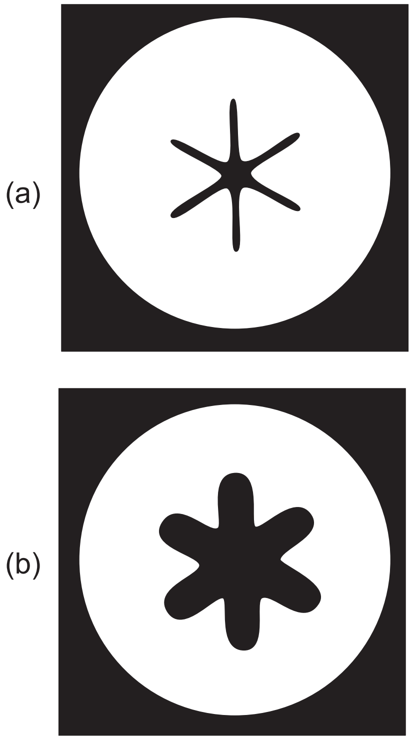


Figure 23. Cross-sectional star-shaped grain of Propellant C before combustion (a) and after being extinguished (b) one second into the burn.

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Pyrotechnic Spark Generation

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ABSTRACT

Pyrotechnically generated sparks are probably the earliest augmentation of pyrotechnic burning for entertainment. While much is known about spark production both scientifically and as a craft, new effects and enhancements continue to be made. This review article presents a summary of the basic science of incandescent bodies, which establishes the range of possibilities for sparks as well as their limitations. This is followed by a discussion of the pyrotechnic production of carbon and metal sparks, including control of spark duration and color. Finally, there are limited discussions of the control of corrosion of metal spark materials and the control of spark branching.

Introduction

The intentional production of pyrotechnic sparks contributes significantly to the beauty and spectacle of fireworks and was developed very early in the history of pyrotechnics. An early example of the use of sparks is the "fire-club" carried by the "green-man" (originally also called the "wild-man") shown on the title page of the second volume of John Bate's Book *Mysteries of Nature and Art*.[1] (See Figure 1.)

THE
SECOND BOOKE
Teaching moſt plainly, and withall
moſt exactly, the compoſing of all
manner of Fire-works for Tryumph
and Recreation.

By IOHN BATE.

LONDON,
Printed by *Thomas Harper* for *Ralph Mab*.
1635.

Figure 1. Illustration of "green-man" holding a "fire club" from reference 1.

Upon first consideration, the production of attractive spark effects may seem trivial; simply add an amount of some spark producing material to a basic pyrotechnic composition. For example, when titanium is added to rough Black Powder and pressed into comets, attractive white sparks can be produced (see Figure 2). However, upon closer examination, not all spark production is that simple. For example, consider effects such as Senko Hanabi,[2a] "fire-fly" spark effects,[3a] and even the duration of simple carbon sparks,[4a] all have complexities beyond the simple model suggested above.

This review article presents the basic chemistry and physics of spark incandescence; however, some questions will remain unanswered. This is because many interesting aspects of

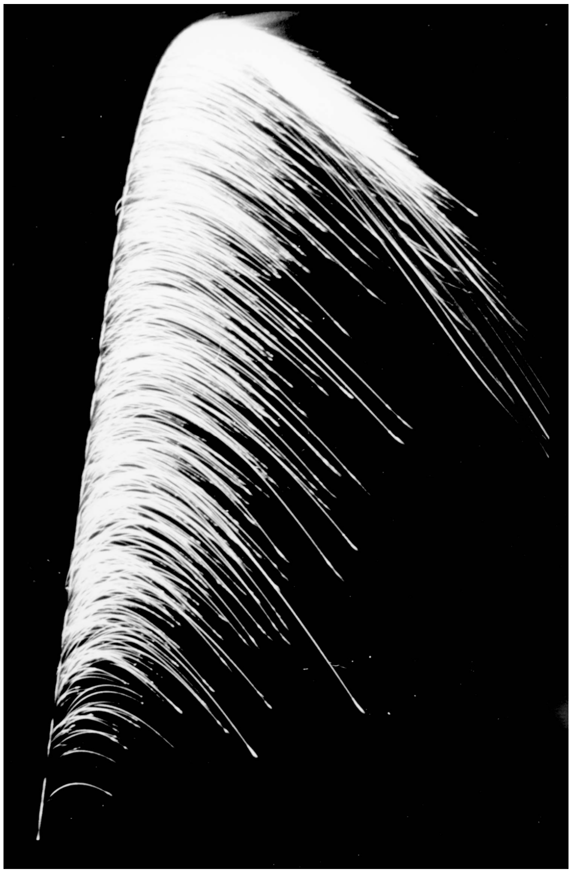

Figure 2. A Black Powder comet with 10% flake titanium (10–20 mesh).

spark production are still unknown; for example, the mechanism causing spark branching.

The attributes of spark producing pyrotechnics generally considered attractive are high spark density and long spark duration. To some extent, these are interrelated because when individual sparks last a long time, the appearance will be that of greater spark density. Another most attractive attribute, when the viewer is close enough to observe it, is spark branching, such as produced by cast iron sparks.

Incandescence

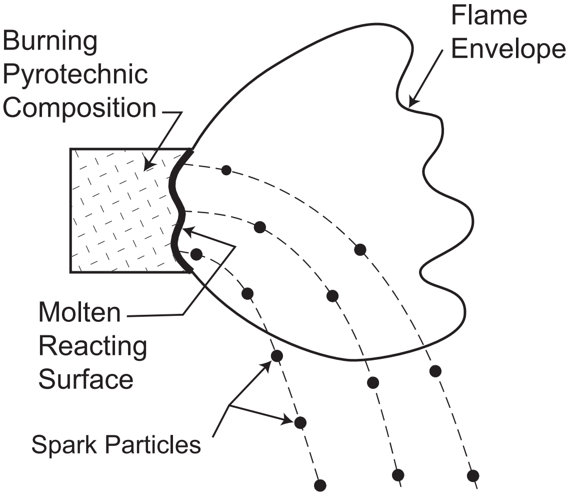

Figure 3. Illustration of the generation of pyrotechnic sparks.

In the simplest terms, pyrotechnic sparks are tiny pieces of glowing material emitted from the burning surface of a pyrotechnic composition. (See Figure 3.) Any liquid or solid particle will emit light (incandesce) when it is heated to a sufficiently high temperature. The brightness and color of the emitted light are both functions of temperature. This is demonstrated in Figure 4 for black bodies (ideal absorbers and emitters of thermal radiation).

Note in Figure 4 that an increase in temperature from 727 to 1727 °C results in an increase in peak emission by a factor of approximately 30. Note further that, in the range of visible emis-

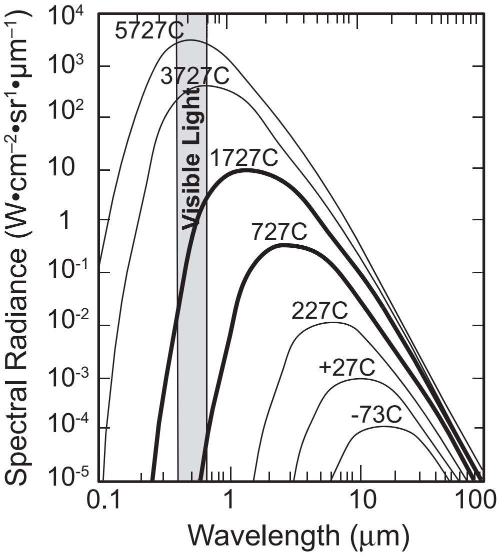

Figure 4. Spectral radiance of a black body at various temperatures.[5]

sions, there is an increase by a factor of approximately 100,000. At 727 °C, the visible emissions predominate at the extreme long wavelength (red) end of the spectrum. Accordingly, such an incandescent body will appear reddish to an observer. Whereas, at 3727 °C, the emissions are more evenly distributed across the entire visible range, producing nearly white light. The possibilities for color and relative brightness of black body sparks are summarized in Table 1.

Table 1. Color and Relative Brightness of Black Body Sparks.

Temperature (°C)	Descriptive Color[4b]	Relative Brightness(a)
500	Red	1
850	Reddish-Orange	4
1500	Orange	7
2200	Yellowish-White	9
3000	White	10

(a) Relative brightness is an estimate based on the Planck radiation formula and the assertion that human eyes have an approximate logarithmic response to light intensity when viewing points of light in a void.[6]

Some pyrotechnic spark particles are probably quite close to being black bodies (e.g., some carbon sparks); others (e.g., aluminum sparks) deviate noticeably from ideal[4b] black bodies and may be referred to as "gray bodies". Shimizu illustrates the perceived colors of black and gray bodies as a function of temperature in Figure 5. Note that, unlike black bodies, gray bodies have the ability to produce yellow sparks.

Based on the above discussion, it should be apparent that the color and brightness of pyrotechnic sparks are linked, and that the range of possibilities is rather limited. Red sparks will always be dim and white sparks must be bright. For the most part, it is not possible to produce bright red or dim white sparks. However, when points of light are viewed at a distance such that their size is less than the observer's visual acuity, size and brightness of the point of light are linked to some extent. That is to say, brighter objects appear somewhat larger, and larger objects appear somewhat brighter.[7] This presents an opportunity to make small adjustments in a spark's perceived brightness without affecting its color. For example, consider two sparks at the same temperature (color), one that is twice the diameter of the other. The larger spark will have 400% more surface area emitting light, and thus emits 400% more light. If these light sources are small enough and are seen in the dark there will be an approximate logarithmic relationship between intensity and perceived brightness.[6] Accordingly, the larger spark should be perceived as being about 60% brighter, but with the same color as the smaller spark. If this is correct, while spark color and brightness are linked, there is the possibility to make some independent adjustments. However, note that changing a spark's size will change its surface to mass ratio, which is likely to change its chemistry to some extent (discussed further below).

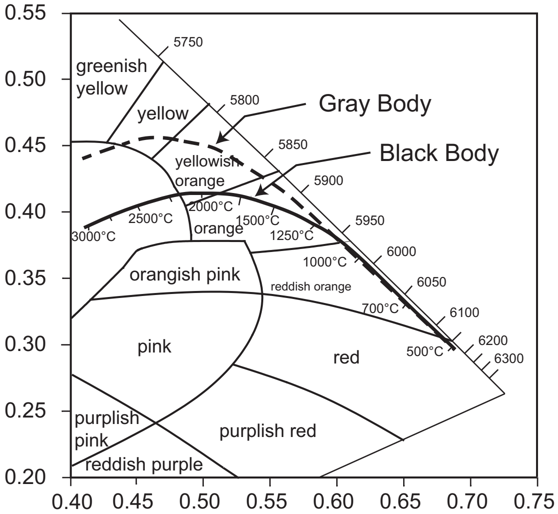

Figure 5. A portion of the chromaticity diagram illustrating the color of light emitted by black and gray bodies.[4c]

Pyrotechnic Spark Duration

Based on the discussion of incandescence, it would seem that merely introducing inert particles into a flame could produce useful pyrotechnic sparks. There the particle would be heated to high temperature and would leave the flame glowing brightly. In practice this does not work at all well; see Figure 6, which is of two essentially identical fountains (gerbs). Both fountains were made using the same compressed handmade Black Powder, the added spark producing materials were of the same size, were essentially the same material (mostly iron), and both fountains had a choke of 1/3 the tube diameter. Nonetheless, there is a stark difference in the performance of the two fountains. The difference is that the fountain on the left was made using stainless steel grains, while the one on the right was made using cast iron grains.

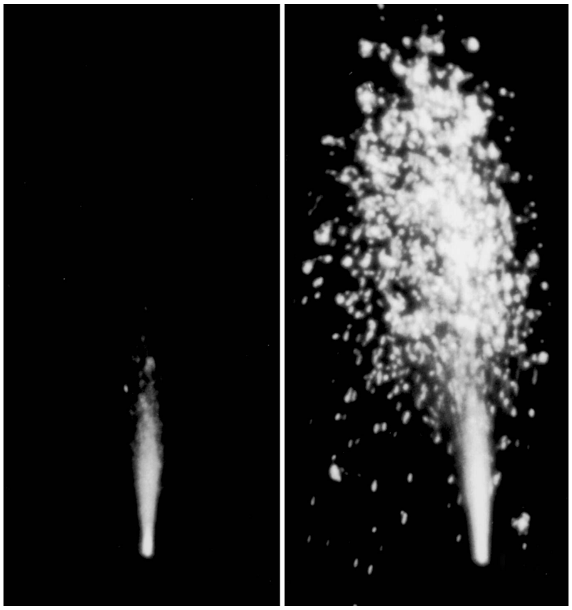

Figure 6. Pictures of two essentially identical fountains, both producing incandescent sparks; however, only the fountain on the right produced sparks that were bright enough and had long enough duration to be attractive.

In each case the spark particles were heated to high temperature and left the flame incandescing. However, the stainless steel grains quickly became invisible after leaving the flame. Not only are such sparks not aesthetically pleasing, they burn out so quickly that they actually seem depressing to the viewer. Such performance is not unique for stainless steel; it is common for all relatively inert spark particles. This is the result of the low mass of spark particles, which causes them to loose their thermal energy (become invisible) quickly after they leave the high temperature environment of the flame. This will always be true unless there is some mechanism for the spark particle to produce additional energy. For the cast iron sparks, which persisted a long time (and then produce attractive branching sparks), the mechanism for producing this additional energy is air oxidation.

$$4\ \mathrm{Fe}_{(\mathrm{High\ Temp.})} + 3\ \mathrm{O_2} \rightarrow 2\ \mathrm{Fe_2O_3} + \mathrm{Heat} \quad (1)$$

The difference for the stainless steel spark grains is that stainless steel, while mostly iron, is formulated such that air oxidation (rusting) is essentially precluded. Without the ability to produce additional thermal energy, these sparks quickly cool to invisibility (i.e., to below the temperature of significant visible light emission).

Common Spark Producing Elements

For the reason discussed above, all common spark producing materials are capable of self sustained air oxidation after being heated to a high temperature, for example:

$$\mathrm{C}_{(\mathrm{High\ Temperature})} + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{Heat} \qquad (2)$$

$$\mathrm{Ti}_{(\mathrm{High\ Temperature})} + \mathrm{O_2} \rightarrow \mathrm{TiO_2} + \mathrm{Heat} \qquad (3)$$

Table 2 lists the most common chemical elements used for the production of pyrotechnic sparks. Also included are zinc, zirconium, and magnesium, which are occasionally used as spark producers.[8–10]

The color and brightness of a spark particle depend on the temperature that is maintained during its air oxidization. To some extent, the spark particle’s temperature depends on the amount of heat released in the oxidation reaction (heat of combustion). Unfortunately, while it is easy to calculate the heat of combustion (see Table 2), there are other complicating factors. It is obvious from the data in Table 2 that, by itself, the amount of energy produced is not a completely successful predictor of spark color (temperature). For example, the heats of combustion for carbon and iron are essentially the same, and yet there is a significant difference in typical spark color. Also, it would not be predicted that magnesium would produce white sparks. Table 2 includes each material’s electronegativity, which is an indicator of the ele-

Table 2a. Properties of Spark Producing Elements.

Element	Spark Color	Heat of Combustion(a)	Combustion Product(b)	Electronegativity[11]
Carbon(c)	Orange	–94	CO_2	2.55
Iron	Yellow	–98	Fe_2O_3	1.83
Zinc	Yellow(d) (green/blue/white)	–84	ZnO	1.65
Aluminum	Yellowish White to White	–200	Al_2O_3	1.61
Titanium	Yellowish White to White	–225	TiO_2	1.54
Zirconium	White	–263	ZrO_2	1.33
Magnesium	White	–144	MgO	1.31

Table 2b. Properties of Spark Producing Elements (Continued).

Element	Melting Point °C(e)	Boiling Point °C(e)	Combustion Product(b)	Melting Point °C(e)	Boiling Point °C(e)
Carbon(c)	~3550	3825(g)	CO_2	–57(f)	–78(g)
Iron	1535	2750	Fe_2O_3	1565	—
Zinc	420	907	ZnO	1975	—
Aluminum	660	2467	Al_2O_3	2072	2980
Titanium	1660	3287	TiO_2	~1840	~2800
Zirconium	1852	4377	ZrO_2	~2700	~5000
Magnesium	649	1100	MgO	2852	3600

(a) The Heat of Combustion at 25 °C (more correctly termed Enthalpy of Combustion) is derived from reference 12, and the units are kilocalorie per mole of fuel. Note further that Heat of Combustion is temperature dependent.

(b) This is the assumed principal product.

(c) Note that charcoal commonly used in pyrotechnics is not pure carbon. Charcoal is typically only about 82% carbon,[4d] and it principally has an amorphous structure.[2b] However, the listed heat of combustion is for carbon as graphite.

(d) Sparks produced in a gas flame (Bunsen burner) eventually appear yellow, but when produced pyrotechnically, they appear greenish–bluish white.

(e) Values are from reference 12.

(f) Melting point at a pressure of 5.2 atmospheres.

(g) Temperature of sublimation.

ment's relative tendency to acquire additional electrons. Electronegativities are known for all elements and seem to be a good predictor of spark color.

Other important factors in determining spark color are the melting and boiling points of the spark material and their air oxidation products (also presented in Table 2). The reason the spark material's melting and boiling points are important is that they will determine the physical state in which most of the air oxidation reaction takes place. For example, carbon will be a solid at its expected spark reaction temperature, while most other materials will be liquid. This is not of overwhelming importance, but it affects our understanding of the nature of carbon sparks (discussed below). Of more importance is the fact that zinc and magnesium will be vaporizing as they react and that only solids and liquids incandesce. This is an important part of the reason why these potentially useful materials are only infrequently used as spark materials.

The melting and boiling points of air oxidation products are important because they can affect the degree of protection afforded the spark particle (discussed below) and generally set a limit on the maximum temperature (color and brightness) reached by a spark particle. The reason for this is that thermal energy is consumed or released in the processes of vaporizing and solidifying, respectively.

$$\text{Liquid} + \text{Heat of Vaporization} \rightarrow \text{Gas} \quad (4)$$

$$\text{Liquid} \rightarrow \text{Solid} + \text{Heat of Fusion} \quad (5)$$

For example, the amount of energy produced by a typical spark particle will be sufficient to cause it and its oxidation product to be molten. However, because of their high heat of vaporization, sufficient energy is not produced to allow the spark particle to completely vaporize. This acts to prevent the temperature reached by a spark particle from exceeding its boiling point. On the other hand, once air oxidation is complete and the spark particle cools, the liberation of the heat of fusion can help maintain the spark's temperature a little longer.

Control of Carbon Sparks

For spark particles ignited in the flame of a gas burner (e.g., Bunsen burner), equations of the type 1 through 3 apply. The control of spark duration is straightforward; large particles take longer to burn than small particles. Thus, if one wished to produce longer duration spark particles, simply use larger particles of the spark material (providing they are not so large that the flame fails to ignite them). Control of spark color is even less complicated; it is not possible. The color produced is exclusively a function of the material being used.

For pyrotechnically generated sparks, the combustion products of the primary fuel(s) and oxidizer(s) complicate spark chemistry. As it turns out, this is a good thing, because it provides the basis for some control over spark duration and color. Combustion products can be gases, liquids or solids, depending on temperature and the chemicals used. For example, consider equation 6, a chemical equation for the confined burning of potassium nitrate, charcoal and sulfur. (Note that while this example is based on information from references 2, 4, 13, and 14, for this illustration it has been idealized and simplified.)

$$8\,KNO_3 + 11\,C + 2\,S \rightarrow 2\,K_2CO_3 + 2\,K_2S + 4\,N_2 + 9\,CO_2 + \text{Heat} \quad (6)$$

In the presence of oxygen, such as when burning the composition in air, there is a further exothermic reaction of potassium sulfide to form potassium sulfate, equation 7.

$$K_2S + 2O_2 \rightarrow K_2SO_4 + \text{Heat} \quad (7)$$

The nitrogen and carbon dioxide produced are gases. The melting points of potassium carbonate, potassium sulfide and potassium sulfate are 891, 840 and 1069 °C, respectively.[12] Based on the expected temperature of most pyrotechnic sparks, these three combustion products will be liquid.

The liquid (molten) combustion products are of primary consequence for sparks. Gases play a role in helping to eject droplets of molten combustion products from the burning surface, but for the most part, the gases must then be lost to the atmosphere. Generally the solid combustion products are relatively inert at typical spark temperatures. If the ratios of reactants in equation 6 are altered by the addition of more charcoal, some will not react in the flame and will come to reside within the molten droplets of combustion products, as suggested in Figure 7, to form a composite spark particle.

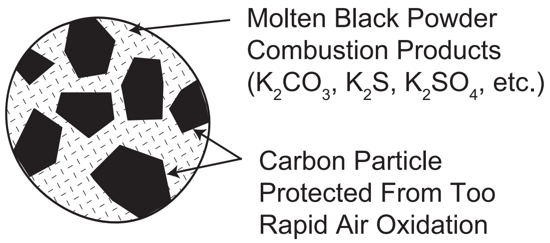

Figure 7. Illustration of a composite carbon spark droplet, consisting of solid charcoal particles residing in droplets of molten combustion products.

One function of some of the liquid components in the charcoal spark particle is to produce additional thermal energy by their reaction with atmospheric oxygen (equation 7). However, the more important function is to retard the air oxidation of the charcoal particles. The importance of this can be appreciated if one ignites even large charcoal particles (20 mesh) in a gas flame. These sparks are totally consumed in approximately one second. Whereas the duration of pyrotechnic charcoal sparks can easily be many seconds, even when the charcoal particles are smaller than 100 mesh. The increase in spark duration is thought to be the result of greatly reducing the direct exposure of the carbon particles to atmospheric oxygen. However, since oxygen from the air can be expected to dissolve into the molten spark droplet, oxygen can still reach carbon particles that are buried within a molten spark droplet, although at a much lower rate. The molten combustion products help achieve both of the most desirable spark attributes, long duration and high visual density. (In part, this is because more and smaller particles of the spark material can be used, but it is mostly because each spark particle lasts so long that more sparks are visible at any one time).

The ability to alter the type and amount of molten combustion products provides the opportunity to control carbon spark duration, and, to some extent, spark color. If the formulation is adjusted to produce a relatively high percentage of liquid products, the charcoal particles will have greater duration (because they are better protected from air oxidation), and their color should tend to be more red (because they are reacting more slowly and thus maintain a lower temperature). If the formulation is adjusted to increase the ratio of reactive to inert products (i.e., potassium sulfide to potassium carbonate), the sparks may be more orange (because the additional energy production will raise their temperature).

As an example of control of spark duration, consider the two gold charcoal spark formulations in Table 3. These formulations have been written to list handmade meal powder as the primary ingredient. This helps to explain the reason for the difference in the spark durations. If it is assumed that in air, meal powder reacts fairly completely, then it produces mostly inert combustion products. The formulation producing short duration sparks has only charcoal added to the meal powder (and binder). The long duration formulation has about the same amount of charcoal, but it also has a significant additional amount of sulfur. The extra sulfur produces more molten combustion products, which provides additional protection for the carbon particles. The long duration formulation also produces more sulfides, and thus has an additional source of spark energy while competing with the residual charcoal for air oxygen.

Table 3. Gold Charcoal Spark Formulations.

Ingredient[(a)]	Short Duration[2c]	Long Duration[15]
Handmade meal [(b)]	73	65
Charcoal (Air Float)	22	20
Sulfur	—	10
Binder[(c)]	5	5

(a) Ingredients are given in mass percent.

(b) This is a mixture of 75% potassium nitrate, 15% air float charcoal, and 10% sulfur.

(c) The binder is glutinous rice starch and dextrin, for the short and long duration formulations, respectively.

The size of the individual carbon particles within the composite spark particle does play a role in determining the duration of carbon sparks, but it is not of paramount importance. This is because the charcoal particles are contained within these larger spark droplets. For example, consider that some sparks produced using lampblack are among the longest lasting carbon sparks, yet lampblack has much smaller particles than common charcoals.

While it has not been reported in the literature on sparks, the relative size of the composite carbon spark droplets must also have an effect on spark duration. That is because both the relative reaction rate with atmospheric oxygen and the rate of energy loss must be functions of the droplet's surface area (proportional to particle diameter squared), while the amount of reacting material within the droplet is a function of its volume (proportional to particle diameter cubed). Accordingly, all else being equal, larger droplets should have longer durations. This is because the rate of oxygen absorption is proportional to the spark particle's surface area and not its mass.

There are a number of factors that must affect the size of composite carbon spark droplets, among these are: the fraction and rate of production of gaseous combustion products; the viscosity of the liquid combustion products; for a comet star, the velocity of the star through the air, or for a gerb, the diameter of the choke. Accordingly, rapidly burning comets with much gas production, that generate low viscosity liquid combustion products, and that are rapidly moving through the air, must tend to produce relatively smaller (shorter duration) composite spark particles.

Control of Metal Sparks

In an earlier section it was suggested that the control of sparks produced in a gas flame was rather straightforward. Spark duration is controlled by particle size, with larger spark particles burning longer, provided they are not too large to be successfully ignited while they remain in the flame. In this case, spark color is controlled only by the choice of spark material. The control of pyrotechnically generated metal sparks is often treated as simply as if they were produced using gas flames. While this simple treatment has been sufficient to explain some aspects of pyrotechnic metal sparks, there are complexities that deserve discussion.

For the metals listed in Table 2, considering their expected spark temperatures (based on their colors and the temperature information in Table 1), most of these spark particles and their oxides will be liquid[2d] (see Table 4). Thus, for iron, aluminum, titanium and zirconium, the oxides can be expected to collect on the metal particle surfaces and act to retard their air oxidation in somewhat the same way as discussed for carbon sparks.

Beyond the protection afforded by the molten metal oxides, additional protection may be provided by the combustion products of the primary fuel(s) and oxidizer(s), in much the same way as discussed for charcoal sparks. Consider the pairs of aluminum and titanium spark formulations given in Table 5. While the pairs of formulations differ in the flame temperatures produced, that is unlikely to be the primary reason for the different spark colors produced. This is because the effect of high flame temperature will persist for only a short time after the spark particle leaves the flame; recall the example shown in Figure 6. For the aluminum and titanium formulations, it is believed that the difference is mostly the result of

Table 4. Observations Regarding Spark Producing Elements.

Element	Physical State(a) Element	Physical State(a) Oxide	Common Forms	Common Size Range (Mesh)	Other Use References
Carbon	solid	gas	Charcoal Lamp Black	10 to 325 –325	2e
Iron	liquid	liquid	Iron Filings Steel Filings	20 to 60 ~100	16b 16c
Zinc(b)	gas	liquid (?)	Dust Filings	325 20 to 60	9
Aluminum	liquid	liquid	Flake Atomized	20 to 80 60 to 150	16b, 17
Titanium	liquid	liquid	Sponge Turnings	10 to 100 10 to 100	18 19
Zirconium(b)	liquid	liquid	Sponge Turnings	10 to 80 10 to 80	(b)
Magnesium(b)	gas	liquid	Atomized	10 to 50	10

(a) The most likely abundant physical state.

(b) Rarely used in fireworks for spark production.

Table 5. Aluminum and Titanium Spark Formulations.

Ingredient[(a)]	Aluminum Sparks		Titanium Sparks	
	White	Yellow	White	Yellow
Potassium perchlorate	43	—	45	—
Potassium nitrate	—	38	—	54
Aluminum powder	52	48	—	—
Titanium (10–20 mesh, flake)	—	—	20	16
Sulfur	—	9	—	13
Charcoal (air float)	—	—	—	13
Zircalium (Al_2Zr, –100 mesh)	—	—	20	—
Accroides resin	—	—	10	—
Binder[(b)]	5	5	5	4
Reference	4e	4e	20	21

(a) Ingredients are given in mass percent.

(b) This is glutinous rice starch and dextrin, for the aluminum and titanium formulations, respectively.

the protection provided to the metal by the reaction products. In both cases, the formulations producing yellow sparks contain a moderately large amount of sulfur, and thus are expected to produce a relatively high abundance of molten combustion products that are capable of retarding the air oxidation of the metal particles. If this is true, some of the same measures used for the control of carbon sparks should apply to metal sparks.

Another method that can sometimes be used to alter the color of white aluminum sparks is to add a source of sodium to the composition. In this case, it is believed that the strong atomic emissions from sodium can act to add a yellow component to the light emitted by the spark. Although not documented, this may also be the case for other metals.

Unlike the more common spark elements, the boiling points of magnesium and zinc are quite low, 1100 and 907 °C, respectively. Accordingly, the spark particles must be in the process of vaporization, with some of the oxidation occurring with metal vapor while still inside the flame. This can be confirmed by observing these sparks when ignited in a gas burner; both types of sparks appear to be propelled such as from gas production, and both leave a smoke trail from condensing combustion products. Their low boiling points make these materials somewhat less useful for the production of pyrotechnic sparks. For example, only quite large magnesium particles seem capable of surviving long enough to exit the pyrotechnic flame to produce sparks.[10] Also, when metals are partially consumed in the flame, they will tend to brighten it, which generally detracts from any sparks produced. However, to the contrary, zinc dust can be used to make quite attractive comets such as electric spreader stars. In this case, the star burns to produce a large number of fragments, each burning greenish-bluish-white. It seems likely that an important part of the mechanism for fragmenting the stars may be the production of zinc gas, which then burns to produce the attractive flame. The source of the greenish-bluish-white flame is most likely a combination of spectral emissions from gaseous zinc (blue[22]), high temperature incandescence of liquid zinc oxide particles in the flame, and possibly spectral emissions from gaseous zinc oxide (yellow green[23]).

Alloys and Corrosion

In addition to the elements listed in Table 4, alloys are often used for spark production. Among the most common are magnalium (magnesium-aluminum, typically 50% magnesium), ferro-titanium (typically 30% iron), and ferro-aluminum (typically 35% iron). In addition, cast iron and carbon steels are alloys of mostly iron with a small amount of carbon. Generally, the spark related properties of these alloys are an average of their constituents' properties. Accordingly, both ferro-titanium and ferro-aluminum produce light yellow sparks. Ferro-titanium is easier to ignite than ferro-aluminum, which apparently acquires some ignition difficulty from its aluminum content.

Corrosion can be a problem for some spark materials, especially for iron and magnesium. The most common method for handling this corrosion for iron is to coat the particles with linseed oil, which air cures to form a protective film. Protection for iron can also be accomplished using alloys with either of the corrosion resistant metals—aluminum or titanium. Thus, ferro-titanium and ferro-aluminum typically need no treatment, providing the alloys contain no more than 30 to 40% iron.[24] Magnesium, typically, needs to be protected from corrosion. For magnesium, treatment with linseed oil is usually reasonably effective except when using ammonium perchlorate.[25] Protection can also be accomplished by formation of a conversion coating on the surface of the particles.[2g,25,26] Similar to iron alloys, magnalium (magnesium-aluminum alloy) that contains at least 30 to 40% aluminum generally does not need protection. Aluminum generally requires no protection even in water dampened compositions; however, when protection is needed, the addition of a small amount of boric acid will generally be sufficient.[2f] Another approach to solving corrosion problems is the use of thoroughly dried materials in addition to non-aqueous binding techniques.

"Fire-Fly" or Transformation Effects[3]

In the "fire-fly" effect, also sometimes called transformation or transition effects, initially rather normal appearing long duration orange charcoal sparks are produced, which ultimately transform to produce yellow-white sparks. In some instances, a single orange spark may produce a series of short-lived bright yellow-white sparks, thus giving somewhat the appearance of a fire-fly. These spark formulations contain both charcoal particles and aluminum flakes.

In the initial several seconds of the spark's duration, the air oxidation reaction is limited to converting potassium sulfide to potassium sulfate, and consuming the excess carbon in the spark particle, with the aluminum remaining essentially dormant. Then at some point, conditions allow the aluminum to ignite to produce the yellow-white spark effect. It has been suggested that the aluminum ignition process may be repeated more than once as suggested in Figure 8, to produce the fire-fly effect.[3] Proper functioning of the fire-fly effect requires that the burning composition produces flame temperature that is not sufficiently high to cause the immediate ignition of the aluminum. Also required is the use of a charcoal with the capability of engendering the correct conditions to produce a sustained low temperature spark and then cause the ignition of the aluminum flakes. If the late stage spark temperature is too low, the aluminum will fail to ignite and not produce the transition to bright yellow-white.

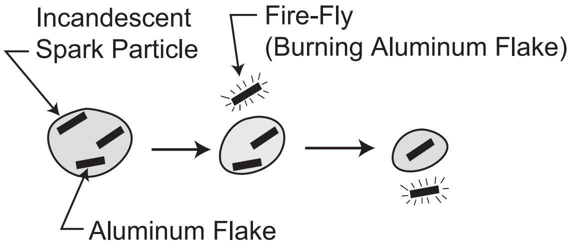

Figure 8. Shimizu's model of the mechanism for the production of Fire-Flies.[3b]

An excellent treatment of the subject of the fire-fly effect[3a] implies that the use of coarse flake aluminum (flitters) is required. However, the temperature of the spark particle (during the carbon burning) is sufficiently high and sufficiently long in duration to melt the aluminum. This would seem to make the original shape of the aluminum irrelevant. That flake aluminum is not necessary for the fire-fly effect is confirmed by a report[27] of using coarse atomized aluminum to produce the effect. It is also reported[27] that magnesium, magnalium and titanium[28] can be used to produce somewhat similar delayed ignition metal sparks.

Branching Sparks and Senko Hanabi

Sparks that branch, such as illustrated in Figure 9, are extremely attractive when one is close enough to observe the effect. Most spark materials provide a limited degree of branching; however, none are close to rivaling those produced by cast iron and high carbon steels. While details of the mechanism resulting in branched sparks is not reported in the literature, it is known that the percentage of dissolved carbon in the iron is important. It is reported[2h] that 0.7 to 0.8% carbon is the most effective for producing finely branched sparks. [The combustion product(s) of carbon (carbon monoxide or carbon dioxide) is unusual to the extent that it is a gas. Accordingly, one wonders if this is a part of the explanation.]

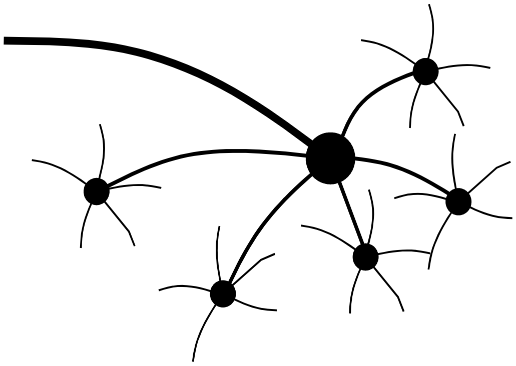

Figure 9. Illustration of the appearance of branching spark particles.

Attractive branching sparks are also produced by the traditional Japanese item, Senko Hanabi[2a] and the European spur-fire fountain, called flowerpots. Senko Hanabi is typically made in one of two forms, one is a thin straw coated with a wet composition (Figure 10-a1), and the other has dry composition twisted inside tissue paper. (Figure 10-a2). The effect is produced using a sulfur-rich Black Powder composition that burns rather slowly to produce a ball of molten combustion products suspended from the straw or twisted tissue paper. Initially, for a period of several seconds, not much appears to happen. Then branching sparks begin to be projected from the molten ball, increasing in intensity and producing a delicately beautiful display of branching orange sparks.

During the initial apparently quiescent period, there is continuing air oxidation of the reactive combustion products. One possible series of reactions, based on information from reference 2a are shown in equations 8–10.

$$2\,K_2CO_3 + 5\,S \rightarrow 2\,K_2S_2 + 2\,CO_2 + SO_2 \qquad (8)$$

$$K_2S_2 + O_2 \rightarrow K_2S + SO_2 \qquad (9)$$

$$K_2S + 2O_2 \rightarrow K_2SO_4 \qquad (10)$$

$$C + (?) \rightarrow \text{Sparks} \qquad (11)$$

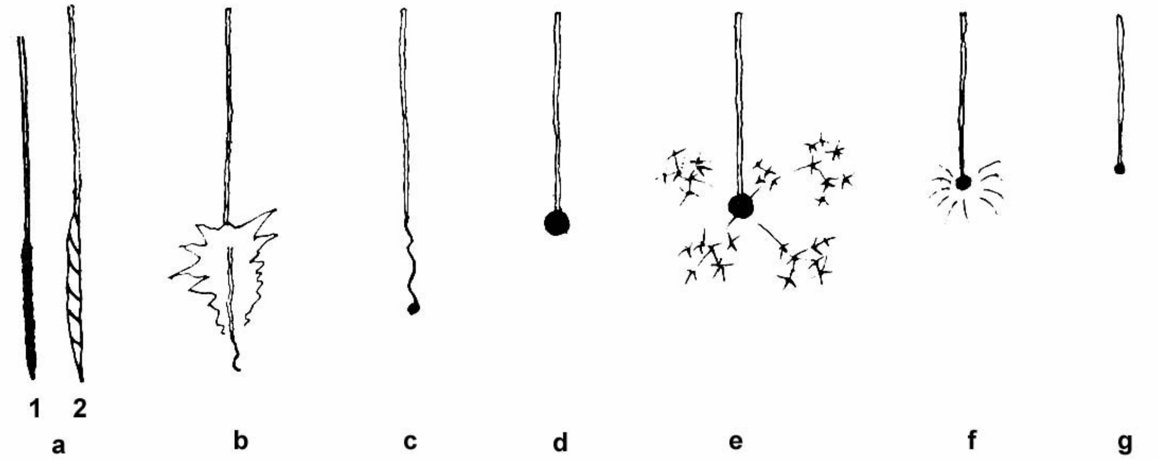

Figure 10. (a) Two typical forms of senko hanabi. (b–g) The typical senko hanabi process.[4f]

These reactions (equations 8–10) produce heat that maintains the temperature of the molten ball of combustion products and alters its chemical components. In addition, an amount of carbonized material from the straw or tissue paper is continually adding to the molten ball. At some point minor explosive reactions of the carbon particles produce the branching sparks (equation 11). While details of the spark mechanism are unknown, the nature of the source of carbon (charcoal or soot) plays an important role in the character and abundance of the sparks produced.[2i]

Glitter and Microstars

The glitter effect can be thought of as a spark effect wherein initially orange sparks are generated, then after a brief time delay they proceed to produce a bright flash. That flash may range in color from yellowish-orange to white. Figure 11 illustrates the glitter effect, which should not be confused with the simple continuous aluminum spark effect, often referred to as flitter. The glitter effect and its chemistry have been fairly extensively treated in the literature,[29–36] although there remains some disagreement about certain aspects of its chemistry. For this reason, and because the subject has recently been covered in a review article,[34] the discussion of glitter in this article will be rather limited in its scope. The initial chemistry is similar to that for carbon sparks. Equation 12 suggests a simplified chemical reaction for sulfur-rich Black Powder, which produces the yellowish-orange sparks (molten droplets). Equations 13 and 14 were seen above as equations 9 and 10 and provide thermal energy to maintain the temperature of the spark droplets sometimes referred to as the “spritzels”.[32] Equation 15 is the reaction producing the terminating glitter flash. In equation 15 the exact nature of the fuel is not specified, because there is some disagreement as to what it is: Fish[30] implies it is aluminum sulfide, Oglesby[32] suggests it is aluminum metal, and Stanbridge[31] suggests it is aluminum carbide.

$$2\,KNO_3 + 3\,C + 2\,S \rightarrow K_2S_2 + 3\,CO_2 + N_2 \qquad (12)$$

$$K_2S_2 + O_2 \rightarrow K_2S + SO_2 \qquad (13)$$

$$K_2S + 2\,O_2 \rightarrow K_2SO_4 \qquad (14)$$

$$K_2SO_4 + (\text{Al-based fuel}) \rightarrow \text{Flash} \qquad (15)$$

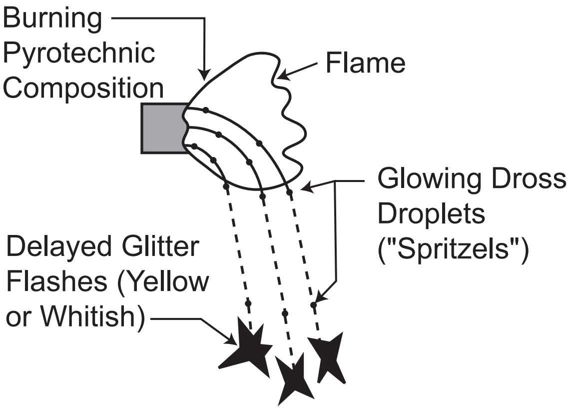

Figure 11. Illustration of the appearance of glitter sparks and flashes.

The attributes of attractive glitter effects are long delay and large bright flashes. Glitter delay is most commonly achieved using antimony sulfide or alkali metal or alkaline earth oxalate, carbonate or bicarbonate in the composition. Flash size and brightness can be increased using barium nitrate, a spherical atomized aluminum, or magnalium. If larger particle size aluminum is used, the glitter flashes will produce a radial spray of yellowish-white sparks.

Microstars[37,38] are small pellets of composition, usually emitted by fountains that react invisibly (at low temperature) as they move through the air and eventually produce a bright flash of light. Microstars may be thought of as a strobe effect[39] where only a single flash is produced. Although there is some similarity between microstars, glitter and simple pyrotechnic sparks, microstars are not typically considered to be a spark effect, and they will not be discussed in this article. There is, however, the exception that conventional metal sparks can be produced in the microstar flash reaction. Presumably, this is accomplished using metal particles that are too large to be fully consumed by the flash reaction.

Conclusion

Spark effects have been used to augment firework effects for a very long time, yet new and improved effects continue to be developed. In some cases, our understanding of spark effects is quite good, in others, much remains to be learned. Hopefully this review article has summarized much of what is known and identified some things deserving further study.

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Glitter Chemistry

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ABSTRACT

Pyrotechnic glitter is characterized by a liquid spark terminating in a delayed flash. The chemical mechanisms responsible for the delay and the flash are not known with certitude. Several pyrotechnists have proposed hypothetical mechanisms to account for the phenomena. The different proposals engender different predictions regarding how a glitter performs as a function of its composition. Consequently the behavior of experimental glitter compositions sheds light on the validity of the various proposals.

Although experiments on colored glitter are hitherto disappointing, with the exception of yellow, further work may yet yield useful results.

The most significant safety concern that glitter compositions present is a potential exotherm upon dampening. This can largely be avoided by careful selection of the combination of metal and glitter additives.

Keywords: glitter, formulation, potassium, nitrate, barium, theory

Introduction

The characteristic property of a burning glitter composition is that it produces rather dim sparks, which suddenly undergo a short lived but tremendous increase in light output. This is illustrated in Figure 1. The glowing of the sparks prior to the glitter flash may not always be obvious when observing a glitter effect in fireworks, but is readily apparent in photographs. Thus there must be at least two different kinds of spark chemistry occurring after the spark has left the burning pyrotechnic composition.

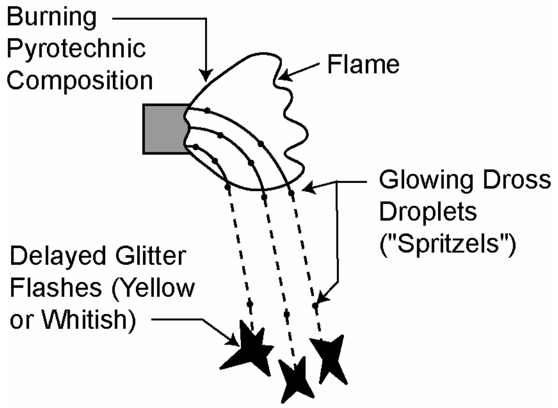

Figure 1. Pyrotechnic glitter.

The first phase of a glitter spark resembles that of a classic golden streamer composition utilizing charcoal, not only in color and brightness, but also in that they have both been shown to consist of liquid droplets. The flash phase of a glitter spark, by contrast, resembles the functioning of a pyrotechnic flash powder. Somehow these two disparate elements have been hybridized in the essence of a glitter composition.

An excellent golden streamer formulation, given by Freeman,[1] is shown as formulation 1 in Table 1. The green powder component is a simple intimate mixture of finely powdered potassium nitrate, charcoal, and sulfur, in proportions 75:15:10, without any milling or wet processing. The use of green powder in this composition, and in the glitter compositions discussed later, is not essential, and it may be replaced by its components or sometimes by commercial meal powder without substantially affecting the chemistry involved. However, it is convenient to discuss glitter chemistry by considering the green powder components collectively as an independent chemical entity.

Table 1. Formulations.

Ingredients	1	2	3	4	5	6	7	8	9	10	11	12	13
Green powder	65		65	75	65	64				65	70	65	65
Barium nitrate		55	11										
Sodium nitrate							50						
Rubidium nitrate								55					
Potassium perchlorate									48				
Sulfur	10		10		10		12	10	19			5	5
Charcoal (air float)	20						11	10	9				
Dextrin	5		5	5	5	5	4	5	4	5		5	5
Aluminum (atomized, 120–140 mesh)				10		9			7	10			
Aluminum (atomized, 325 mesh)											7		
Magnalium (20:80, 200 mesh)		10	2										
Magnalium (50:50, –60 mesh)		35	7		10		10	10				10	10
Titanium (20–40 mesh)						3							
Antimony sulfide (fine powder)				10	10	14	8	10		10			10
Strontium oxalate						5							
Barium sulfate										10			
Molybdenum sulfide											13		
Sodium oxalate							5				10		
Indium sulfide												15	
Sodium bicarbonate									13				5

Key to Formulations:

1	Golden streamer	8	Potassium-free bright silver glitter (excellent but expensive)
2	Flash powder compatible with golden streamer (better to use –200 mesh magnalium for flash powder)	9	Perchlorate glitter
3	Pearl glitter (short delay)	10	Silver glitter (good)
4	Silver glitter	11	Glitter fountain (off-white color of glitter flashes is aesthetically displeasing)
5	Bright silver glitter (long delay)	12	Bright silver glitter (very expensive)
6	Silver glitter fountain	13	Vivid yellow glitter
7	Sodium nitrate glitter (not very useful in practice)		

A pyrotechnic flash powder that is compatible with the golden streamer components is shown as formulation 2 in Table 1. The observations discussed so far lead one to think that one may be able to make glitter by replacing the additional charcoal content of the golden streamer composition with the flash powder, as shown in formulation 3. Remarkably enough, given the rather naive assumptions and the lack of more sophisticated formulation development, this composition does indeed produce quite good glitter stars of the short delay type known as “pearl”.[2]

So far the chemistry that may be involved in glitter reactions has not been considered, and for this we must turn to various glitter mechanism theories which pyrotechnists have proposed.

Lloyd Scott Oglesby: Potassium Sulfide Theory[2,3]

The vast majority of glitter compositions contain potassium nitrate, charcoal, and sulfur, many of them in the proportions present in Black Powder or green powder. One may therefore reasonably suppose that the first chemistry to occur is the combustion of such materials. According to Partington,[4] "The proportions of the constituents and the main products of combustion correspond roughly with the following equation:

$$2\,KNO_3 + S + 3\,C \rightarrow K_2S + N_2 + 3\,CO_2$$

Carbon monoxide, however, is also evolved, and the residue contains potassium carbonate and sulfate." Note that the equation is only a first approximation to the combustion of gunpowder. However, glitter is substantially more complex than gunpowder, and so consideration of all the equations pertinent to the combustion of gunpowder may hinder rather than aid the understanding of glitter.

The pearl glitter composition, formulation 3, contains an excess of sulfur. This extra sulfur can participate in a slight modification of the gunpowder reaction to produce potassium disulfide:

$$2\,KNO_3 + 2\,S + 3\,C \rightarrow K_2S_2 + N_2 + 3\,CO_2$$

Oglesby describes reactions such as this, occurring in the reacting layer of a glitter star, as "on board reactions". Potassium disulfide has a melting point of 470 ºC and is thus formed as liquid droplets that Oglesby calls "spritzels". Accordingly, the subsequent set of reactions, occurring in these glitter droplets, can be called "spritzel reactions". Oglesby suggests a two-stage oxidation of the spritzels using atmospheric oxygen:

$$K_2S_2 + O_2 \rightarrow K_2S + SO_2$$

$$K_2S + 2\,O_2 \rightarrow K_2SO_4$$

There is precedent for this sequence of reactions. These are the reactions that are thought to occur in high-sulfur golden streamer compositions, such as formulation 1, as well as in "senko-hanabi".[5] In such compositions the liquid potassium disulfide forms a matrix in which the unreacted charcoal is suspended. These droplets of potassium disulfide together with charcoal are commonly referred to as "charcoal sparks". Not only does the charcoal gradually oxidize from atmospheric oxygen, but so does the potassium disulfide, first to potassium monosulfide and then to potassium sulfate. All of these reactions generate heat.

Meanwhile, what becomes of the aluminum that is present in some form in almost all types of glitter? According to Oglesby the aluminum has remained chemically unchanged so far in the process and is present as a suspension in the spritzels. Then as the potassium sulfate concentration increases, a critical point is reached when the glitter flash reaction occurs:

$$2\,K_2SO_4 + 8\,Al \rightarrow 3\,K_2S + 4\,Al_2O_3$$

Again, there is precedent for such a reaction. Sulfates are known to function as oxidizers in pyrotechnic flash powders.[6,7]

The set of four reactions depicted above form the core of Oglesby's theory of glitter chemistry. Yet they are not sufficient. The ingredients potassium nitrate, sulfur, charcoal, and aluminum alone do not produce an effective glitter composition. Something else is needed.

The glitter composition, formulation 3, contains barium nitrate, and this indeed suffices as an extra ingredient to make the glitter work. Oglesby suggests that barium nitrate undergoes a sequence of reactions analogous to those of potassium nitrate:

$$Ba(NO_3)_2 + S + 3\,C \rightarrow BaS + N_2 + 3\,CO_2 \qquad \text{(on board reaction)}$$

$$BaS + 2\,O_2 \rightarrow BaSO_4 \qquad \text{(spritzel reaction)}$$

$$3\,BaSO_4 + 8\,Al \rightarrow 3\,BaS + 4\,Al_2O_3 \qquad \text{(flash reaction)}$$

Why does this make a difference if the reactions are so similar? The difference is that potassium sulfate (m.p. 1069 ºC) is a liquid at the spritzel temperature, whereas barium sulfate (m.p. 1580 ºC) is a solid. If the flash reaction is initiated by a critical concentration of sulfate

$$2\,KNO_3 + S + 3\,C \rightarrow K_2S + N_2 + 3\,CO_2$$

$$3\,K_2S + Sb_2S_3 \rightarrow 2\,K_3SbS_3$$

(on board reactions)

$$4\,K_3SbS_3 + 3\,O_2 \rightarrow 6\,K_2S_2 + 2\,Sb_2O_3$$

$$K_2S_2 + O_2 \rightarrow K_2S + SO_2$$

$$K_2S + 2\,O_2 \rightarrow K_2SO_4$$

(spritzel reactions)

$$3\,K_2SO_4 + 8\,Al \rightarrow 3\,K_2S + 4\,Al_2O_3$$

(flash reaction)

Figure 2. The series of reactions that may occur when antimony sulfide is used in glitter.

oxidizer present as a solution in potassium sulfide, then barium sulfate plays no part in *initiating* the flash reaction. There are two consequences of this. Firstly, barium sulfide takes up some of the oxygen available to the spritzel, and so the potassium sulfate concentration builds up more slowly. Consequently there will be a greater delay time until the initiation of the flash reaction. Secondly, the total amount of oxidizer available for the flash reaction is increased, resulting in a brighter flash.

Barium nitrate is neither the most common, nor the most effective glitter additive. That honor goes to antimony sulfide. Any theory of glitter must take into account the role of antimony sulfide.

Spur fire, the characteristic composition used in the fountain called a flower pot, also frequently contains antimony sulfide.[8] These fountains produce large and long-lasting spark droplets with much fire-branching, each droplet a senko-hanabi. When viewed at short range, the effect is incredibly beautiful.

Oglesby suggests the series of reactions (see Figure 2) when antimony sulfide is used in glitter.

Notice that this mechanism does not require any extra sulfur, as reflected in formulation 4, and so the first step is the standard gunpowder reaction. There are two key steps resulting from the use of antimony sulfide: Firstly is the formation of potassium thioantimonite (K_3SbS_3). Secondly is the oxidative decomposition of this in the spritzel to produce potassium disulfide and antimony oxide (Sb_2O_3). The latter is a relatively volatile material and may be partially lost from the spritzel as it falls through the air. The more extensive sequence of spritzel reactions allows for a greater delay until the flash reaction.

One can go further and combine the use of additional sulfur together with antimony sulfide, such as in formulation 5. In this case the potassium sulfides can combine with antimony sulfide to form potassium thioantimonate (K_3SbS_4). Oxidative loss of sulfur in the spritzel can then give potassium thioantimonite (K_3SbS_3), and the reactions proceed as before. The key parts of the sequence are depicted below:

$$2\,K_2S_2 + K_2S + Sb_2S_3 \rightarrow 2\,K_3SbS_4$$

(on board reaction)

$$K_3SbS_4 + O_2 \rightarrow K_3SbS_3 + SO_2$$

(first spritzel reaction)

As one might expect, the addition of yet another spritzel reaction to the sequence allows particularly long delays to be achieved.

Formulation 6, for a glitter fountain based on Lancaster's white glitter star formulation,[9] introduces yet another glitter additive, strontium oxalate. Oglesby suggests that such materials function in a way described by the following equations:

$$SrC_2O_4 \rightarrow SrCO_3 + CO \quad \text{(on board reaction)}$$

$$SrCO_3 \rightarrow SrO + CO_2 \quad \text{(on board reaction)}$$

$$2\ SrO + 3\ K_2S_2 \rightarrow 2\ SrS + 3\ K_2S + SO_2 \quad \text{(spritzel reaction)}$$

$$SrS + 2\ O_2 \rightarrow SrSO_4 \quad \text{(spritzel reaction)}$$

$$3\ SrSO_4 + 8\ Al \rightarrow 3\ SrS + 4\ Al_2O_3 \quad \text{(flash reaction)}$$

The initial decompositions of strontium oxalate consume heat, thereby slowing down concurrent reactions and adding to the delay, perhaps by allowing larger spritzel size. The melting point of strontium sulfate (1605 ºC) is comparable to that of barium sulfate (1580 °C), and so there is a similar additional contribution to the delay and to the flash brightness.

Strontium oxalate is but one of a range of carbonates and oxalates with utility as glitter delay agents. (See Table 2.) Carbonates function in a similar way, as can be seen by their intermediacy in the oxalate reaction sequence.

Table 2. The Role of Carbonates and Oxalates.

	Oxalate	Carbonate	Bicarbonate
Barium	×	×	
Strontium	×	×	
Calcium	×	×	
Magnesium	×	×	
Lithium	×	×	
Sodium	×		×
Potassium	×		×
Antimony	×		

× = useful materials

Note that the postulated mechanism for the functioning of these materials requires the presence of potassium disulfide. Consequently, such glitter delay agents cannot function as such by themselves, but only in the presence of additional sulfur or antimony sulfide.

Note that formulation 6 retains dextrin even though it is for a dry fountain composition. Oglesby suggests that carbohydrates, such as dextrin, serve a function in glitter—beyond that of binding—by furnishing water as a combustion product, which affects the spritzel viscosity and "enhances the formation of sulfides rather than carbonates in glitter mixtures". Lancaster[10] also concurs stating, "Dextrin is quite useful in the right proportions and we actually put it in some dry mixes, which it tends to make rather 'bubbly'".

Ferric oxide is a glitter additive that does not fall within the categories discussed so far. Oglesby suggests that it is reduced to iron and iron sulfides as on board reactions; then "The iron serves as a low energy fuel after the spritz [ejection of spritzels] and as a simple physical barrier to fluid motion in the spritzel."

Oglesby's theory is expounded in more depth in reference 2.

Myke Stanbridge: Aluminum Carbide Theory[11]

This theory is analogous to Oglesby's theory except for the key role proposed for aluminum carbide. The theory may be summarized by the following set of equations:

$$2\ KNO_3 + 2\ S + 3\ C \rightarrow K_2S_2 + N_2 + 3\ CO_2 \quad \text{(on board reaction)}$$

$$4\ Al + 3\ C \rightarrow Al_4C_3 \quad \text{(on board reaction)}$$

$$K_2S_2 + O_2 \rightarrow K_2S + SO_2 \quad \text{(spritzel reaction)}$$

$$K_2S + 2\ O_2 \rightarrow K_2SO_4 \quad \text{(spritzel reaction)}$$

$$3\ K_2SO_4 + 8\ Al \rightarrow 3\ K_2S + 4\ Al_2O_3 \quad (\textit{spritzel reaction})\text{— not flash}$$

$$3\ K_2SO_4 + Al_4C_3 \rightarrow 3\ K_2S + 2\ Al_2O_3 + 3\ CO_2 \quad \text{(flash reaction)}$$

The easiest way to understand what is going on is to consider the differences between this and Oglesby's theory. Firstly, a portion of the aluminum is postulated to be converted to aluminum carbide as an on board reaction. The remaining aluminum reacts with potassium sulfate as soon as the latter is formed in the spritzel flying through the air. Note that, for Stanbridge, Oglesby's flash reaction is part of the delay mechanism. When all the aluminum is consumed, the concentration of potassium sulfate rises until criticality is reached, and the flash reaction proceeds with aluminum carbide as the fuel.

The reader is referred to the articles by Stanbridge for the more subtle points of the theory. There do not appear to be any major points of departure from Oglesby's theory other than those mentioned here.

Troy Fish: Aluminum Sulfide Theory[12]

This theory is quite similar to that of Stanbridge with the critical difference of aluminum sulfide formation in place of aluminum carbide formation. A quote from Ellern exemplifies the principle behind this theory: "An extremely potent, but seemingly very little known, mixture is the one of flake aluminum and sulfur in approximately stoichiometric ratio of about one to two parts. It can be ignited with an ordinary match and reacts slowly with brilliant white glow, forming beads of aluminum sulfide".[13] Under certain conditions the reaction can be quite violent.[14] Stanbridge makes thermodynamic arguments that either aluminum carbide or aluminum sulfide, but not aluminum, could be the fuel in the flash reaction.

Fish does not describe the theory in detail and provides no equations. The author has therefore taken the liberty of interpreting the theory in the form of the equations that follow:

$$2\,KNO_3 + S + 3\,C \rightarrow K_2S + N_2 + 3\,CO_2 \quad \text{(on board reaction)}$$

$$2\,Al + 3\,S \rightarrow Al_2S_3 \quad \text{(on board reaction)}$$

$$K_2S + 2\,O_2 \rightarrow K_2SO_4 \quad \text{(spritzel reaction)}$$

$$3\,K_2SO_4 + 2\,Al_2S_3 \rightarrow 3\,K_2S_2 + 2\,Al_2O_3 + 3\,SO_2 \quad \text{(flash reaction)}$$

Fish makes use of this theory in formulating glitter compositions. The first two equations are taken to represent "base fires", which are then mixed with the other glitter components. The first equation simply represents green powder. The second equation represents the stoichiometric mixture of aluminum and sulfur. Fish actually uses a slight excess of sulfur in this second base fire, presumably to allow for some loss due to its volatility at high temperatures.

A key point of departure for this theory, compared with the others, is that the excess sulfur commonly present in glitter compositions is not considered to react to form potassium disulfide. Aluminum sulfide is formed instead, with potassium monosulfide as the other sulfur-containing primary-reaction product. Note that each of the theories discussed so far proposes a different fuel for the flash reaction.

Fish considers the delay effect of antimony sulfide to be firstly physical, on account of its high latent heat of fusion. The process of melting absorbs heat, thereby retarding the on board reactions. Then in the spritzel the following delay reaction occurs:

$$2\,Sb_2S_3 + 9\,O_2 \rightarrow 2\,Sb_2O_3 + 6\,SO_2$$

This reaction generates heat and retards potassium sulfate formation by virtue of its oxygen consumption.

Michael Swisher: Thermitic Theory[15]

None of the theories presented so far provides a good explanation of the role of ferric oxide in certain glitter compositions. The most familiar combination of ferric oxide and aluminum is the thermite reaction:

$$Fe_2O_3 + 2\,Al \rightarrow Al_2O_3 + 2\,Fe$$

Swisher postulates this as the flash reaction in such glitter compositions. How does this idea relate to more common compositions that do not contain ferric oxide? The classic preparation of metallic antimony involves heating antimony sulfide with iron.[16]

$$Sb_2S_3 + 3\,Fe \rightarrow 3\,FeS + 2\,Sb$$

One may immediately recognize this as being closely analogous to the standard thermite reaction. Thus, Swisher postulates a similar reaction with aluminum as the flash reaction for glitter compositions containing antimony sulfide:

$$Sb_2S_3 + 2\,Al \rightarrow Al_2S_3 + 2\,Sb$$

It is interesting to contrast the idea of aluminum sulfide being a product of the flash reaction with that of Fish's theory, where aluminum sulfide is consumed in the flash reaction. Note that the suggestion of Fish that antimony sulfide is converted to the oxide prior to the flash reaction is also consistent with the latter being thermitic in nature:

$$Sb_2O_3 + 2\,Al \rightarrow Al_2O_3 + 2\,Sb$$

Takeo Shimizu: Polysulfide Reduction Theory[17]

Shimizu concurs with the formation of potassium sulfides, as previously described:

$$2\,KNO_3 + 2\,S + 3\,C \rightarrow K_2S_2 + N_2 + 3\,CO_2 \quad \text{(on board reaction)}$$

However, for Shimizu these sulfides are the oxidizing agent for the flash reaction: "The bloom is produced by the reaction of the aluminum with the K_2S_x."

$$3\,K_2S_2 + 2\,Al \rightarrow 3\,K_2S + Al_2S_3 \quad \text{(flash reaction)}$$

Thus Shimizu is in agreement with Swisher in proposing that aluminum sulfide may be the product of the flash reaction, but at odds with Fish and Stanbridge who suggest that aluminum sulfide may be a fuel for the flash reaction. Oglesby suggests no role for aluminum sulfide in glitter chemistry.

Note that no specific spritzel reaction is key to the production of flash reactants in Shimizu's theory. Indeed Shimizu acknowledges that sulfur is lost from the potassium sulfides during the spritzel phase. Rather, the flash reaction is initiated upon reaching a critical temperature: "when small particles of molten residue pass through the air, they increase in temperature while being oxidized by atmospheric oxygen. If they achieve a sufficiently high temperature, then blooms are produced". Presumably, this feature is also common to Swisher's theory, in contrast to the other three theories all of which require a build up of critical concentration of potassium sulfate in order to initiate the flash reaction, though perhaps also via a temperature rise mechanism.

Experimental Observations

The different theories of glitter chemistry outlined in this paper were developed by the respective authors in response to their own observations and theoretical considerations. This constitutes the first two stages of the scientific process. The next step is to distinguish between the validity of different theories by means of experiments. Fortunately all the theories were couched in such a way as to allow testable predictions of changes in the behavior of glitter as a result of changes in compositions. (Theories that do not allow for testable predictions are not in the realm of science.)

Experiments will not necessarily lead us to conclude that one of the theories is "correct". Some theories (notably Oglesby's) are so extensive that they may be found to be "partially correct". Also, the theories are not entirely mutually incompatible. Indeed there are common features shared between some of them. Finally it is possible that all of the theories could be shown to be incorrect, in which case we should all have to think again.

In general, the theories postulate the formation of certain transient chemical intermediates that are then destroyed in a later stage of the glitter process. Thus one cannot simply analyze combustion products to determine which path the reaction took. One can, with substantial difficulty, quench the glitter reaction at an intermediate stage, such as the spritzel, and analyze the mixture for the proposed intermediates.

Both Oglesby and Stanbridge provide some micro analytical data to support their theories but, as Oglesby points out, "Some of the sulfide melts studied were not stable for more than one half second after capture". Similarly, Shimizu states, "It is difficult to establish the mechanism of the flash solely through chemical analysis". Ultimately the success of the theories must depend on their ability to predict the actual behavior of glitter compositions.

The author's glitter star tests used pumped stars of 7/16" diameter fired from 1/2" i.d. Roman candles and observed visually.

1. The Necessity for Potassium

Several of the glitter theories postulate the formation of potassium sulfides, K_2S_x, as key intermediates in the process of glitter. Indeed, Oglesby states, "Potassium sulfide is therefore a necessity from the theoretical view and has been experimentally determined to be necessary".[2] If this is strictly correct, one would predict that a composition devoid of potassium will not function as a glitter. One of the obvious ways to attempt a yellow glitter is to replace the potassium nitrate content of a white glitter with sodium nitrate. Sodium is the element directly above potassium in the periodic table and so the substitution is chemically analogous.

The author prepared a variety of star compositions consisting of sodium nitrate, sulfur, charcoal, antimony sulfide, aluminum, and dextrin. The results were invariably a bright yellow star with no sign of the glitter effect.

It is interesting to put oneself in the mind of a chemically oriented pyrotechnist one hundred years ago, when aluminum was being introduced as a firework material. Such a pyrotechnist might well have predicted the yellow illumination star described above, but surely would never have guessed what would happen with potassium nitrate as the oxidizer.

On the other hand Winokur has been able to devise a composition utilizing sodium nitrate as the sole oxidizer (formulation 7) that can function as a glitter under certain conditions.[18] Following Winokur's suggestions the author confirmed that five grams of the composition, when burnt in a loose pile, ejected numerous short delay flashes with excellent yellow color, along with a large yellow flame. In addition Winokur exactly described the burning behavior of the composition pressed in an unchoked 1/2" i.d. tube as starting with an excellent yellow glitter, shortly degenerating into a yellow flame. The composition does not function as a glitter when used for stars. Despite its lack of much practical utility, this composition is of theoretical importance for it shows that the glitter effect can take place without any potassium salts, albeit under very limited circumstances.

It would appear then that the complete replacement of potassium with sodium does allow a glitter to function, but only marginally so. Oglesby is explicit about what is required of potassium: "Potassium sulfide melts below the melting point of potassium sulfate and that is what it takes to make glitter". The melting points are 840 °C for potassium sulfide and 1069 °C for potassium sulfate. By contrast the melting points of sodium sulfide and sodium sulfate are 1180 and 884 ºC, respectively, in the reverse order from the potassium salts. Thus Oglesby's theory predicts that sodium nitrate cannot function as a replacement for potassium nitrate in most glitter compositions.

The element most closely related to potassium in the opposite direction from sodium is rubidium, situated directly beneath potassium in the periodic table. The author prepared potassium-free compositions utilizing rubidium nitrate as the oxidizer, such as formulation 8. In contrast to the experience with sodium nitrate, the rubidium nitrate composition produced truly excellent glitter stars. The requirement for potassium is unambiguously disproved. However, before completely rejecting the theory, one should note that the melting point of rubidium sulfide is 530 ºC, compared with 1060 °C for the sulfate. Thus the success of rubidium as a replacement for potassium is actually in accord with the predictions of Oglesby's theory. Rubidium glitters have no discernable color imparted to the glitter flashes. The element below rubidium in the periodic table is cesium. The author found that cesium nitrate can also function as the sole oxidizer in a glitter composition, in this case producing a particularly impressive terminal delay (the final large droplet produced by a burning glitter star resulting in a particularly large and delayed flash[19]).

2. The Necessity for Sulfur

The potassium sulfide intermediates require not only the presence of potassium (or other alkali metal) but also the presence of sulfur. The prediction is that one cannot make a glitter composition devoid of sulfur. Winokur has succeeded in making a good glitter composition devoid of elemental sulfur,[19] but it contains antimony sulfide and it is quite reasonable to assume that potassium sulfides may still be formed in this circumstance.

If one adopts the same approach of chemical analogy taken for potassium, then one should examine the elements directly above and below the sulfur in the periodic table, namely oxygen and selenium. Oxygen, of course, is already present in the glitter composition, as a component of potassium nitrate, as well as in the surrounding air as the element. Consequently the expedient of removing sulfur, in both elemental and combined form, from a glitter composition should allow the production of potassium oxides, K_2O and K_2O_2, in place of the corresponding sulfides. To the author's knowledge no-one has succeeded in producing a glitter in the absence of sulfur although Winokur has specifically attempted such a feat.[19]

The use of selenium in a glitter composition has also been tested by Winokur and found to be ineffective.[19] Thus it would appear that glitter compositions have a requirement for sulfur.

3. The Necessity for Nitrate

Almost all published glitter formulations use potassium nitrate as the principal oxidizer. The necessity for potassium was examined above. Another question is the necessity for a nitrate oxidizer. Von Baum[20] has discussed glitter compositions containing potassium perchlorate as the sole oxidizer, such as his "A1" shown in Table 1 as formulation 9 with amounts rounded to the nearest percent. This composition, pressed into a lance tube, as suggested by von Baum, or into an unchoked 1/2" i.d. tube, does indeed produce a very beautiful effect with the appearance of being a true glitter, albeit quite distinctive.

It is generally considered that the byproduct of using potassium perchlorate as an oxidizer is potassium chloride. This would be inconsistent with most of the proposed glitter theories. However, one cannot rule out the possibility that in a high-sulfur composition, such as this, sufficient potassium sulfide is generated so as to allow any of the proposed glitter mechanisms.

Von Baum[20] notes that both charcoal and sulfur are necessary in these compositions, with antimony sulfide being ineffective as a substitute for sulfur. Also, magnalium cannot substitute for aluminum, and ammonium perchlorate cannot substitute for potassium perchlorate. While none of the current glitter theories can fully explain these observations, none of them can be eliminated on this basis.

4. The Necessity for Aluminum

The glitter theories all postulate a key role for aluminum, but the role is different for each of the theories. If it were possible to replace aluminum with a different element then, depending on the element, some, but not all, theories may be able to explain the observation. Following the same rationale as before, the elements above and below aluminum in the periodic table are boron and gallium, respectively.

The addition of even small percentages of boron to a glitter composition destroys the glitter effect.[21] Gallium inconveniently melts on a warm day (30 ºC, 86 ºF), but this could be circumvented by the use of an alloy such as gallium antimonide. The author is unaware of any glitter experiments with these materials. Next below gallium in the periodic table is indium, which the author has found to be an ineffective substitute for aluminum in glitter compositions.[22]

In addition to the kinship among elements of the same column in the periodic table, there also exists the so-called "diagonal relationship", particularly within the first two rows. The element so related to aluminum is beryllium. Feher[23] has tested beryllium in a glitter composition, in place of aluminum, and found it to be quite effective. Thus aluminum is not an essential component of a glitter composition. The chemistry of beryllium is quite similar to that of aluminum, including the existence of an analogous carbide, Be_2C. The observation of an effective beryllium glitter is therefore consistent with the Stanbridge theory. However, there also exists an analogous sulfide consistent with the Fish theory. The electronegativity of beryllium is virtually identical to that of aluminum, and so it should serve as a fuel in the flash reaction, consistent with any of the theories that postulate aluminum in such a role. Thus the interesting observation of a functioning beryllium glitter sheds no light on the relative viability of the different theories of glitter. However, note that beryllium is extraordinarily toxic. Its use in fireworks should be limited to research by those with the requisite experience.

The theory of Stanbridge allows for the possibility of using manganese in place of aluminum in a glitter composition, on account of the favorable thermodynamic properties of manganese carbide.[11] The author has tested manganese as a replacement for aluminum in glitter compositions without success. Although these experiments bear unfavorably on the prediction of manganese as a potential glitter material, they should not be interpreted too strongly as evidence against the Stanbridge carbide theory in general.

Stanbridge also suggests that aluminum carbide may be used as a component in glitter compositions. However, the present author's experiments along the lines recommended resulted in no glitter flashes at all. In addition, aluminum carbide was tested by the author as the sole aluminum source in glitter compositions for fountains. Only orange sparks with no trace of glitter effect were observed. This result is consistent with all of the glitter theories including that of Stanbridge.

Aluminum may be present in alloyed form, for example with magnesium, iron, or cobalt.[19,24,25] By contrast certain other alloys of aluminum, for example with zinc or zirconium, have not been found to function in glitter compositions.[2,22] Alloys with copper and nickel appear to be marginal cases of little use for glitter.[19] A comprehensive theory explaining why certain alloys of aluminum are effective, while others are not, has yet to be proposed.

5. The Role of Barium Salts

Only Oglesby has provided a detailed explanation of the mechanism by which barium salts benefit a glitter composition. Regardless of whether the glitter additive is barium carbonate, barium nitrate, or barium oxalate, delay reactions are proposed leading eventually to barium sulfate. The barium sulfate then acts as a co-oxidizer in the flash reaction, enhancing the brightness of the flash.

This theory is capable of making specific predictions. For example if barium sulfate itself were to be used as a glitter additive there should be no delay reactions associated with it, and the delay should therefore not be increased. However, it should still participate in the flash reaction, enhancing its brightness. These predictions were tested by the author using formulations such as number 10 in Table 1. It was found that the flash brightness was indeed enhanced relative to the composition without any barium salt. Moreover, the delay was not increased, unlike the behavior when other barium salts are used. The theoretical predictions were exactly born out, in confirmation of Oglesby's theory. The barium sulfate composition is excellent in fact, and recommended for practical use.

6. The Role of Antimony Sulfide

Oglesby gives antimony sulfide a special role in its reaction with potassium sulfides to give potassium thioantimonate as a spritzel intermediate. In searching for analogous materials the author came across potassium thiomolybdate, which could be formed from potassium disulfide and molybdenum sulfide as below:

$$K_2S_2 + MoS_2 \rightarrow K_2MoS_4$$

Thus, in principle, Oglesby's theory predicts that molybdenum sulfide could be used in place of antimony sulfide in glitter compositions. Most glitter additives are effective only when additional sulfur is present such that potassium disulfide could be formed. Antimony sulfide is unique in requiring no additional sulfur, producing potassium thioantimonite in this case. Thus a more stringent test of the ability of molybdenum sulfide to replace antimony sulfide would be in a composition that contains no additional sulfur. Formulation 11 was tested in a 5/8" fountain by the author and found to produce an excellent off-white glitter. Oglesby's theory is again vindicated since it can specifically accommodate the function of molybdenum sulfide as a glitter additive. By contrast, the proposal of Fish that antimony sulfide functions as a heat sink by virtue of its low melting point (550 ºC) is inconsistent with the success of molybdenum sulfide whose melting point of 1185 °C is much higher. Thus it seems that antimony sulfide plays a chemical role rather than a physical role in glitter.

The author also tested indium sulfide in glitters. The lack of stable potassium thio-salts of indium leads Oglesby's theory to predict that this material cannot be used as a replacement for antimony sulfide. In fact good glitters such as formulation 12 can be made using indium sulfide, although the glitter flashes have absolutely no hint of the potential blue coloration from indium emissions. This composition is a vast improvement on simple mixtures of green powder, magnalium, sulfur and dextrin. However, three similar experiments in which the indium sulfide was not accompanied in the composition by additional sulfur resulted in no glitter effect whatsoever. This is exactly as predicted by Oglesby's theory: regardless of the presence of other glitter additives, a necessary requirement for a good glitter is that the composition contains either additional sulfur to allow for the formation of potassium disulfide, or else a material such as antimony sulfide or molybdenum sulfide that allows the formation of a stable potassium thio-salt.

Winokur tested the sulfides of arsenic, mercury, lead, bismuth, barium, copper, and iron.[19] It is clear from the published descriptions that none of these can function as effectively as molybdenum sulfide. Thus the particular function proposed for antimony sulfide by Oglesby is supported by the specificity of what can be used as a replacement.

7. Tests of Swisher's Thermitic Theory

In order for a thermitic reaction to take place, the glitter composition must contain a compound of a metal whose electronegativity is greater than that of aluminum. While this condition is met by many glitter compositions, it is not met by all. Consequently the thermitic theory is not a candidate for the explanation of all kinds of glitter compositions. However, the thermitic mechanism may still operate in specific cases. Note, in particular, that the other theories do not provide a satisfactory explanation for the function of ferric oxide.

Swisher suggests that antimony sulfide may take part in a thermitic reaction with aluminum. The author tested the stoichiometric mixture of antimony sulfide and 30 micron atomized aluminum. Five grams of this mixture, pressed in a 1/2" i.d. tube, was hard to light but could be initiated with a standard ferric oxide thermite mixture. The light output was very weak and the mixture was slow burning. A regulus of antimony remained. Although it must be admitted that the result bore little resemblance to a glitter flash reaction, it should be remembered that the conditions experienced by a spritzel flying through the air are rather different from those pertaining to this experiment. Moreover, the proposal of Fish that antimony sulfide may be converted to antimony oxide in the spritzel would allow for a more energetic thermite reaction.

A specific prediction of the thermitic theory is that other oxides and sulfides capable of a thermite reaction with aluminum should be useful glitter additives. Chromic oxide (Cr_2O_3) is another material known to undergo thermitic reaction with aluminum and Swisher reports making excellent glitters using it.[15] The author has found that bismuth subnitrate is a useful glitter additive, and this too can engender a thermitic reaction after initial decomposition to bismuth oxide (Bi_2O_3). The effectiveness of molybdenum sulfide is also consistent with the thermitic theory.

Another prediction of the thermitic theory is that elemental sulfur need not be an essential component of glitter composition, provided that there be present a compound capable of undergoing thermitic reaction with aluminum. Winokur[19] has shown this to be possible with antimony sulfide. However, there do not seem to be any other examples, and one may postulate potassium thioantimonite formation even in the absence of elemental sulfur, in accord with Oglesby's theory:

$$12\ KNO_3 + 4\ Sb_2S_3 + 15\ C \rightarrow 4\ K_3SbS_3 + 2\ Sb_2O_3 + 15\ CO_2 + 6\ N_2$$

In contrast with these experiments, Winokur has reported using manganese dioxide (MnO_2) and lead oxide (Pb_3O_4),[19] both known to undergo thermite reaction with aluminum,[13] and found them to be useless. Thus the evidence regarding the thermitic theory of glitter is mixed at this point.

8. What Is the Fuel in the Flash Reaction?

Three of the theories of glitter postulate that the aluminum component of a glitter composition constitutes the fuel for the flash reaction. The other two theories postulate that the aluminum undergoes a chemical reaction prior to the flash reaction. The two different postulates give rise to two different predictions as to the way the nature of the glitter flash depends on the nature of the aluminum used in the glitter composition. Specifically, if aluminum is the fuel in the flash reaction, then the particle size and alloying of the aluminum component could markedly affect the flash reaction. Conversely, if the aluminum undergoes chemical reaction prior to the flash reaction, the information about its original form should be lost, and the nature of the flash reaction should be relatively constant in regards to this variable. Note, however, that all theories allow for the possibility of excess coarse aluminum being flung burning from the glitter flash, thus excluding such effects from distinguishing between the theories.

A flash parameter that can be used for comparison between compositions is the color of the flash when a sodium salt is used as a glitter additive. The author visually compared the colors produced by using aluminum (atomized, 120–140 mesh), aluminum (atomized, 325 mesh), ferro-aluminum (35:65, –60 mesh), cobalt-aluminum (31:69, –100 mesh), and magnalium (50:50, –60 mesh). The aluminum carbide and aluminum sulfide theories predict that the flash color should be essentially invariant. The other theories allow for the possibility that the flash color may vary between the different compositions.

The results of the experiments are as follows. With the coarser aluminum, ferro-aluminum or cobalt-aluminum alloys, only pure white flashes were produced despite the presence of the sodium salt. The finer aluminum produced pale yellow glitter flashes and the magnalium produced vivid yellow glitter flashes. Similar observations have also been reported by Winokur.[19]

The results are consistent with the theories of Oglesby, Shimizu, and Swisher, but are poorly accounted for by the aluminum carbide and aluminum sulfide theories.

It should be possible to reproduce a flash reaction by mixing the postulated chemicals involved and determining the behavior upon ignition. Both Oglesby and Shimizu state that a mixture of potassium sulfate and aluminum does not ignite to produce a simulation of a glitter flash. Stanbridge goes further, implying that this reaction can be ruled out on theoretical thermodynamic grounds.

In contrast to the opinion of these several pyrotechnists, a 50:50 mixture of potassium sulfate and aluminum (2µ), when heated in a deflagrating spoon with a Bunsen burner, does indeed produce a very convincing and vigorous flash reaction accompanied by a moderate explosion.[26] This reaction is clearly a viable candidate for the glitter flash mechanism. The additional presence of sulfides, as suggested by Oglesby, is not a necessary condition for the occurrence of the flash reaction.

This experiment negates the supposed “disproofs” of Oglesby’s theory by Stanbridge and Shimizu. However, the author found that a similar mixture of potassium sulfate and aluminum carbide also undergoes a flash reaction upon heating, albeit less bright and less vigorous than with aluminum. The residue produces hydrogen sulfide upon dampening, thereby demonstrating the oxidative role of potassium sulfate in the reaction. Thus both aluminum and aluminum carbide are capable of acting as fuel in combination with potassium sulfate.

Stanbridge postulates a role for aluminum as a fuel in the delay mechanism as opposed to the flash reaction. Thus his theory predicts that not only will a simple mixture of green powder and aluminum produce glitter, but that the glitter delay should increase with the amount of aluminum in the composition. None of the other theories predicts this relationship between the amount of aluminum and the glitter delay. Consequently an experiment to measure the length of glitter delay as a function of aluminum content can unambiguously determine the viability of Stanbridge’s theory relative to the other theories.

Such an experiment has been performed by photographing stationary glitter stars in a wind tunnel and measuring the number of glitter flashes within one foot increments of the glitter star.[27] The compositions used were made according to a standard gold glitter formulation,[28] with the aluminum content being 5, 7 or 10%. The result was that the glitter delay *decreased* as the amount of aluminum was increased. This effect is the opposite of that predicted by Stanbridge's aluminum carbide theory but is consistent with the other four glitter theories. Moreover, Oglesby provides an explanation for the observed relationship: "When a glitter formula is overloaded with aluminum, the spritzels produced will have insufficient sulfide melt material to cover and chemically isolate the aluminum from air ... A thin layer of potassium sulfide on aluminum is insufficient to cause delay." Oglesby's explanation is also consistent with the observation that decreasing the aluminum particle size causes a decrease in the glitter delay.[27,29]

9. Physical Observations

Presumably in referring to Shimizu's theory, Stanbridge states "Reactions based only on K_2S_x are too slow to meet the observed duration of the glitter flash...".[11] However, Stanbridge's postulated glitter flash duration of one millisecond may be as much as an order of magnitude shorter than flash durations determined experimentally.[27] Certain glitter flashes, such as those from some compositions utilizing bismuth subnitrate as a glitter additive, have the appearance of being very much longer in duration. Thus, the argument against Shimizu's theory based on flash duration may be erroneous.

The theories of both Shimizu and Swisher require, and predict, that there must be an increase in spritzel temperature prior to the flash in order to trigger the flash reaction. The other theories rely on an increase in potassium sulfate concentration to trigger the flash reaction. Experimental studies indeed suggest that the light intensity of the spritzel, and thus its temperature, rapidly increases just prior to the flash.[27] This result is as predicted by Shimizu and Swisher. However, it does not count against the other theories for, while not being a requirement, the observation is nonetheless consistent with them.

Discussion

There is as yet no universally agreed upon chemical mechanism that explains the pyrotechnic phenomenon of glitter. However, the five theories discussed here all agree upon a certain basic sequence of events. "On board" reactions produce some chemical intermediates. These chemical intermediates are modified as the spritzels fall through the air. Finally, there is a flash reaction involving the oxidation of an energetic fuel.

The experimental evidence is not yet sufficient to reach a definitive verdict regarding the validity of the various theories of glitter. However, the evidence so far would appear to be strongly supportive of Oglesby's theory. The aluminum carbide and aluminum sulfide theories are less consistent with the experimental observations.

Sturman[30] has published a detailed and cogent discussion of the thermodynamics of the aluminum carbide and aluminum sulfide theories. It would appear that one may also eliminate these theories from consideration, based on such theoretical grounds. Dolata[31] has performed thermochemical measurements on glitter compositions, as well as related compositions whose intermediacy is predicted by various glitter hypotheses. While many of the conclusions are tentative, Dolata states, "First of all, it is clear that the nature of the aluminum doesn't play a thermodynamically important role in the on-board reactions". Again, the observations specifically contradict both the aluminum carbide and aluminum sulfide theories.

No doubt further experiments will gradually shed more light on the chemistry of glitter. However, the practical control of glitter delay is already well understood.

Regardless of the theoretical considerations, the basis of glitter may be considered to be the combination of green powder (or equivalents), aluminum (including certain alloys), and delay agents. The practical mastery of glitter centers around the choice of delay agent, which falls into one of three categories: firstly, antimony sulfide as the sole delay agent; secondly, the combination of sulfur with another delay agent, most commonly a carbonate, an oxalate, barium nitrate, or ferric oxide; finally, the combination of antimony sulfide with any other delay agent(s). Only the theories of Fish and Shimizu unambiguously predict that the simple mixture of green powder and aluminum will not produce glitter. Moreover they specifically require the presence of either additional sulfur or antimony sulfide, allowing for the possibility that Swisher's thermitic flash reaction with antimony sulfide could be an "on board" reaction in the Fish scheme. Besides these chemical delay agents, one can also make use of the minor contribution of physical delays. These are primarily poor incorporation, by use of green powder in place of commercial meal powder, and increased metal particle size.

Colored Glitter

An exciting prospect for the future is the production of various colored glitters, a feat that, with the sole exception of yellow, remains tantalizingly out of reach. Shimizu has tested the combination of Parlon® with barium carbonate and copper carbonate glitter additives without success.[17] Sturman[32] has pointed out that rare earth metal monoxides are roughly isoelectronic with alkaline earth metal monohalides but have greater thermal stability. He also notes that some of these monoxides produce excellent colored emissions in high temperature gas flames. These observations led to his suggestion of rare earth compounds as potential color imparters for glitter flashes. The author has tested the addition of chlorine donors to glitter compositions containing barium nitrate or strontium nitrate, as well as the use of a number of glitter additives that may be thought to have the potential of imparting color (see Table 3). None of these experiments led to a clearly colored glitter flash.

If the perchlorate glitters of von Baum[20] do indeed proceed via the intermediacy of potassium sulfide, then there must necessarily be some available chlorine and they are thus potential candidates for producing colored glitter. However, von Baum[20] notes that the use of strontium carbonate in such formulations does not produce colored glitter flashes. The author has found that the substitution of lithium oxalate for sodium bicarbonate in this system does not produce a glitter.

Table 3. Materials Not Yet Found To Produce Colored Glitter.

Name	Formula
Barium nitrate	$Ba(NO_3)_2$
Boron	B
Calcium carbonate	$CaCO_3$
Cesium nitrate	$CsNO_3$
Erbium oxyfluoride	ErOF
Indium metal	In
Indium carbonate	In_2CO_3
Indium sulfide	In_2S_3
Lithium-aluminum alloy	LiAl
Lithium carbonate	Li_2CO_3
Lithium oxalate	$Li_2C_2O_4$
Rubidium nitrate	$RbNO_3$
Strontium nitrate	$Sr(NO_3)_2$
Thallium nitrate	$TlNO_3$
Ytterbium oxide	Yb_2O_3
Ytterbium sulfide	Yb_2S_3
Yttrium oxalate	$Y_2(C_2O_4)_3$
Yttrium oxide	Y_2O_3

Both Winokur[19] and Oglesby[2] claim to have made pink glitter, using strontium salts or lithium salts, respectively. The author has tested such compositions in front of audiences psychologically prepared in two different ways. One group was specifically asked ahead of time to look for the pink glitter flashes. The other group was told nothing about the purpose of the experiment. After the glitters had performed (in Roman candles), some, but not all, of the first group reported that they had seen that the glitter flashes were pink. Members of the second group were asked what was the color of the glitter flashes. None reported that they were pink and were by no means easily convinced by the suggestion that perhaps they might have been pink. Clearly the subjective experience of the pink color is influenced by the pre-bias of the observer (a well known psychological phenomenon). In other words, it is not beyond possibility for eager experimenters to delude themselves as to the success of their experiment. A colored glitter should not count as a colored glitter unless it is clearly recognized as such by an unbiased audience.

The most successful colored glitter is the yellow produced by the combination of magnalium with sodium bicarbonate as in formulation 13 adapted from Winokur.[19] If one proceeds from analogy with this, then the most likely candidate for the production of a different color is the combination of magnalium with lithium carbonate. However, so far such compositions produce only white.[21] Perhaps the problem is simply the quantity of lithium, which constitutes only 19% of lithium carbonate. One solution may be to load up the lithium content of the composition, in the form of lithium-aluminum alloy as suggested by Winokur: [19] "It is possible that alloys containing lithium or strontium could be used to produce pink or red glitter. The high cost of such alloys makes it doubtful that such material could ever become commonly used in commercial items." On the other hand, Partington[4] states, "Lithium burns when heated in air above its melting point, with a *white* flame..." (author's italics).

The author was able to obtain some lithium-aluminum alloy (20:80, LiAl, 40 to 200 mesh) for testing in glitter compositions. The first test of water compatibility resulted in an extremely violent reaction, although not resulting in ignition. Consequently no attempt was made to prepare glitter stars with this material and only fountains were tested. Mixtures (20 g) with various glitter additives and 5 or 10% of lithium-aluminum alloy were prepared and pressed into a 5/8" tube with a clay choke of a type that works well in standard glitter fountains. One exception to this was for the composition that contained a combination of 10% bismuth subnitrate and 10% antimony sulfide as the glitter additives. In this case, when the lithium-aluminum alloy was added to the other premixed dry components, a substantial exotherm ensued with concomitant emission of hydrogen sulfide. Although ignition did not occur, the author was not comfortable with the safety aspects of pressing this composition in a tube, and the test was performed by ignition of the loose powder. This large exotherm did not occur with the compositions containing the combination of bismuth subnitrate and sulfur or the combination of lithium carbonate and antimony sulfide.

In all cases the result of the test was the production of white sparks with no delayed glitter flashes and no observable pink coloration. In one case, when the glitter additive combination of lithium carbonate and sulfur was used, there appeared to be a slight increase in brightness of the sparks towards the end of their trajectories. The compositions containing 10% each of lithium carbonate and lithium-aluminum alloy have a total lithium content of 4%, apparently insufficient for coloration if insufficiency is the problem. However, it would appear unwise to increase further the lithium content of the lithium-aluminum alloy as the 20% material reported here is already dangerously reactive and disabling of the glitter mechanism.

Safety Considerations

Two kinds of safety considerations pertain to fireworks in general: toxicity and accidental ignition. The most commonly cited toxicity issue for glitter compositions concerns the use of antimony sulfide. For example, Fish[12] asks, "Is this poison necessary?" However, Fish provides no data in support of his hypothesis that antimony sulfide may be unduly toxic, and the toxicological literature suggests to the contrary: "The fact that two men, one employed for one year, where the air concentrations at their highest were 52 mg/m^3 showed no ill-effects, suggested that the trisulfide has a low toxicity".[33] Such low toxicity is entirely in accord with its low solubility of 0.000175 g/100 cm^3.[34] The assertion that antimony sulfide is particularly toxic would appear to have no basis in fact, and perhaps came about due to erroneous comparison with other more soluble antimony compounds that are indeed very poisonous. Oglesby correctly points out that other antimony compounds tested for use in glitter compositions are much more poisonous than the sulfide. Of more concern might be acute poisoning by ingestion of sodium oxalate.

Besides the safety considerations common to dealing with any pyrotechnic composition, glitter compositions are renowned for their potential for an exothermic reaction upon dampening with water. This is reasonable since all glitter compositions contain an active metal, in the form of aluminum or an alloy of aluminum.

The most common problem stems from the use of fine flake aluminum that can undergo an alkaline decomposition with a nitrate in the presence of water. This may be avoided by the addition of a boric acid buffer, or simply by the use of atomized aluminum. In addition, certain combinations of glitter additives with aluminum or magnalium must be avoided. These are listed in Table 4. The pattern of unwanted reactivity is in accord with chemical expectations; note that the pH of saturated lithium carbonate solution is 11 (strongly alkaline), whereas that of saturated lithium oxalate is 7 (neutral). Thus, aluminum, which is sensitive to alkaline conditions, can not be used with lithium carbonate, and lithium oxalate should be used instead. It is interesting that Fish[12] has stated that lithium carbonate is not effective in glitter. This is certainly not the case when magnalium is being used in combination with lithium carbonate.[21] Presumably, the problem with aluminum is the decomposition upon dampening, rather than any inherent deficiency of lithium carbonate. Shimizu[35] has reported that magnalium is actively attacked by wet sodium oxalate, and this is also true for lithium oxalate[21] and antimony oxalate (the latter suggested for use with aluminum by Kosanke[36]). In these cases it is safer to use as alternatives more alkaline materials such as lithium carbonate or sodium bicarbonate, which do not cause such decomposition with magnalium.[35]

Table 4. Adverse Reactivities of Metals with Glitter Additives in an Aqueous Environment.

Ingredient	Aluminum	Magnalium
Lithium carbonate	×	
Sodium carbonate	×	
Lithium oxalate		×
Sodium oxalate		×
Antimony oxalate		×

× = unwanted reaction upon dampening.

Curiously, Lancaster[10] has stated, "One last point on glitter mixes: when using finely-powdered magnalium be very careful to add boric acid, or else the mix can heat up (on damping) ...". Such advice flies in the face of both theory and experiment. Magnalium (unlike aluminum) is more reactive under acidic conditions than under alkaline conditions, and thus theoretically should have such reactivity exacerbated rather than alleviated by the addition of boric acid. The relevant published experiments support this theoretical prediction.[35,37] The combination of boric acid with magnalium should be considered hazardous and best avoided. Indeed, Lancaster[38] may have changed his opinion on this issue for recently he has stated: "Magnalium is attacked by weak acids (e.g., boric acid)".

This controversy, like the glitter flash discussion, highlights an important principle of science, stated here in the words of two great scientists: Richard Feynman[39] (Nobel laureate in Physics) "Science is the belief in the ignorance of experts" and Carl Sagan[40] (Astronomer extraordinary) "One of the great commandments of science is mistrust arguments from authority". The author hopes that the arguments presented in this article will also be treated with the skepticism they deserve.

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Some of the glitter theories are not explicit in every detail. Consequently the author may have made errors of interpretation and, in taking responsibility for these, remains open for correction. In addition to the pyrotechnists

mentioned above, the experimental contributions of Robert Winokur are particularly noteworthy.

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Strobe Chemistry

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ABSTRACT

Pyrotechnic strobe compositions burn in an oscillatory manner such that there is a marked variation of emitted light intensity as a function of time. The most common theoretical explanation for the phenomenon is that such compositions contain within them sub-compositions that may be regarded as a smoulder composition and a flash composition. The smoulder reaction would have a lower activation energy and low heat output. The flash reaction would have a high activation energy and high heat output. The actual chemical components of strobe compositions are extremely diverse, confounding a unified chemistry of the phenomenon. Nevertheless the majority of strobe compositions can in fact be reasonably deconstructed into smoulder and flash compositions. However, there appear to be a few strobe compositions that defy such explanation; although it is possible that the author lacks the wit to comprehend the chemistry. It is also possible that the prevailing theory applies to some, but not to all, strobe compositions; and it is yet possible that a different theory will provide a more encompassing explanation with better predictive power.

Keywords: strobe, formulation, theory, flash, magnalium, smoulder

Introduction

The pyrotechnic strobe effect is produced by a light-emitting pyrobody, such as a star, wherein the light intensity is a cyclic variable function of time. The minimum light intensity may or may not be zero, but the frequency of the intensity peaks must be sufficiently slow such that the eye can distinguish between them. An example of a possible time course of light intensity is shown in Figure 1. To qualify as a strobe the composition must produce at least two flashes separated by a "dark" phase.

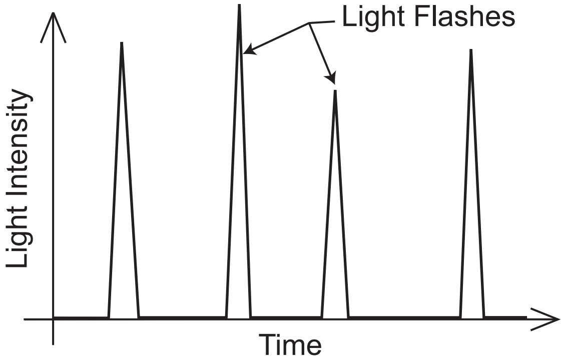

Figure 1. Representative time course of pyrotechnic strobe.

Shimizu has hypothesized that two different kinds of pyrochemistry are involved; one in the "light" or "flash" phase of a pyrotechnic strobe, and one in the "dark" or "smoulder" phase.[1] These will be referred to as the "flash reaction" and the "dark reaction". Shimizu suggests that a strobe composition may be thought of as a mixture of a flash composition and a smoulder composition. This is not the only possible hypothesis for the mechanism of strobe. For example, one could have postulated that a single pyrochemical reaction could occur at different rates for some reason (e.g., oscillatory thermal feedback or oxygen influx due to a pyrobody tumbling in air); or that a smoulder reaction gives rise to products capable of producing a flash reaction; or that a flash reaction gives rise to products capable of producing a smoulder reaction.

Shimizu's hypothesis engenders very specific predictions regarding what type of composition could or could not function as a strobe. If Shimizu's hypothesis is correct, then every composition that is capable of functioning as a strobe must contain ingredients that are capable of reacting as a flash composition, as well as ingredients that are capable of producing a dark reaction. Any exceptions to this would mean that Shimizu's hypothesis is not universally applicable.

Genesis of the Shimizu Hypothesis

Firstly, Shimizu gives due credit to Wasmann[2] and Krone[3] for originating this line of thinking regarding the theoretical mechanism of pyrotechnic strobe. However, it will be referred to as the "Shimizu Hypothesis" here since he has made the largest contribution to our understanding of this phenomenon.

Shimizu had noticed in his studies on strobe compositions that, during the dark phase, "hot spots" develop in the smouldering slag layer that grow in size and temperature until a critical point is reached when the flash reaction commences. Thus it would appear that the dark reaction should have a small activation energy together with a relatively small heat output. By contrast the flash reaction should have a large activation energy (thereby allowing a delay before initiation) as well as a large heat output (thereby producing a relatively bright flash).

Testing the Shimizu Hypothesis

Various theories of glitter chemistry propose specific ingredients and/or intermediates and/or reactions.[4] Such theories can be tested by, for example, manipulating the ingredients of the glitter composition and observing the resultant pyrotechnic effect. However, Shimizu has not proposed that any specific ingredients are necessary or that any specific reaction takes place, for the functioning of a pyrotechnic strobe.

Consequently, the testing of the flash composition, smoulder composition hypothesis will be more general. Indeed, one of the first testable predictions is that there should be not just one strobe chemistry but many strobe chemistries. Therefore stringent testing of Shimizu's strobe hypothesis would catalog as many widely different strobe compositions as possible, focusing on their predicted commonalities such as those listed below:

1) One should be able to write a plausible equation for the flash reaction.
2) One should be able to write a plausible equation for the dark reaction.
3) The strobe composition should be reconsitutable as a mixture of a flash composition and a smoulder composition.
4) Quenching a strobe composition shortly after a flash should yield a mixture depleted in the proposed flash components.
5) Quenching a strobe composition shortly before a flash should yield a mixture depleted in the proposed smoulder components.

Caveats:

a) "Plausible" equations are ones that utilize ingredients of the composition and that are chemically reasonable.
b) Shimizu's hypothesis does not predict that any mixture of a flash composition and a smoulder composition will be capable of strobing. It is proposed as a necessary condition, not a sufficient condition.
c) There exists strobe composition consisting of only two components, neither of which is capable of independent functioning as either a flash composition or a smoulder composition. At first sight this would appear to contradict prediction No. 3. However, note that a mixture of 50A + 50B is also equivalent to a 1:1 mixture of 80A + 20B and 20A +80B. These latter could be flash composition and smoulder composition.
d) Atmospheric oxygen may be a plausible reactant in a smoulder composition (e.g., burning sulfur).
e) It is possible that there may be more than one plausible flash reaction or dark reaction for a given strobe composition. Indeed, there may be more than one in actuality. A dictum of chemistry is that any reaction that can occur will occur. Consequently, the real chemistry involved in pyrotechnic strobes is necessarily more complex than can be depicted by a set of two equations. However, for the purpose of testing the Shimizu hypothesis, it is sufficient only to find one equation for each reaction type.
f) Quenching experiments should be possible for long cycle strobes, but may be prohibitively difficult for fast strobes.

g) Quenching experiments are left to those with more sophistication in the required techniques than has the author, and are therefore beyond the scope of this article.

Various Strobe Compositions

A set of diverse strobe formulations was chosen with the intent of maximizing the differences of ingredients between the formulations. Substitution of similar ingredients, such as one alkaline earth sulfate for another alkaline earth sulfate, was not considered as one may reasonably assume that these compositions function through an analogous sequence of reactions. Formulations are either previously published or devised by the author. For testing, compositions (6 g) were pressed into a short (1½-inch long) ½-inch i.d. tube glued to a metal base. "Hot" prime (1 g) was pressed on top of the composition and lit with a visco fuse. In certain cases no amount of priming would succeed in lighting the composition, but several seconds of direct blowtorch flame would eventually trigger the composition to start strobing by itself.

No consideration was given to the "usefulness" of the test composition. That is it may be hard to light, not reliably stay lit, strobe too fast, strobe too slow, have hygroscopic ingredients, not be stable on storage, be absurdly expensive, etc. None of these factors bear on the utility of the composition for testing theoretical principles. Thus the only inclusion criteria were (a) that the composition must fulfill the definition of "strobe" (i.e., at least two flashes separated by a dark phase), and (b) that the formulation must be significantly different from others under consideration.

Strobe formulations considered for their conformity with Shimizu's theoretical predictions are listed in Table 1.

Table 1. Diverse Strobe Formulations.

Ingredients	A	B	C	D	E	F	G	H	I	J	K	L	M
Barium nitrate	54	50											
Sulfur	23												
Magnalium (50:50)	18	20	33	30	25	20							15
Dextrin	5												
Guanidine nitrate		30	33	42						70	55		
Potassium perchlorate			33										
Ammonium perchlorate				28	60	50	60		50		25	30	
Barium sulfate					15								
Hexamine						30	40	50					
Lithium perchlorate								50					
Magnesium									50				
Mg_2Cu										30			
Tetramethylammonium nitrate												40	
Copper (atomized, –100 mesh)											20	30	
Copper(II) oxide													10
Bismuth(III) oxide													75
Reference	5	6	7	7	8	7	7	7	1	7	7	7	9

"Dark" and "Flash" Binary Mixtures

There are a number of known binary (two-ingredient) compositions capable of a continuous smoulder reaction with little or no light output. More familiarly there are a number of known binary flash powers. A listing of such combinations, particularly those containing commonly used strobe ingredients, allows a shortcut to determining whether a strobe composition satisfies Shimizu's proposed mechanism. That is to say, if the composition contains the ingredients of at least one binary mixture from each list then one need look no further.

Examples of known dark binary mixtures are listed in Table 2. Examples of known flash binary mixtures are listed in Table 3. Hypothetical strobe reaction equations for the strobe compositions under discussion are listed in Table 4.

Table 2. Known Binary Dark Mixtures.

No.	Ingredient 1	Ingredient 2	Ref.
1	Magnesium	Ammonium perchlorate	1
2	Magnalium	Ammonium perchlorate	1
3	Zinc	Ammonium perchlorate	1
4	Copper	Ammonium perchlorate	1
5	Cyanoguanidine	Ammonium perchlorate	7
6	Guanidine nitrate*	Ammonium perchlorate	7
7	Magnesium	Sulfur	1
8	Magnalium	Sulfur	1
9	Titanium	Sulfur	1
10	Copper	Sulfur	1
11	Air	Sulfur	10
12	Copper	Guanidine nitrate	7
13	Cupric oxide	Guanidine nitrate	8
14	Magnesium-copper alloy	Guanidine nitrate	7

* Guanidine nitrate is a common informal name for the substance more properly called guanidinium nitrate.

Table 3. Known Binary Flash Mixtures.

No.	Ingredient 1	Ingredient 2	Ref.
1	Barium nitrate	Magnalium	4
2	Barium sulfate	Magnalium	11
3	Ammonium perchlorate	Magnalium	11
4	Potassium perchlorate	Magnalium	12
5	Barium nitrate	Magnesium	1
6	Barium sulfate	Magnesium	1
7	Ammonium perchlorate	Magnesium	1
8	Potassium perchlorate	Magnesium	1

Discussion of the Strobe Formulations from Table 1

A. The key components of this excellent classic white strobe star are barium nitrate, sulfur, and magnalium. This contains dark mixture No. 8 from Table 2, and flash powder No. 1 from Table 3. The Shimizu hypothesis is therefore satisfied by this formulation.

B. Sulfur is by no means necessary, since here it is replaced by guanidine nitrate. The flash powder remains the same, but no combination appears in Table 2 as the dark mixture. In this case an experimental test of the Shimizu hypothesis is therefore necessary. The prediction is that some subset of materials present in formulation B is capable of producing a smoulder composition. Examination of Table 2 indicates that both magnalium and guanidine nitrate are components of known dark binary mixtures, and consequently constitute a candidate dark binary in admixture. Testing showed that the mixture 20% magnalium/80% guanidine nitrate will smoulder, though not reliably staying lit. An occasional flash also presented. This is sufficient to satisfy the Shimizu hypothesis.

C. This is a similar composition to "B", but the oxidizer is changed from barium nitrate to potassium perchlorate. Thus the flash powder is switched from No. 1 to No. 4 in Table 3. The Shimizu hypothesis is satisfied.

D. The oxidizers are switched again, this time to ammonium perchlorate. The ammonium perchlorate/magnalium flash powder is No. 3 from Table 3. The Shimizu hypothesis is satisfied.

E. This time the guanidine nitrate is replaced with barium sulfate, and our smoulder composition is gone. Barium sulfate and magnalium constitute a flash powder (No. 2 from Table 3), but it does not smoulder. However the ammonium perchlorate/magnalium mixture can function as a smoulder composition (No. 2, Table 2), as well as a flash powder, and so any composition containing both these components will automatically satisfy the Shimizu hypothesis regardless of other ingredients. Note, however, that in these sulfate type strobe compositions the sulfate is usually considered to act as the principal oxidizer in the flash reaction and the ammonium perchlorate acts as the principal oxidizer in the dark reaction.[1] Specifically Shimizu has suggested that the magnesium content of the magnalium reacts with ammonium perchlorate in the dark reaction, leaving primarily barium sulfate and aluminum for the flash reaction.[1] This is also consistent with the magnalium combustion mechanism proposed by Popov et al,[13] involving preferential oxidation of the magnesium content.

F. Hexamine is used here in place of barium sulfate. This does not further test the Shimizu hypothesis however because, as noted above, any composition containing both ammonium perchlorate and magnalium automatically qualifies.

G. The simple omission of magnalium leaves a binary composition of ammonium perchlorate and hexamine that is still capable of strobing behavior. Now bereft of both known dark or flash binary mixtures, this composition would appear to pose a serious problem for the Shimizu hypothesis. Let us see if we can rescue the situation:

The sulfur strobes typified by "A" (Table 1) are hard to observe in the dark phase because the bright flash requires that one's eyes have some time to readjust, by which time another bright flash occurs. However, there is a closely related kind of composition for making "microstars" that in performance essentially produce a single dark phase followed by a single flash phase.[14] While this does not qualify as a strobe composition, which would require a minimum of two flashes, both the formulation and the effect are clearly related to strobe. The delay can be increased by increasing the sulfur content. So with a high-sulfur composition one may observe the dark reaction for some time before observing the flash. A typical formulation for such a composition would be: 40% barium nitrate, 30% sulfur, and 30% magnalium.[14] The composition is made into microstars using a nitrocellulose binder. One may observe the microstars after being lit with a blowtorch. The appearance of the dark reaction is simply the typical dim blue flame of burning sulfur. This is followed by a single bright flash; so do not observe too closely.

Thus, although a reaction between magnalium and sulfur was postulated as the dark reaction for this kind of composition, it is also plausible that it could be a reaction between sulfur and air (No. 11 from Table 2) depleting the sulfur content until a suitable flash powder composition is reached. Hexamine is a fuel, like sulfur, that burns easily in air with a dim flame. So the burning of hexamine in air can be postulated as the dark reaction for strobes of type G.

Now we have an apparently even more intractable problem: No metal fuel, so where is the flash powder? An answer is perhaps found in the apparent capability of hexamine/potassium perchlorate mixtures (such as 30:70) of producing a sharp report when functioning as a flash powder.[15] It is known that ammonium perchlorate can also function as the oxidizer in a flash powder.[15] Thus one indeed might reasonably argue, based on literature precedent, that the ammonium perchlorate/hexamine mixture should be able to function as a flash powder after sufficient hexamine has burnt off, bringing the mixture closer to stoichiometric proportions (86% ammonium perchlorate, 14% hexamine). The proposed mechanism thus makes this composition analogous to various pyrotechnic compositions wetted with alcohol, wherein a portion of the alcohol burns off the surface layer allowing the composition to flash; and the cycle repeats.

H. If the explanation above suffices for this ammonium perchlorate/hexamine mixture (G), then it also suffices for the lithium perchlorate/hexamine mixture (H).

I. Simple binary oxidizer/metal mixtures can also function as a strobe. In this case we have the known dark binary No. 1 from Table 2 and the known flash powder No. 7 from Table 3.

J. Similarly to the case above, it is easy to make a dark binary composition by mixing magnesium-copper alloy with guanidine nitrate, No. 14 from Table 2. This is quite reasonable since the mixture of copper and guanidine nitrate, No. 12 from Table 2, will do the same. The flash powder might seem a little odd since guanidine nitrate is a net fuel rather than a net oxidizer. Nevertheless guanidine nitrate does contain available oxygen and so might function in a flash powder in a similar way to barium sulfate in the presence of a highly energetic metal fuel.

K. The dark binary composition is here fulfilled by either the copper/ammonium perchlorate combination or the copper/guanidine nitrate combination (Nos. 4 and 12 from Table 2). The fact that simple omission of ammonium perchlorate from this composition results in a smoothly burning smoulder composition perhaps favors the latter. No ammonia smell is produced, and the brown residue is insoluble in water. Unlike the previous guanidine nitrate strobes discussed,

Table 4. Hypothetical Strobe Reaction Equations.

Strobe	Flash Reaction	Smoulder Reaction
A	$3\,Ba(NO_3)_2 + 10\,Al \rightarrow 3\,BaO + 3\,N_2 + 5\,Al_2O_3$	$Mg + S \rightarrow MgS$
B	$3\,Ba(NO_3)_2 + 10\,Al \rightarrow 3\,BaO + 3\,N_2 + 5\,Al_2O_3$	$(H_2N)_3CNO_3 + Mg \rightarrow (H_2N)_2CO + H_2O + N_2 + MgO$
C	$3\,KClO_4 + 8\,Al \rightarrow 3\,KCl + 4\,Al_2O_3$	$(H_2N)_3CNO_3 + Mg \rightarrow (H_2N)_2CO + H_2O + N_2 + MgO$
D	$6\,NH_4ClO_4 + 10\,Al \rightarrow 3\,N_2 + 12\,H_2O + 2\,Al_2O_3 + 6\,AlOCl$	$(H_2N)_3CNO_3 + Mg \rightarrow (H_2N)_2CO + H_2O + N_2 + MgO$
E	$3\,BaSO_4 + 8\,Al \rightarrow 3\,BaS + 4\,Al_2O_3$	$2\,NH_4ClO_4 + Mg \rightarrow 2\,NH_3 + H_2 + Mg(ClO_4)_2$
F	$6\,NH_4ClO_4 + 10\,Al \rightarrow 3\,N_2 + 12\,H_2O + 2\,Al_2O_3 + 6\,AlOCl$	$2\,NH_4ClO_4 + Mg \rightarrow 2\,NH_3 + H_2 + Mg(ClO_4)_2$
G	$5\,C_6H_{12}N_4 + 36\,NH_4ClO_4 \rightarrow 30\,CO_2 + 84\,H_2O + 36\,HCl + 28\,N_2$	$C_6H_{12}N_4 + 9\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O + 2\,N_2$
H	$2\,C_6H_{12}N_4 + 9\,LiClO_4 \rightarrow 9\,LiCl + 12\,CO_2 + 12\,H_2O + 4\,N_2$	$C_6H_{12}N_4 + 9\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O + 2\,N_2$
I	$2\,NH_4ClO_4 + 5\,Mg \rightarrow N_2 + 3\,H_2O + 3\,MgO + 2\,Mg(OH)Cl$	$2\,NH_4ClO_4 + Mg \rightarrow 2\,NH_3 + H_2 + Mg(ClO_4)_2$
J	$(H_2N)_3CNO_3 + 2\,Mg \rightarrow 2\,NH_3 + N_2 + CO + 2\,MgO$	$(H_2N)_3CNO_3 + 2\,Cu \rightarrow (H_2N)_2CO + H_2O + N_2 + Cu_2O$
K	$4\,NH_4ClO_4 + 5\,(H_2N)_3CNO_3 \rightarrow 21\,H_2O + 5\,CO_2 + 12\,N_2 + 4\,HCl$	$(H_2N)_3CNO_3 + 2\,Cu \rightarrow (H_2N)_2CO + H_2O + N_2 + Cu_2O$
L	?	?
M	$Bi_2O_3 + 2\,Al \rightarrow 2\,Bi + Al_2O_3$	$Bi_2O_3 + 3\,Mg \rightarrow 2\,Bi + 3\,MgO$

there is no active metal fuel present with which to form an obvious flash powder. However, the low melting point of guanidine nitrate (217 °C) could facilitate the production of a molten mixture with oxidizer, such mixtures having the potential for almost explosive decomposition.[7]

L. The very idea of a black strobe, such as this, does not really fulfill the definition given earlier since no visible light is produced at any stage in the combustion. However, it is very closely related to some blue strobe compositions.[7] Moreover, the combustion gases produced during the "flash" phase may be ignited to produce a blue flame. This flame does not stay lit in the absence of an external ignition source.

The combustion alternates between a slow smoulder and a fast smoulder accompanied by a loud sizzling sound; an acoustic strobe perhaps? The point here is that the composition can be altered by fine gradations (increasing the ammonium perchlorate to 40%) wherein the combustion gases produced during the flash phase reliably ignite in air of their own accord to produce the blue flame. Therefore the flash phase of this kind of blue strobe actually consists of two separate reactions: the pyrochemical reaction that is essentially the same as that operating in this black strobe (L, producing no light), and the combustion of the resulting gases in air to produce a blue flame. Thus, regardless of whether we address the black strobe or the related blue strobe, we would still need to postulate a flash reaction that produces no light. The triangle diagram for the similar system, K, with guanidine nitrate in place of tetramethylammonium nitrate (TMAN) did not show any areas of black strobe.[7] Consequently one may not assume that the mechanisms are necessarily analogous. However, the peculiarity of the black strobe phenomenon is not limited to compositions containing TMAN. Investigations of various potential blue strobe systems also revealed a black strobe in combinations of ammonium perchlorate, cupric salicylate, and hexamine.[7] It would appear that the explanatory power of the Shimizu hypothesis breaks down here. These compositions have a flash phase consisting of a fast smoulder, and contain nothing like the ingredients expected of a flash powder.

What of the "dark" reaction, or should we say "slow" reaction in these cases? TMAN is a net fuel that has very similar burning properties to hexamine: easy to ignite, burning at a low temperature, with small light output. The author postulated the burning of hexamine in air as the dark reaction for cases G and H.[7] One might thus similarly postulate the burning in the air of TMAN as the dark reaction for strobes containing this material. However, the ammonium perchlorate/cupric salicylate/hexamine system mentioned above has been found NOT to produce a visible flame during the dark phase, and this was also observed to be the case for some TMAN compositions. The dark reaction for TMAN strobes is therefore just as non-obvious as the flash reaction.

M. The acoustic strobe effect was referred to in the section above. Certain crackling microstar compositions, such as this one, have a propensity for multiple reports along with flashes and so also fit in the acoustic strobe category.[9] Shimizu has proposed a mechanism for the lead based crackling microstars that is analogous to his strobe suggestions.[16] One may note that most crackling microstars contain magnalium, just as do the most common kinds of strobes. Thus Shimizu proposes that the magnesium primarily takes part in the dark reaction, and the aluminum primarily takes part in the explosive flash reaction. It would not seem unreasonable that a similar mechanism could operate in the bismuth based microstars.

Conclusions

The principal mechanism that has been proposed to explain the chemistry of pyrotechnic strobe compositions is based on alternating reactions corresponding to the "dark" and "flash" phases of the strobe.[1–3] The dark reaction should have a low activation energy, together with a low heat of reaction. The flash reaction should have a high activation energy, together with a high heat of reaction. These qualities are characteristic of a smoulder composition and a flash composition respectively. Thus the hypothesis predicts that a pyrotechnic strobe composition is capable of deconstruction into a smoulder composition and a flash composition. It is not necessary for the components of these compositions to be different, since certain binary mixtures are capable of each reaction mode at different compositional ratios.

Theoretical analysis of the diverse strobe formulations above indicates that, for the most part, pyrotechnic strobe compositions can indeed be plausibly deconstructed into a smoulder composition and a flash composition. By and large this is supportive of the prevailing hypothesis. However, there nevertheless exist some strobe compositions for which an opponent of this hypothesis could reasonably claim that such deconstruction is "clutching at straws". There is room for doubt. There are several possibilities. It could be that the prevailing hypothesis is correct and general, but we do not have sufficient understanding of some strobe compositions to see the applicability. It could be that the prevailing hypothesis is applicable to most strobe compositions, but not to all. It could be that the prevailing hypothesis is not really the most appropriate description of strobe mechanism, and that there may yet be a hypothesis of more general validity and predictive value. The hypothesis that a strobe composition can be thought of as a mixture of a smoulder composition and a flash composition may have value as a post facto explanation. Nevertheless, it does not have much predictive value since mixtures of a smoulder composition and a flash composition will not generally produce a strobe composition. Perhaps it is a necessary, but not sufficient condition. Our understanding of the pyrotechnic strobe would be furthered by a theoretical analysis of the thermodynamics and kinetics involved. Quenching experiments should provide valuable evidence regarding the chemical changes that have occurred in different phases of the cycle.

Strobe Frequency

While we do not yet have a good theory to enable discovery of new strobe compositions, it is nevertheless possible to tailor the properties of existing compositions in order better to serve our needs. In particular there are some reliable methods for fine tuning the strobe frequency to suit one's purpose. The majority, but by no means all,[17] of practical strobe compositions contain a metal powder. It seems that in these cases the frequency may be increased by increasing the available surface area of the metal. Most commonly this is achieved either by increasing the percentage of metal in the formulation or by decreasing the particle size of the metal powder. In order to decrease the frequency, the opposite is done.

In addition, altering the physical form of a strobe composition can affect the frequency. Increasing the thermal feedback will usually increase the frequency. Thus, a composition in a tube will exhibit a greater frequency than the same composition as a naked star flying through the air.

Safety Considerations

Firework composition safety considerations most commonly fall into the categories of accidental ignition hazard or toxicity hazard. Many strobe compositions contain ingredients that are also found in flash powders. Moreover, the hypothetical mechanism proposes that strobe compositions could be regarded as being partly comprised of flash powder. Thus one might reasonably assert that strobe compositions should be treated with the same respect that one would afford flash powder. Practical experience of many pyrotechnists has borne this out. Strobe compositions have been known to explode catastrophically when subjected to impact. Strobe mines have been known to shred metal mortars. Nor should one assume that strobe compositions devoid of active metal fuel are free from such considerations.

A wide variety of firework chemicals are used in the preparation of strobe compositions, and it is necessary to be aware of particular combinations that engender a greater than normal predisposition for spontaneous combustion. Most notable in this context is the combination of magnesium and ammonium perchlorate. As stated by Lancaster, "Magnesium is particularly liable to heat up in the presence of ammonium salts".[18] Unfortunately this happens to be a combination that otherwise has been shown to be especially effective for the production of variously colored strobe compositions.[1] The usual expedient for accommodating this situation is to pacify the magnesium surface with potassium dichromate or ammonium dichromate. The techniques have been mostly developed by Shimizu, and nicely summarized by Lancaster.[18] The use of dichromates, however, introduces a toxicity hazard significantly greater than typically associated with pyrotechnic compositions.[19] Dichromates are known to be carcinogenic, with potential long latencies after exposure. For use in fireworks, therefore, it is necessary to take greater than normal precautions to prevent access to lungs and skin during manufacture. There have been some efforts to solve the magnesium/ammonium perchlorate incompatibility problem in a way that avoids undue toxic hazard.[20]

The use of magnesium aluminum alloy (magnalium) instead of magnesium, in combination with ammonium perchlorate, goes a long way in reducing the probability of an unintended exothermic reaction. However, magnalium and ammonium perchlorate, in combination with some other materials, have also been known to heat up in the presence of water.[21] Non-aqueous binding generally solves the problem, nitrocellulose being popular for strobe stars.

Crackling microstars may be classified as a pyrotechnic strobe. The use of lead oxide in these compositions presents significant toxic hazard.[22] The neurotoxicity for the developing brain is of particular concern. While infants may not be engaged in fireworks manufacture, they can nevertheless still smell the smoke.

Acknowledgments

While many pyrotechnists have contributed to the development of the pyrotechnic strobe, the principal theoretical contributions have come from Friedrich Wasmann and Takeo Shimizu. The author would also like to thank Ken Kosanke, Frank Feher, and Trevor Griffiths for their helpful suggestions in the preparation of this article.

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A Study of the Combustion Behaviour of Pyrotechnic Whistle Devices (Acoustic and Chemical Factors)

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ABSTRACT

Pyrotechnic whistles have long been used in both civilian and military applications. It is known that, under certain conditions, these compositions burn in an oscillatory manner and have exhibited a tendency occasionally to explode with great power during combustion. Based on the results of experimental work and a study of the thermochemical properties of whistle fuels, a hypothesis is proposed that attempts to account for the observed high levels of explosive and acoustic power of pyrotechnic whistles. The formation of < 10 μm diameter hollow carbon spheres was observed in laboratory experiments involving the thermal decomposition of potassium benzoate (a whistle fuel) in a reducing atmosphere. At the moment of formation, the spheres may possibly be filled with combustible hydrocarbon gases and would be extremely reactive. If formed during the quiet cycles of an operating whistle device, their existence may explain the higher than expected acoustic power of pyrotechnic whistles. Such a hypothesis may also lead to an understanding of other hitherto unexplained explosions, where under conditions such as 'cook-off', the thermal decomposition of organic fuels used in some other pyrotechnics would result in the formation of new substances which are more reactive than the parent chemicals.

Keywords: whistle, combustion, acoustics, oscillating burning, pyrotechnics

1. Introduction

Pyrotechnic whistle compositions are usually formulations consisting of the salt of an aromatic acid such as potassium benzoate ($KC_7H_5O_2$) or sodium salicylate ($NaC_7H_5O_3$) as the fuel and a strong oxidant such as potassium perchlorate ($KClO_4$). When the powder mixture is consolidated and burnt as an open-faced pellet, it burns at a constant linear rate and emits virtually no sound. However, if the pressed composition is ignited at the bottom of a short tube, it burns in an oscillatory manner and emits a loud, high-pitch whistling sound.

Pyrotechnic whistles have been used in a number of military and civilian applications, however, it has long been known that whistles have a propensity to explode during combustion and have been responsible for serious injuries. As part of a study to reduce the hazards associated with the manufacture and use of whistles, an investigation was undertaken to determine the mechanism by which high intensity oscillatory sound is produced by the combustion of consolidated whistle formulations.

This is described in a more comprehensive report[1] where modern instrumentation techniques, including high speed video, were employed to examine the combustion characteristics of the whistle composition MRL(X) 418, which contains 30% potassium benzoate and 70% potassium perchlorate. In particular instances, comparisons were made between this composition and a US formulation, which incorporates sodium salicylate as the fuel.

In addition, it has been established through acoustic considerations that the energetic output of each cyclic pulse of a burning whistle device is considerably greater than that expected from the thermochemical properties of the simple fuel-oxidiser system. Experimental evidence confirmed that when whistle composition was deliberately made to explode, sufficient energy was released to fragment the metal test cylinders into which it was filled. However, the projected fragments exhibited relatively large dimensions, with velocities not exceeding 100 m/s—factors indicating that detonation of the filling did not occur. When equal masses of other pyrotechnics, including flare composition and gunpowder (Black Powder) were similarly tested, no fragmentation of the cylinders was evident.[1]

These observations have led to the hypothesis that, under the specific conditions extant in the burning zone of a whistle device, highly reactive secondary fuels may be created through the thermal decomposition of the primary fuel. It is proposed that while these conditions occur during the quiescent phase of a burning whistle device, the resultant mass of reactants is limited by inherent physical control factors. However, should uncontrolled changes in the combustion surface geometry occur, the mass of these reactants can increase, leading to the explosion of the device.

2. Computer Modeling of Combustion

The NASA-Lewis CEC 76 computer code was used to predict the reaction products of a mixture of 70% $KClO_4$ and 30% $KC_7H_5O_2$ burning within a tube (i.e., in the absence of excess air). At atmospheric pressure, the predicted species consisted mainly of KCl, H_2O, CO_2 and CO; the latter two being in equal proportions. In an actual whistle device, it was questioned whether the subsequent reaction of hot CO in air at the tube mouth would generate sufficient acoustic energy to produce the oscillating sound inherent in this type of device.

To test this contention, a pyrotechnic whistle was ignited inside an open drum from which the air had been displaced with argon. When compared with an identical whistle burning in an air-filled drum, no difference in either frequency or amplitude could be discerned, inferring that the oscillatory sound is produced within the tube, and most likely, at the burning front.

3. Acoustic Model

The acoustic model presented here is approximate and quite simplistic in as far as the following assumptions were used:

- the model is based on linear acoustic theory (the model is less accurate for large amplitude waves),
- the acoustic propagation properties of the gas in the chimney of the whistle are homogenous,
- the effect of gas flow on the acoustic wave propagation is neglected,
- the free field impedance of the acoustic propagation medium inside and outside the chimney is nearly the same, and
- thermal and viscous losses are neglected in the propagation of acoustic waves.

Figure 1 provides the basic framework for understanding the proposed acoustic model of the whistle device. The acoustic behaviour of the device has been modelled on the classic quarter-wave resonator, where the reaction front of the burning pyrotechnic composition provides both a high acoustic impedance boundary and an acoustic energy source, and the open end, or mouth of the whistle chimney, provides a low impedance boundary.

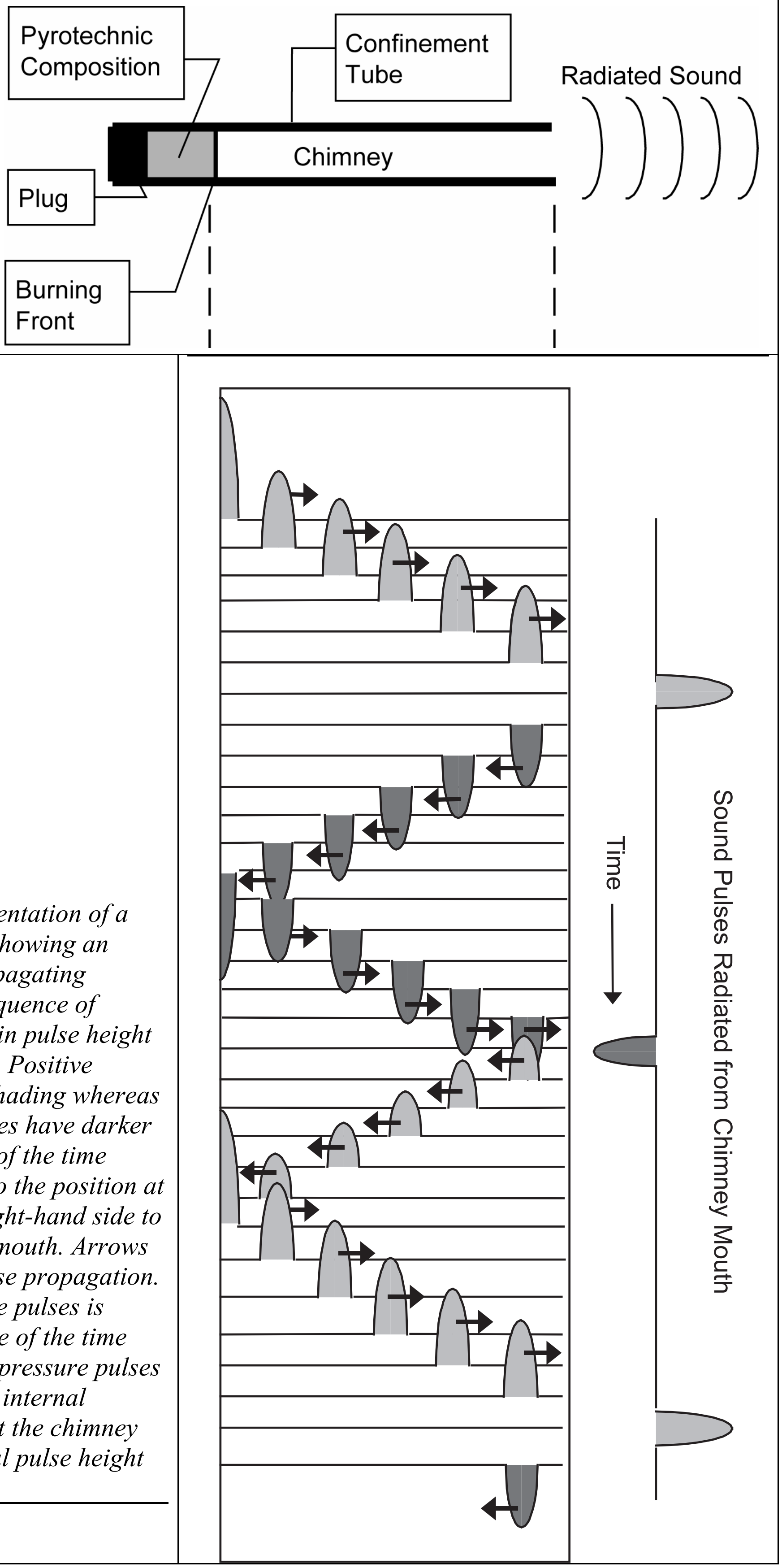

Figure 1. Schematic representation of a pyrotechnic whistle device showing an acoustic pressure pulse propagating through the chimney in a sequence of snapshots in time. Changes in pulse height occur at points of reflection. Positive pressure pulses have light shading whereas negative or rarefaction pulses have darker shading. The left-hand side of the time sequence box corresponds to the position at the burning front and the right-hand side to the position at the chimney mouth. Arrows indicate the direction of pulse propagation. A graph of radiated pressure pulses is shown on the right-hand side of the time sequence box. The radiated pressure pulses are generated each time the internal pressure pulse is reflected at the chimney mouth. A drop in the internal pulse height indicates this radiation loss.

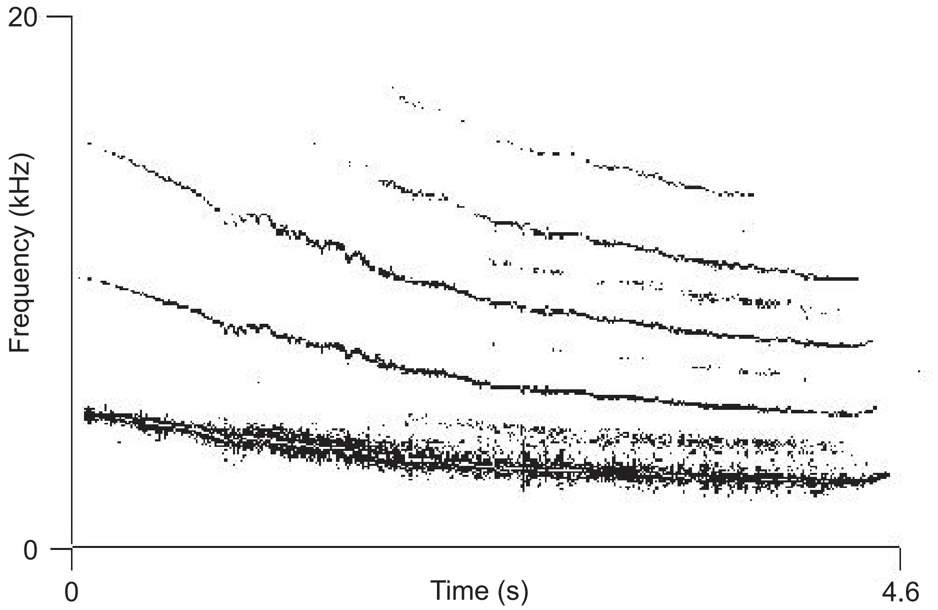

Figure 2. Spectrogram of whistle output, showing the peaks of the whistle spectrum as a function of time. The lowest line represents the first harmonic, or the fundamental, and the upper lines represent the higher harmonics.

There appears to be some confusion about such a model in the literature, where an open organ pipe model was suggested by Maxwell.[2] The open organ pipe model represents a half-wave resonator with two low impedance boundaries[3] where the ratio of the frequencies of the upper harmonics and the fundamental follows a simple 1, 2, 3, 4, ... relationship, termed here as the modal ratio. While the experimental data show such a relationship between the mode frequencies (see Figure 2), it does not fit the half-wave resonator model, which yields unrealistically low acoustic propagation velocities when calculated as the product of frequency and wavelength, with the wavelength equal to twice the effective chimney length. The modal ratio for a quarter-wave resonator, however, normally follows a 1, 3, 5, 7 … relationship, but it can be shown that non-linear distortions in the acoustic wave output are capable of producing the observed 1, 2, 3, 4 … modal ratios. So far, it has been found to be extremely difficult to account for the non-linear acoustic behaviour in the absence of suitable experimental measurement techniques capable of operating in a very hostile environment, and to simulate the process computationally would require considerable developmental effort. However, the simplified acoustic model still offers useful insights, particularly when the whistle chimney, or quarter-wave tube resonator, is considered as an acoustic wave trap. This helps to provide a better basis for understanding the possible effect of acoustic feedback on the chemical reaction rates in the whistle composition burn.

Experiments show that the whistle oscillations build up gradually after initiation.[3] It is presumed that before the periodic whistle noise is established, the initial pyrotechnic burn generates its own random noise, which is trapped by the whistle chimney and fed back towards the reaction front where it may be reinforced under favourable conditions. Therefore, the initial stage of the development of the oscillatory burn is considered to be a random process as shown in frame (b) of Figure 3, where random fluctuations precede the onset of coherent oscillations.

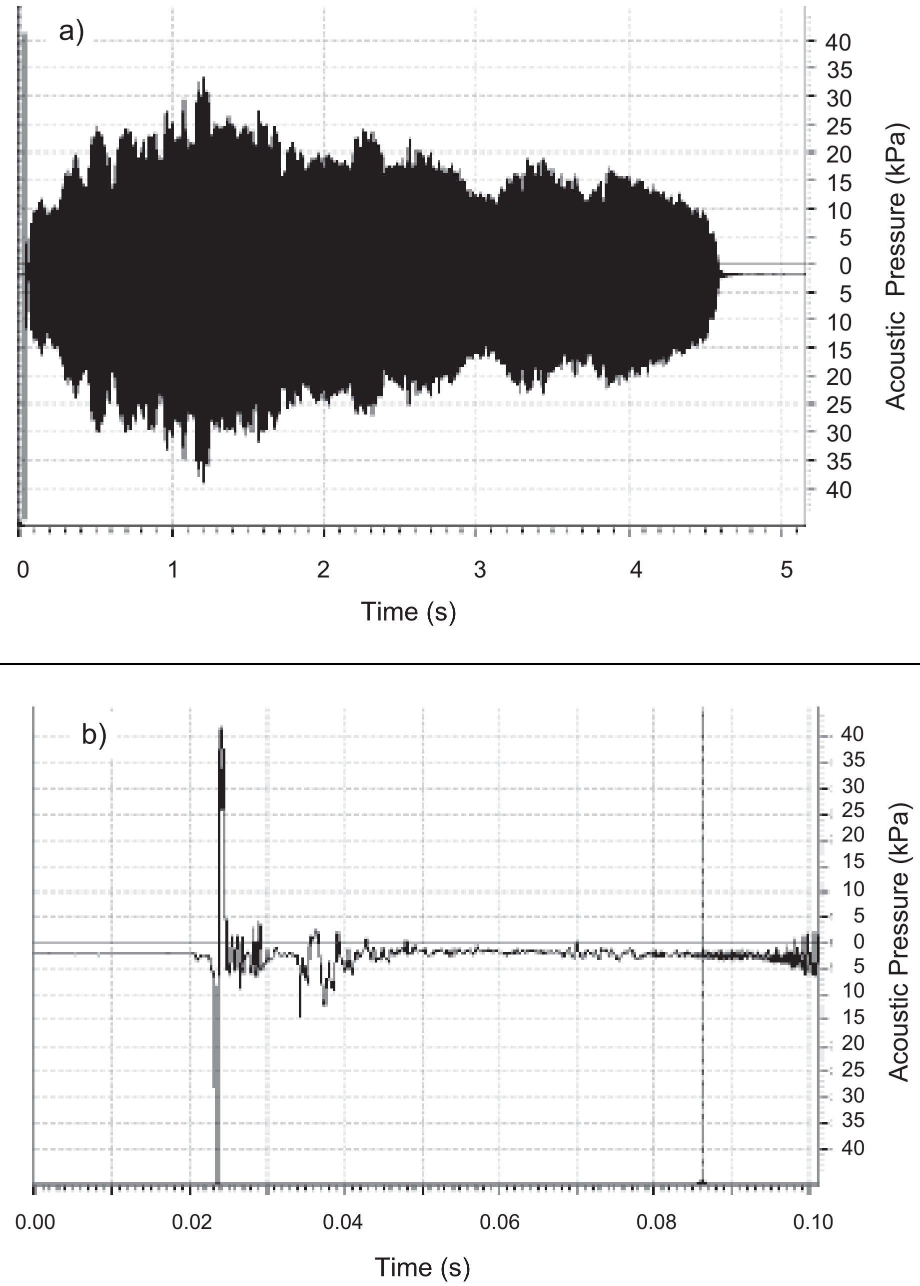

Figure 3. An example of the acoustic output of a pyrotechnic whistle device as a function of time with a vertical scale of approximately ± 40 kPa. Frame a) shows the complete record of sound output of nearly 5 seconds duration and frame b) shows the first 0.1 s comprising an initial transient due to the electric match-head initiator, random reverberant sound decay, and onset of coherent narrow-band oscillations. Unsuccessful attempts at resonant feedback are evident from the random fluctuations just to the left of the cursor at approximately 0.087 s followed by the onset of build up in coherent whistle resonance.

The effect of the acoustic pressure on the reaction rate of whistling pyrotechnic compositions is not yet properly understood, but it is clear from the literature as well as experimental evidence that the acoustic pressure wave trapped in the chimney controls the combustion process. Moreover, the energy of the combustion feeds back positively into the trapped acoustic wave.

This process is sometimes called thermo acoustic feedback since the combustion is expected to impart energy to the acoustic wave through the addition of heat. The wave-trap model highlights one feature, which may be of considerable significance in the acoustic control mechanism of the combustion, namely acoustic pressure doubling at the reaction front. In the model, as portrayed in Figure 1, a compressional pulse is generated at the reaction front and propagates towards the chimney mouth where it is reflected, but proceeds as a rarefaction pulse of somewhat diminished magnitude back towards the reaction front. At the chimney mouth, the pulse magnitude becomes nearly zero due to the low acoustic impedance boundary condition, and all of the potential energy of the pulse is momentarily converted into kinetic energy. During this reflection process, some of the pulse energy is dissipated through acoustic radiation into open space. At the reaction front, the rarefaction pulse is reflected and its pressure magnitude is momentarily doubled because of the high acoustic impedance at the reaction front boundary. The doubling is due to conversion of all of the kinetic energy of the pulse into potential energy while in the rebound phase. The pulse then reverts to its previous magnitude (assuming zero losses) and proceeds back towards the chimney mouth. There it undergoes a reflection as described previously, but now it returns as a compressional pulse to the reaction front and completes the cycle, doubling temporarily in magnitude during the rebound phase.

3.1. Thermo Acoustic Feedback Mechanism

To build up oscillations in the pyrotechnic whistle device, a mechanism must exist that periodically adds energy to the trapped acoustic wave. Rayleigh[4] stated that vibrations in a resonant column might be generated through periodic addition of heat in phase with pressure wave condensation (compression). In an attempt to understand how this energy is imparted by the combustion process, the relationship between pressure and reaction rate was considered. Maxwell[2] asserted that the rate of burning of whistle compositions is not abnormally sensitive to pressure and that the acoustic pressure fluctuations do not appear to change the reaction rates sufficiently to account for the observed acoustic power of whistling compositions. These assertions are supported by the data (reference 1) set out in Figure 4, which demonstrate that pressure fluctuations about the atmospheric mean of 100 kPa of absolute pressure produce little more than a six-fold difference in average mass burning rate. Note that gun powder (Black Powder), which produces a similar volume of permanent

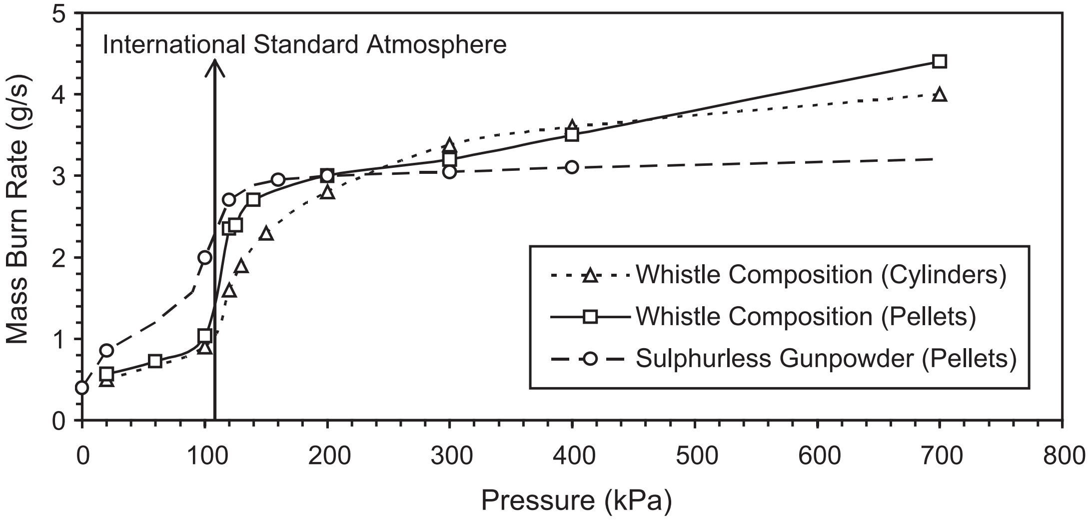

Figure 4. The relationship between static pressure (kPa) and mass burn rate (g/s) for whistle composition burning both as inhibited pellets in the open air, and at the bottom of open cylinders; in comparison to pellets of sulphurless gunpowder (Black Powder). The combustion of whistles ceased at pressures below 20 kPa, probably due to thermal losses from the burning front.

gas as whistle composition (~300 L/g), exhibits a similar increase in the mass burn rate with pressure, but does not exhibit oscillatory burning.[1]

Based on experimental observation and the above acoustic wave-trap model, it is believed that the acoustic pressure doubling at the reaction front controls the reaction process through thermochemical switching. It is suggested that acoustic pressure wave doubling at the reaction front is able to influence the temperature and pressure in the reaction zone and lead to differential fuel and oxidant decomposition rates. Thermochemical analysis of whistle fuels and oxidants by Wilson[1] showed that lowering of reaction temperature in a whistle composition is expected to lead to decreased decomposition rate of the oxidant while the fuel decomposition rate may continue relatively unabated. According to Wilson the layer of aromatic fuel thermally decomposes, producing solids and combustible gases including hydrocarbons and a highly reactive form of carbon. Thus, a doubled rarefaction pulse at the reaction front may lower the temperature and pressure at the reaction front and hence increase the net production of secondary fuels while decreasing the oxidant decomposition rate. A one half-cycle later, the doubled compression pulse will increase the temperature and pressure at the reaction front with a concomitant increase in the decomposition rate of the oxidant. The resultant combustion will be more energetic than in the preceding half-cycle and is therefore capable of adding energy to the acoustic wave, meeting the Rayleigh criterion. A build-up in the acoustic pulse height is possible via this mechanism with increasing contrast between the decomposition rates of the fuel and oxidant as the pulse height increases. In a fully developed oscillatory burn, the occurrence of distinct alternating half cycles of active and quiescent phases would be expected. Such behaviour was observed in experiments involving the recording (at 12,000 pictures per second) on a Kodak SP 2000C high-speed video system of combusting whistle devices pressed into transparent test blocks (see Figure 5).[1]

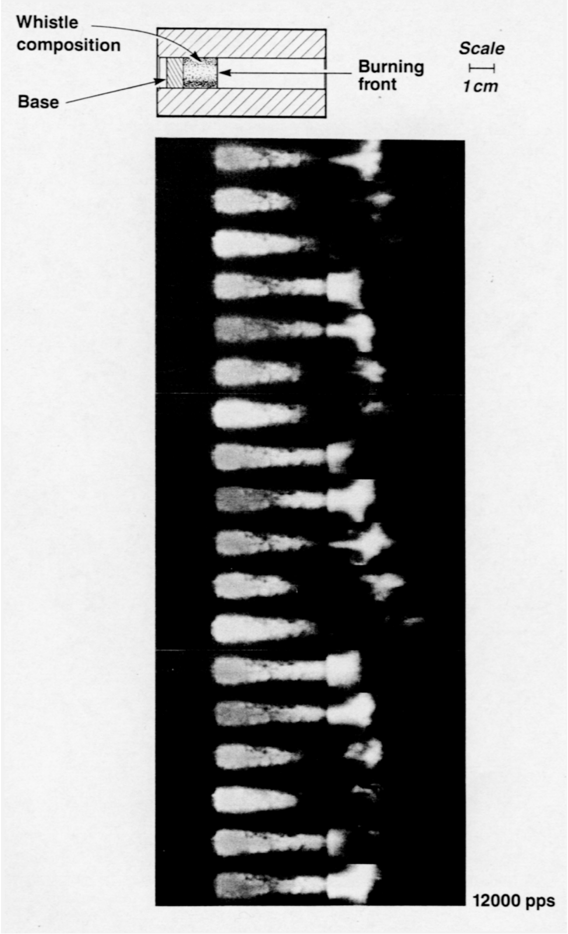

Figure 5. High-speed video record of a burning (3 kHz) whistle device showing combustion cycle 'switching' at the burning front.

Maxwell demonstrated that the acoustic frequency of a pyrotechnic whistle decreases as the length of chimney above the burning front increases.[2] A series of experiments with 0.45 m long chimney extensions was designed to reduce the oscillation frequency to enable the combustion process to be more effectively recorded on high-speed video. The records of these devices exhibited a very clear distinction between the active (light) and quiescent (dark) phases of the combustion cycle as seen in Figure 6. Maxwell also made similar observations using streak camera photography.

It should be noted that during the dark period, the reaction is not extinguished, but is sustained, possibly as a smouldering process of hot carbon particles in an oxygen deficient, low-pressure environment. If the environmental temperature were to fall below that at which the fuel decomposes, the combustion reaction would likely be extinguished. This probably explains why the whistles would not burn reliably at pressures much below atmospheric values, as indicated in Figure 4.

3.2 Quantitative Analysis of Acoustic Data

Useful information can be obtained from quantitative analysis of the acoustical data, such as acoustic pressure levels generated at the reaction front of a whistle device and specific impulse output, when compared with other energetic materials. The acoustic output of experimental whistle devices was measured (reference 1) with a Bruel and Kjaer Impulse Precision sound level meter located at a safe distance from the chimney mouth, and the sound pressure levels at the chimney mouth were calculated according to spherical spreading law. The acoustic pressure levels at the reaction front may be estimated from the acoustic properties of the chimney, considered here as a closed-open cylindrical waveguide. A more detailed derivation has already been performed in reference 1 so this study only considers some of the pertinent data and results.

In most of the experiments, the sound pressure level (SPL) was measured at a distance of one metre from the mouth of the whistle, with the SPL meter positioned at right angles to the whistle body. The initial chimney length, L, was 19.5 mm and the bore diameter, d was 12.5 mm. To calculate the effective wavelength, λ, of the wave trapped in the chimney, an end correction was applied to L so that

$$\lambda = 4L + 1.2\,d \cong 93 \text{ mm}$$

For the MRL(X) 418 whistle composition, the starting frequency was a little over 5 kHz and the recorded acoustic pressure waveform was nearly sinusoidal. Using the standard definition of SPL, the recorded waveform was converted to sound pressure and the spherical spreading law was applied to deduce the pressure amplitude just outside the chimney mouth. To calculate the pressure amplitude within the chimney, it is necessary to apply a transfer factor based on the reflection coefficient at the chimney mouth. This is called the resonant amplification factor (RAF), which determines the required build-up of internal wave amplitude until the acoustic energy imparted by the combustion is equivalent to the acoustic energy radiated from the chimney mouth. The RAF may be derived

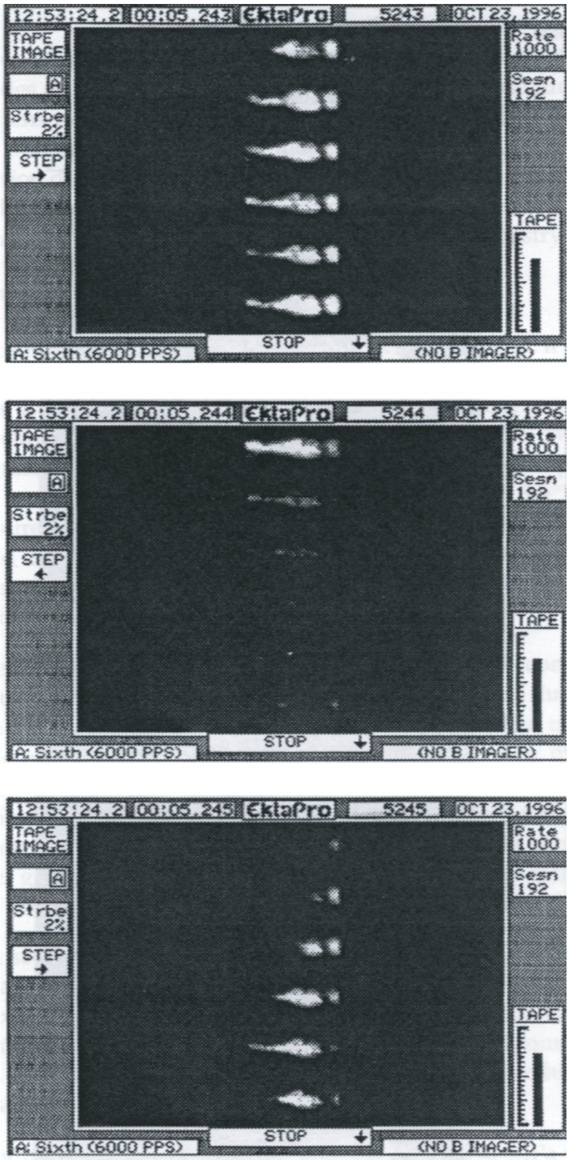

Figure 6. High-speed video record of a low frequency pyrotechnic whistle, showing the active (bright) and quiescent (dark) combustion cycles. To slow the whistle frequency to enable a full cycle to be recorded, an extended chimney tube was fitted to the device. When, in another experiment, a 'normal' 3 kHz whistle was located and ignited at a distance of 15 mm from the end of the low frequency whistle, pointing directly at the mouth of the extended tube, the combustion frequency of the first whistle was observed to increase.[1] This experiment demonstrated that the whistling frequency is controlled by the incoming pressure pulses (normally as a result of reflection from the tube mouth).

from first principles using acoustic theory for waves radiated from open cylinders, assuming no acoustic losses except by radiation from the chimney mouth. Adopting the approach and formulation of Fletcher and Rossing,[3] it is found that the RAF varies linearly with chimney length, starting at a value of 2.5 at the beginning of the burn, and closing at a value of about 6 at the end of the burn.

Figure 7 shows an approximate RAF translation between internal and external peak pressure for the same sound-pressure record as depicted in Figure 3. This illustration raises two important issues:

1) The internal wave amplitude is vacuum limited (i.e., it cannot exceed 50% of ambient pressure). Otherwise, pressure doubling at the reaction boundary during the rarefaction phase would demand negative pressures, which cannot be physically achieved. Hence, at atmospheric pressure, the amplitude is limited to about 50 kPa.
2) As the chimney length increases, the RAF increases, and therefore, the maximum possible output of the whistle decreases because of the vacuum limit. For the experiments with 0.45 m extensions, the RAF ≅ 50 and the expected maximum amplitude radiated from the chimney would be of the order of 1 kPa only. This corresponds to a 20-fold reduction in amplitude, or a drop of about 25 dB in sound output.

4. Energetics

4.1 Acoustic Impulse

Normally, pyrotechnic compositions are designed to burn at a relatively slow rate to produce the required physical effect (e.g., light, smoke, heat, gas or a delay interval). This is usually achieved by a combination of ingredient selection and formulation, and by either pressing or casting the composition into a container so that propagation proceeds by inherently slow layer-to-layer thermal processes. In certain cases, however, the burning rate must be greatly increased to produce the required effects.

In the case of photoflash compositions, where a pulse of light, sound and smoke must be produced in a very short time (e.g., in a spotting

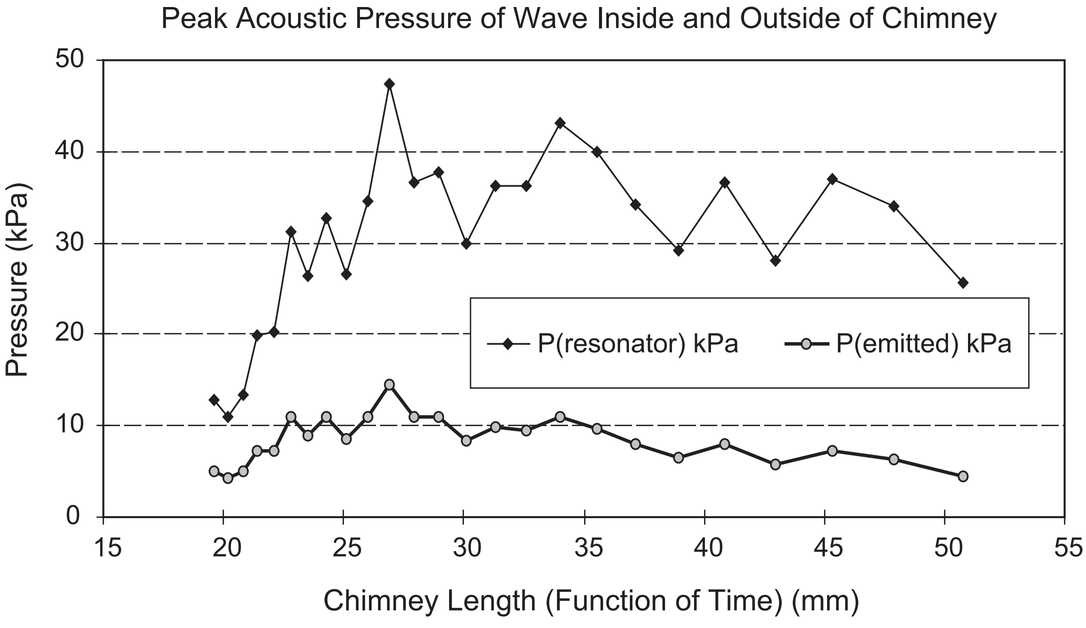

Figure 7. Translation of peak acoustic pressure for waves radiated from the chimney ($P_{emitted}$) to peak pressure for waves trapped inside the chimney ($P_{resonator}$). The translation is a function of chimney length, which varies with time as the whistle composition is consumed, and is governed by RAF (the resonant amplification factor).

charge for an artillery shell), the composition is filled as a loose powder into a container; greatly increasing the surface area available for combustion. The container provides a level of confinement, which serves to increase the internal pressure rapidly. The high thermal output of photoflash compositions (over 8 kJ/g, compared with gun powder (Black Powder), approximately 3 kJ/g) is a result of the use of metallic fuels and this, in conjunction with the other factors, produces a fast reaction rate (often several hundreds of metres per second) and high pressures. The reaction proceeds throughout the void spaces present in the filling and the entire mass of composition combusts, virtually simultaneously. The container ruptures and a single, high amplitude acoustic impulse is produced. Hitherto, the deflagration of loose, metal-fueled photoflash compositions has been regarded as probably the most energetic of the more common pyrotechnic sound-producing reactions when considered on a mass for mass basis.

To compare the acoustic output of loose-filled photoflash composition with loose-filled whistle composition, cardboard-cased test charges were prepared, each containing 50 mg of:

- the magnesium fueled photoflash composition MRL(X) 206, which contains 40% magnesium, 59% potassium perchlorate, and 1% acaroid resin and
- the whistle composition MRL(X) 418.

The electrically-initiated charges were tested for acoustic output; the specific impulse produced by the charges was 1.1 and 0.76 Pa s/g, respectively. Because the positive phase duration of the events was similar, the value produced by the whistle composition can be considered as a surprisingly high result, given the non-metallic nature of its fuel. It is important to note that the specific impulse produced by a single active cycle at the reaction front of *consolidated* whistle composition is estimated to be about 3,500 Pa s/g (using an 11 kPa half-sinusoidal pulse, a frequency of 3,000 Hz and an average burn rate of 1 g/s).[1]

High amplitude, non-cyclic impulse sound can also be produced using primary explosives, but neither the container nor the need to use a loose filling is a critical requirement. This is because the propagation mechanism of primary explosives is often detonation resulting from the formation of a supersonic shock wave. However, Wilson[1] demonstrated that whistle composition, when initiated with a detonator, did not produce an indentation in the witness plate—a test designed to indicate the formation of a detonation wave.

Clearly, a pyrotechnic whistle device is a very efficient converter of chemical to acoustic energy, but the mechanism of sound production from the consolidated burning front within an open tube is evidently different (producing a greater acoustic impulse) from that when the composition deflagrates in the normal sound-producing mode (i.e., when filled as a loose powder and ignited under confinement).

4.2 The Consumption of Mass

The mass of the reactants involved in the production of each acoustic impulse in an operating whistle device would normally be expected to be determined by the area of the burning surface and the degree of thermal energy intrusion into the pressed compact ahead of the reaction front (which is in turn determined by its gas permeability). However, under examination, pressed whistle compositions exhibited very low void spaces,[1] a characteristic likely to limit the mass of composition available to contribute to each acoustic impulse. The mass burning rate figures quoted in this work for whistling MRL(X) 418 are average values; that is the sum of the mass required to produce the acoustic impulses and the mass consumed during the quiescent periods per second. It has been demonstrated (Figure 4) that the mass burning rate of a 12.5 mm calibre, 3000 Hz whistle functioning at ambient pressure is about 1 g/s and that the lowest mass burn rate at which linear combustion is reliably sustained is about 0.5 g/s. But, even if it is assumed that during the quiescent interval, the mass consumption rate is zero (e.g., a ‘smouldering’ reaction of hot carbon particles) and that virtually all the available mass of whistle composition is required to produce the observed acoustic pulse, each single acoustic impulse consumes a maximum of only $1/3000 = 3.3 \times 10^{-4}$ g of composition. This mass, burning as a reaction between discrete fuel and oxidiser particles, appears much too low to account for the observed acoustic power.

From the foregoing, pyrotechnic whistles are unusual as acoustic impulse generators in that:

- whistle compositions contain an organic fuel (which would be expected to produce a low combustion temperature and resultant pressure),
- a higher acoustic impulse is produced from the reaction front of a functioning whistle compact than from a greater mass of the same composition ignited as a loose filling under confinement,
- whistle compositions are unlikely to propagate by a cyclic detonation mechanism (inferring a relatively slow reaction rate), and
- the very small mass of reactants consumed to produce each acoustic impulse would likely preclude a simple combustion process involving solids.

4.3 Fuel and Oxidiser Decomposition Temperatures

Thermo gravimetric analyses (TGA) of a typical whistle fuel ($NaC_7H_5O_3$ – Figure 8) and oxidiser ($KClO_4$ – Figure 9) were conducted to determine the relative onset decomposition temperature of the ingredients.

At the relatively slow heating rate of the thermal analysis instrument (40 °C/min), the results indicate approximately a 350 °C disparity between the onset decomposition temperatures of the whistle fuel and oxidiser. While the values of the decomposition temperatures of the individual ingredients may change—both when slowly heated as a pyrotechnic mixture in the TGA instrument and when heated at the greater rate experienced in a burning whistle—it is unlikely that the ingredients will decompose at precisely the same temperature. It has already been demonstrated that, within a burning whistle tube, the pressure level varies greatly with time; this would likely lead to concurrent temperature fluctuations between the active and quiescent cycles and slightly disparate ingredient decomposition times. The fuel would continue to decompose in a low pressure and low temperature environment, while the oxidiser component would not fully decompose until the incoming pressure pulse had sufficiently raised the temperature of the reaction front.

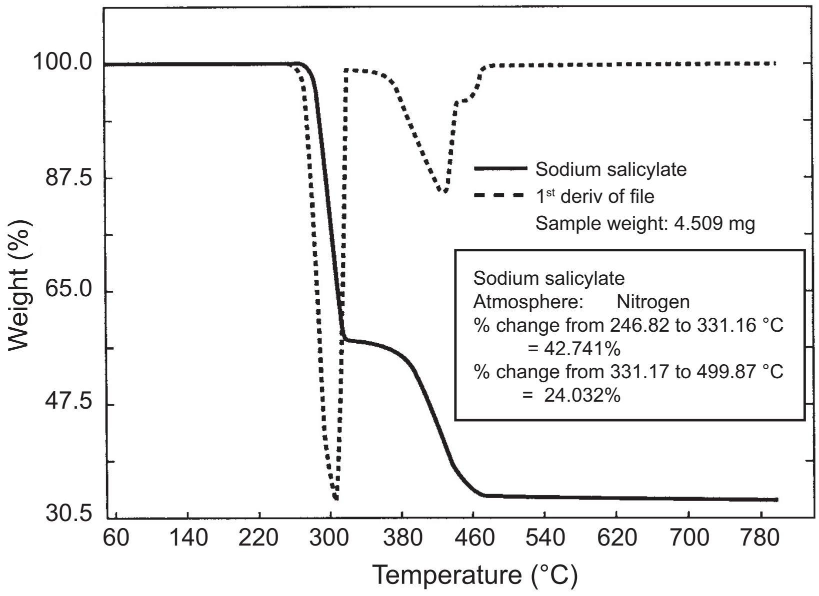

Figure 8. TGA of sodium salicylate. The analysis reveals a two-stage decomposition process commencing at approximately 250 °C.

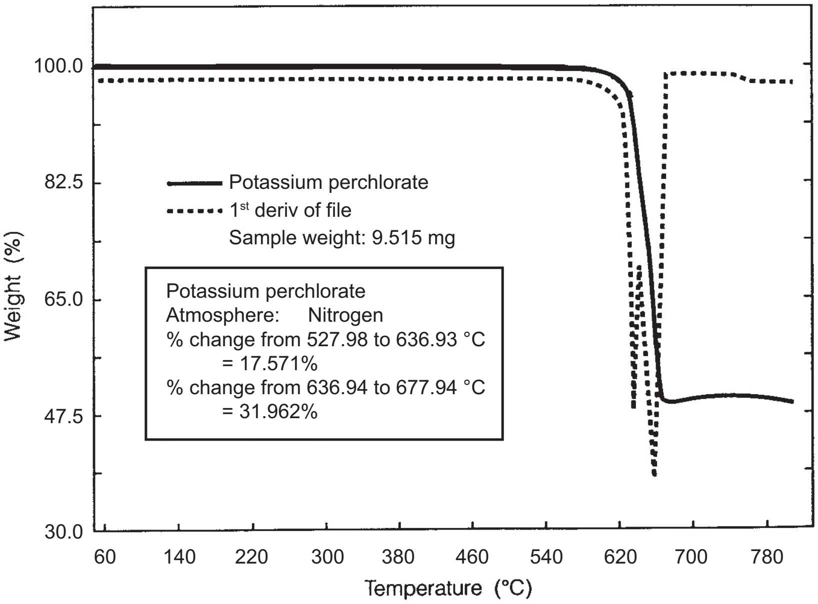

Figure 9. TGA analysis of potassium perchlorate showing onset decomposition temperature at approximately 600 °C.

4.4 Decomposition Products

An experimental analysis of the thermal decomposition of selected whistle fuels in a reducing atmosphere has been performed by Wilson.[1] The dehydration reactions indicated the formation of highly energetic fuel species (confirmed by the explosion of several of the reaction vessels that had likely admitted air during the experiment). While this phenomenon has not been directly observed at the combustion front of a whistle device, it is thought to be a key factor resulting from the oscillating burning environment in whistle compositions. The observation that the whistle fuels exhibit a lower onset decomposition temperature than the ignition threshold temperatures of their pyrotechnic compositions suggests that the physico-chemical properties of the fuels might be altered within the reaction zone, immediately before ignition of the fuel–oxidant mixture occurs. This is not necessarily an uncommon phenomenon in pyrotechnics technology and can normally occur as an ongoing process just ahead of the combustion front as the reactants are preheated as a result of the permeability of the compact, particularly when combustion occurs under pressure.[5] Consolidated whistle compositions, however, have been demonstrated to exhibit very low permeability, probably due to the physical properties of the aromatic fuels.[1] This would restrict the mass of reactants involved to a thin layer on the surface of the consolidated compact.

Thermal decomposition analyses in reference 1 indicated the presence of the following combustible volatiles for potassium benzoate ($KC_7H_5O_2$): CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_6H_6, CO, and for sodium salicylate ($NaC_7H_5O_3$): CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_6H_6, CO, C_6H_5OH. The relative abundance of these species varied with decomposition temperature, and the reader is referred to reference 1 for complete details. It is important to note, however, that the presence of approximately 40% by mass of elemental carbon or carbon compounds was found in the condensed residue. The residue was examined under a Scanning Electron Microscope (SEM) and this revealed that in the condensed state, the residue is mostly carbon and takes the form of spheroids of approximately 1µm diameter (Figure 10).

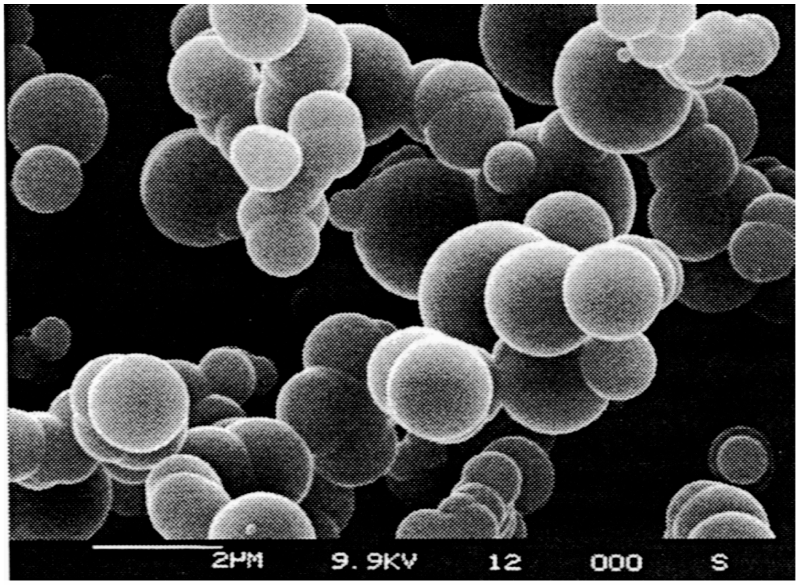

Figure 10. SEM of carbon spheres resulting from the thermal decomposition of whistle fuel in a reducing atmosphere. Crushing the spheres revealed that they were hollow.

Mechanical compression of the carbon spheres has provided strong evidence that at least some of them are hollow. This leads to speculation regarding the dynamics of the formation process and the nature of the gas species that may fill the spheres. The actual form that carbon takes at the moment of the destruction of the aromatic ring at the elevated temperature of the combustion front in a pyrotechnic whistle can only be guessed at, but it is probable that it is in a finely divided state. This hot and highly reactive carbon, together with any combustible gases, which form from the aromatic fuel, would represent a new and relatively energetic fuel mixture. This, when burning under pressure in the oxygen gas resulting from the thermal decomposition of the oxidiser, might account for the observed acoustic efficiency and explosive power of pyrotechnic whistles.

4.5 Explosive Behaviour

The proposed ability of whistle compositions to form a highly reactive fuel–oxygen mixture under certain conditions of temperature and pressure might also explain their tendency to occasionally explode violently, for example when accidentally ignited as a loose powder at the bottom of a filling funnel or as a result of the ‘flash down the side’ phenomenon in a functioning whistle device (see reference 1). In both these circumstances, the mass of reactants is uncontrolled by the normal constraints of a finite and consolidated reaction layer, and a limited combustion pressure environment. Under uncontrolled conditions, the production rate of the energetic fuel species and oxygen would likely become exponential—resulting in the observed explosions.

So far, experimental evidence and some theoretical considerations have lead to the conclusion that the participation of acoustic stimuli in the explosive failure of pyrotechnic whistles is unlikely. The acoustic waves tend to quench the linear combustion rate of whistle compositions and although more reactive fuel species may be created during the quiescent phase of the oscillating burn, they would normally be produced in small discrete quantities before being consumed in the active phase of the combustion cycle.

The role of higher harmonics as stimulants for runaway reactions is virtually ruled out. First, the upper harmonic components are usually weak, and second, only the odd harmonic components are able to physically participate in the reaction control in a quarter-wave resonator. In practical whistle devices, such components will be well above the critical cut-off frequency of the oscillatory burn and will therefore be excluded. However, in experiments with chimney extensions, where the fundamental burn frequency (approximately 270 Hz) was well below the cut-off frequency, switching of the burn oscillations to third harmonic frequency was evident (see Figure 11) and consistent with the model. The switch to a higher mode frequency did not result in runaway reaction, though, and the behaviour could probably be described as preferential mode competition.

Other experiments, in which strong tonal acoustic stimuli were externally applied to functioning whistles, demonstrated an effect on the reaction rate, but only by way of disrupting or altering the control cycle.[1,6] Similarly, experiments with externally applied acoustic shock stimuli have not had a detrimental effect on safe whistle performance, indicating that acoustic pressures are unlikely to induce fragmentation of the fuel–oxidiser compact.

5. Concluding Remarks

The acoustic model shows that acoustic pressure doubling at the reaction front may be critical to the coupling between acoustic waves trapped in the whistle chimney and the combustion process. Temperature and pressure switching is believed to control the decomposition rates of the whistle fuel and oxidant resulting in a two-stage combustion cycle. The first, quiescent stage, involves the decomposition of fuel to form highly reactive species in an oxygen poor atmosphere through acoustically lowered pressure and temperature. The second, active stage, involves the rapid combustion of the new fuel species in an oxygen rich atmosphere through acoustically elevated temperature and pressure. The energy released in the active cycle feeds positively into the acoustic wave trapped in the chimney, but its final amplitude will be governed by the balance of energy injected by the combustion and the radiation and visco-thermal losses. Furthermore, the internal wave amplitude cannot ex-

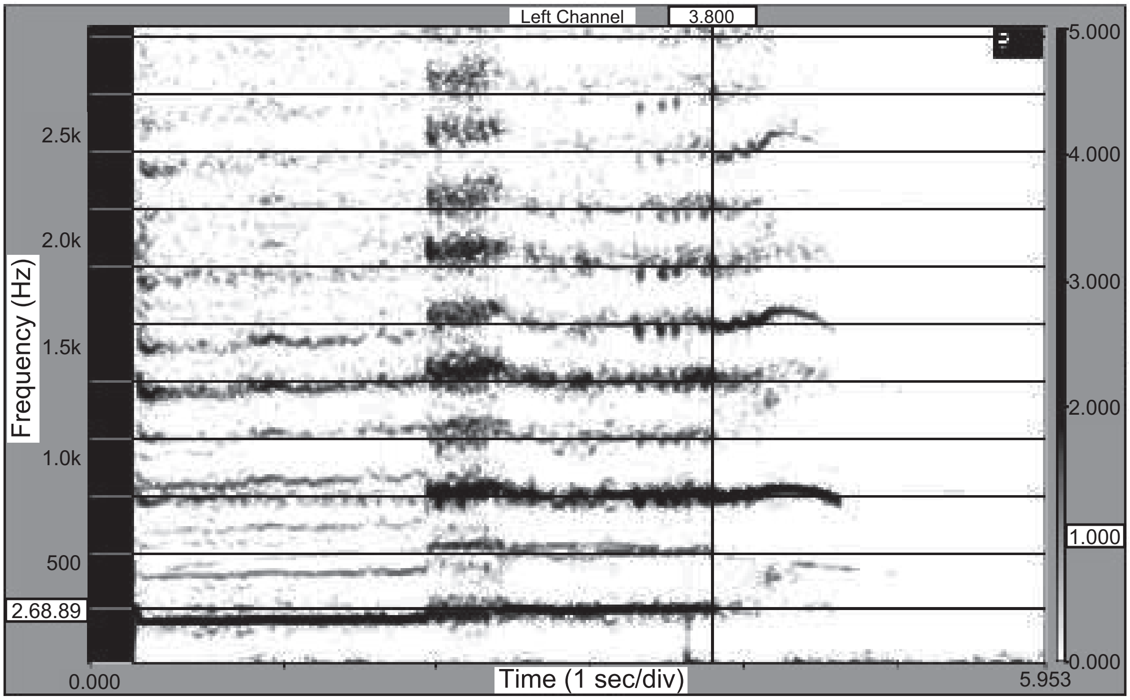

Figure 11. Spectrogram of whistle output for an experiment with a 450 mm chimney extension. It shows the peaks of the whistle spectrum as a function of time and a harmonic cursor has been laid over the temporal spectrum lines. The first harmonic frequency is at approximately 270 Hz. A strong switch to oscillation at the third harmonic frequency is evident at the 2 s marker, and at 3.8 s (position of cursor) the first harmonic is extinguished while the third harmonic component continues—together with its non-linearly generated overtones—until the composition has burnt out.

ceed vacuum during the pressure doubling in the rarefaction phase, so this will be also a limiting factor in the acoustic output, particularly for long chimney lengths. However, further investigation (possibly assisted by sampling the combustion residues at the burning front from a whistle that has been 'switched off' by sudden exposure to vacuum) is required to validate the proposed combustion model before definite conclusions are drawn.

6. References

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Notes

Sensitiveness of Pyrotechnic Compositions

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1 Introduction

Pyrotechnics (along with explosives and propellants) can respond to mechanical and electrical stimulation. They may be designed to be initiated in this way (e.g., cracker snaps) or this may be an accidental response to mishandling. The latter is becoming widely known as sensitiveness[1] and is the subject of this chapter.

1.1 The Term Sensitiveness

The term "sensitiveness" derives from the Sensitiveness Collaboration Committee (SCC) of the UK Ministry of Defence,[2] which produced a manual describing the apparatus and procedures used to assess the safety of "energetic materials" (explosives, propellants and pyrotechnics) for UK Service use. Particular attention is drawn to pyrotechnics as it is often impossible to predict their sensitiveness since a number of key parameters (e.g. particle size, granularity, material purity) exert an influence on the material's response. Sensitiveness is a measure of a composition's response to mechanical stimuli (impact and friction) and to electric spark. All three have implications for the safe handling of pyrotechnic compositions (or any other explosive material) particularly in manufacturing processes where the composition will be exposed and vulnerable. The term sensitiveness is used to differentiate the response to accidental stimulus, and the term sensitivity is used to designate the response to the designed stimulus, mainly flame and spark for pyrotechnic materials. In terms of safety, a pyrotechnic composition should have high sensitivity to flame and low sensitiveness to impact, friction and electric spark.

1.2 Accident Statistics

There have been several studies attributing accidents involving explosive materials (pyrotechnics, propellants and explosives) to their primary cause. McIntyre[3] published a survey of accidents in the US pyrotechnic industry, collecting data from 577 ignitions. The majority of ignitions were attributed to the application of friction to the materials. Similar work by Pape and Napadensky[4,5] covering 389 incidents in the USA found that friction was, again, the major causal stimulus for the accidental ignition of explosives and propellants during processing. In a later study of UK incidents undertaken for the Health and Safety Executive (HSE), Bailey et al.[6] reported similar results from accidental ignition of pyrotechnics. Table 1 lists the results reported by the three sets of workers for pyrotechnic materials.

Table 1. Causal Stimuli for Accidental Ignition of Pyrotechnics.

Stimulus	Percent of Ignitions Caused by Stimulus		
	McIntyre	Pape and Napadensky	Bailey et al.
Friction	64	46	66
Impact	13	23	6
Electrical spark	11	13	5
Other stimuli	12	18	23

1.3 Context of Sensitiveness within Safety Testing

A much wider set of tests is applied in the United Nations (UN) scheme for the transport of dangerous goods[7] (UN "Orange book") where Test Series 3 considers the impact and friction sensitiveness of explosives, propellants and pyrotechnics in ascertaining their safety in transport. Under European Community (EC) legislation, sensitiveness values measured on the Bundesanstalt für Materialforschung und – prüfung (BAM) mechanical sensitiveness tests (impact and friction) are used in assessing: safety for notification and supply of bulk materials,[8] standards for the use in the classification of civil sector explosives[9] and in the control of major hazards involving dangerous substances.[10]

2 Standard Sensitiveness Test Apparatus

There are numerous sensitiveness test apparatus that have all been developed to answer the question "is the material acceptably safe?". To a large extent each unit will have been developed independently of the other apparatus designed to measure the same property. Gradually the BAM mechanical sensitiveness tests have become the most widely used "standard test" for mechanical sensitiveness mainly due to their being the 'recommended test' in the UN Transport scheme and their inclusion in EC legislation and use in European Standards.

2.1 Impact Tests

All impact tests operate on a similar principle. This involves the dropping of a weight onto a sample. All impact machines will have a weight (either a single weight or one from a series) that falls from predetermined heights. Rails will generally guide the falling weight and the sample is held in some form of consumable container. The differences come in the detail of mass used and the extent of confinement in the consumable. Figure 1 shows a schematic diagram for an impact test machine.

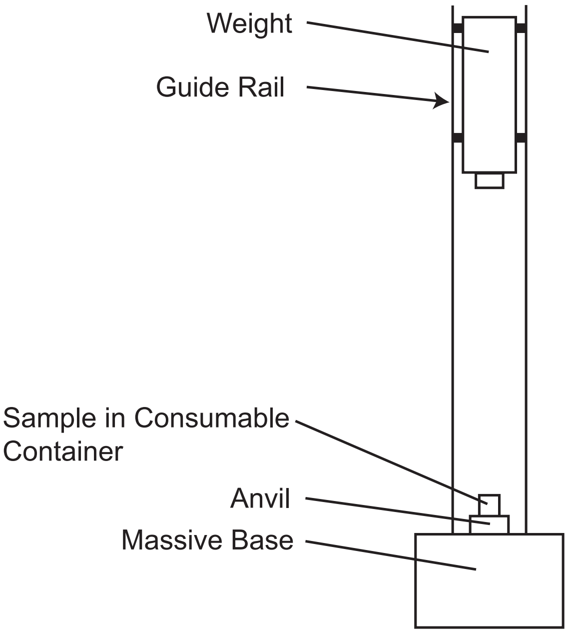

Figure 1. Schematic diagram of an impact sensitiveness test machine.

The UN scheme cites six impact tests in test series 3:

3(a) (i) Bureau of Explosives impact machine,
3(a) (ii) BAM Fallhammer,
3(a) (iii) Rotter Test,
3(a) (iv) 30 kg Fallhammer,
3(a) (v) Modified Type 12 Impact Tool, and
3(a) (vi) Impact Sensitivity Test

Tests from this set are intended to be used to assess the effect of accidental impact on explosives. Highly sensitive materials would be more prone to accidental initiation than less sensitive materials. Transport or handling of highly sensitive materials is probably a more risky activity than storing the material. Hence a material may be acceptable in storage in a sensitive form, while handling the material may require remote facilities. Transport may require specific precautions in the form of dilution or particular packaging to comply with the requirements of the UN scheme.

The tests differ in their approach to the application of the impact stimulus and each test has its own acceptance criterion for transport. However, the general principle is that of dropping a mass onto explosives either directly or via an intermediate striker. The sensitiveness values will give an indication of the ease of initiation (ignition for most pyrotechnics) when working with the material. Certainly a series of data on a single apparatus would allow a set of pyrotechnic compositions to be ranked for their safety in handling. This would be very relevant, for example, where compositions were being pressed using traditional rod and mallet.

2.1.1 Bureau of Explosives Impact Machine

This test measures the drop height required to produce a 50% probability of initiation of a sample, H_{50}. The apparatus drops a 3.63 kg mass (presumably the test started with an 8 lb drop weight) between two parallel cylindrical guide rods. The weight falls onto an assembly containing 10 mg of material. The production of a report (sound) or flame is taken as an "explosion". Materials are considered safe for transport if there are less than five ignitions from a set of ten tests undertaken at a drop height of 10.0 cm (i.e., a H_{50} of 10 cm or less is considered too dangerous for transport in the form tested). Borderline materials may well undergo a larger series of drops using a "Bruceton" method[11] (see section 3.2) to more accurately measure H_{50}.

2.1.2 BAM Fallhammer

The BAM Fallhammer takes a similar approach to the Bureau of Explosives Impact Machine. Two rails guide the weight as it drops, in this case a tooth and ratchet mechanism catches the weight when it rebounds. The machine uses three different masses (m), 1, 5 and 10 kg and a series of heights (h) to generate a series of "impact energies" (e) ranging from 1 J through to 50 J. The impact energy is calculated using $e = mgh$, taking g, the acceleration due to gravity, as 10 ms^{-2}.

Powdered samples are sieved before use. The fraction passing through a 500 µm sieve is used for the test. This sample should also be representative of the bulk material. If one component were in larger-sized particles, this would not be the case. This is unlikely for most pyrotechnic composition but additional grinding of a component may possibly be required to give a "representative sample".

The mass falls onto an assembly consisting of two roller bearings in a collar containing 40 mm^3 of sieved sample. The production of a report or flame is again taken as indication of ignition. The BAM methodology generates a limiting impact energy (LIE) that is the lowest energy that produces at least one ignition in a set of six test (approximately 17% probability of reaction) with the next lower energy giving no ignitions in a set of six tests. LIE values of 2 J or less indicate that the material (pyrotechnic composition) is too dangerous for transport in the form in which it was tested (i.e., as a loose material for pyrotechnic compositions). However, this test is only a screening test and transport of the material may be allowed following further series of trials on packaged material.

2.1.3 Rotter Test

This test is slightly different in approach to the sample containment. There is deliberate clearance for material to flow during the test that is not present in either of the previous two test methods. Again a mass, 5 kg for solid samples, is dropped onto an assembly consisting of a brass cap and steel anvil. The sample, 30 mm^3, is placed into the cap and a pip in the anvil inserted. The assembly can then be turned through 180° and inserted into the housing. The housing is then closed and the drop weight falls onto an intermediate rod that transfers the impact onto the sample. Being a closed system connected to a gas manometer, gas volume change is the normal criterion for an ignition. For non-gassy mixtures the presence of a transient gas volume and smoke on opening the housing can also be used to identify an event. The response is assigned as a "go" or "no go", a "go" being the generation of 1 cm^3 or more of gas and/or smoke in the housing.

A drop height for 50% probability of initiation is found by a Bruceton method (see section 3.2). This is compared to H_{50} produced by a "standard" RDX sample and a "Figure of Insensitiveness", FoI, is calculated. The FoI is defined by:

$$\text{FoI} = 80 \times \frac{H_{50\,(\text{sample})}}{H_{50\,(\text{RDX})}}$$

Any material having a FoI result that is ≤ 80 is regarded as + in the UN test and "the substance is considered too dangerous to transport in the form in which it was tested".

The SCC manual divides explosives into categories based on the value of FoI:

- materials with FoI ≤ 30 are classed as very sensitive,

- materials with FoI 35 to 90 are classed as sensitive, and
- those materials with FoI > 90 are classed as comparatively insensitive in their response to impact.

The Rotter test is often the preferred impact sensitiveness test for incident investigation as it probably reflects processing conditions more accurately than a pure impact (adiabatic compression) test. This is because the test involves motion of the sample around an edge.

2.1.4 30 kg Fallhammer Test

The 30 kg Fallhammer test employs an open test sample. The material is placed into a steel tray, 150 × 50 mm, to a depth of 8 mm and the 30 kg mass, with a defined curved base, is dropped onto the sample such that it impacts with the sample 25 cm from one end. An event is determined by the production of an ignition and its propagation through at least 100 mm of material from the point of impact. Sets of three tests are performed to find a limiting drop height (i.e., the height at which no ignitions occur in a set of three drops). Materials with limiting drop heights of less than 75 mm are considered too sensitive to transport in the form tested.

2.1.5 Modified Type 12 Impact Tool

The modified type 12 impact tool confines 30 mg of sample between an anvil with 32 mm diameter surface and intermediate mass. A second mass is then dropped onto the intermediate mass to produce the impact on the sample. Combinations of drop masses (1.0, 1.5, 1.8 and 2.0 kg) are employed with intermediate masses of 1.5, 2.0 and 2.5 kg. Particularly insensitive samples are tested with garnet paper placed on the anvil. Typically a combination of a 1.8 kg drop mass and 1.5 kg intermediate mass are used for RDX, and a Bruceton method is used to determine H_{50} for the sample. If H_{50} for the sample is less than or equal to that of RDX then the material is considered too sensitive for transport in the form tested.

2.1.6 Impact Sensitivity Test

The impact sensitivity test uses a similar system to the BAM impact test in placing 100 mg of sample between two roller bearings in a collar. However, in this case, the sample is pressed hydraulically (290 MPa) prior to test. A 10 kg mass is dropped from a series of heights to ascertain the height at which no ignitions are obtained in a set of 25 drops. A material with a lower limit of less than 100 mm is taken to be too sensitive for transport in the form tested.

2.1.7 Additional Methods Described in the Encyclopedia of Explosives

The *Encyclopedia of Explosives and Related Items*[12] describes a number of impact machines, some of which are described above. The additional methods described are the Bureau of Mines Impact Apparatus and the Picatinny Arsenal Impact Apparatus.

The Bureau of Mines apparatus employs a grit blasted cup and striker to hold the sample. Drop weights of 1, 2 and 5 kg are employed. Median drop height (H_{50}) is found for the sample.

The Picatinny Arsenal Impact Apparatus uses 2 kg, 1 kg and a 1 lb drop weight, which fall onto a sample held in a small cup, capped with a brass cap and topped off with a vented plug. The lowest drop height that gives at least one initiation in ten drops on a fresh sample is found. There should be no initiations at a 1 inch lower drop height.

2.2 Friction Tests

All current UN friction tests operate on similar principles — a sample is generally held between two friction surfaces and, while a force is applied to the friction surfaces, one of the surfaces is moved generating dynamic friction between the surfaces and the sample. Alternative methods utilise a pendulum. This allows one of the surfaces to swing across the sample placed on a fixed friction surface. Figure 2 shows a schematic diagram for a friction test machine.

There are three tests described in the UN Orange book and a further test is described in the SCC manual:

3 (b) (i)	BAM Friction Apparatus
3 (b) (ii)	Rotary Friction Test
3 (b) (iv)	Friction Sensitivity Test
SCC test No 2	Mallet Friction Test (described in section 2.4.2)

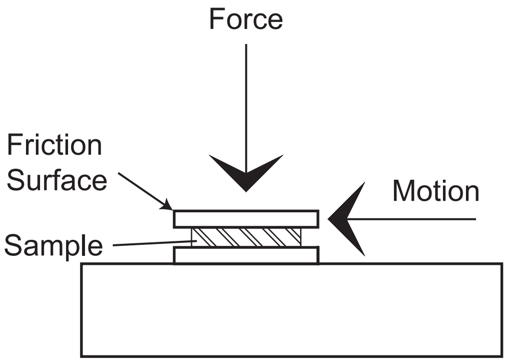

Figure 2. Schematic diagram of a friction sensitiveness test machine.

The UN test 3(b) (iii), the ABL friction test, was removed from the UN scheme.

All tests are assessing a material's response to an accidental frictional stimulus. Such data will have relevance in grinding operations and in pressing where the materials may rub against the surface of the formers. While the acceptance criteria applied in the tests are primarily to assess suitability for transport, the information generated will give an indication of the hazards posed in handling and processing the materials.

2.2.1 BAM Friction Test

This is the recommended test for assessing friction sensitiveness in the UN scheme and comprises two porcelain surfaces, one a moving plate and the other a fixed peg with defined curvature. The plate has a grain due to rubbing with a sponge prior to firing the ceramic. The specified surface roughness is currently 9 to 32 µm. There is no specification as to how the measurement is made. Using modern equipment and specifying the mode of surface measurement is likely to change the value measured.[13] The plate is placed in the machine such that the relative motion of the plate and the peg produces motion across the grain.

The sample (10 mm^3) is placed on the plate and the peg lowered onto the material. A mass is hung along a loading arm to apply pressure to the sample between the surfaces. An electric motor is used to move the plate 10 mm forward and then back. Ignition of the sample (flame or spark), crackling or a report is taken to be an "explosion". Other responses are decomposition or no reaction, both of which count as a non-event.

Using the series of masses and varying positions along the loading arm produces loads in the range of 5 to 360 N with varying step size (larger step sizes at greater loading). Normal usage applies only the loads generated with the masses at the end of the loading arm (10, 20, 40, 60, 80, 120, 160, 240 and 360 N) and the smallest mass on the inner position (5 N). Additional information can be gained by use of intermediate values that can be obtained using the other positions on the loading arm.

A limiting load is determined using fresh material and a new surface for each test. The limiting load is the greatest load that will give no ignitions with the next level producing at least one positive event in six trials with fresh sample. For military pyrotechnics the load for 50% probability (L_{50}) is often found rather than the limiting load. Any material with a limiting load less than 80 N is considered too sensitive for transport in the form tested.

2.2.2 Rotary Friction Test

The rotary friction test employs steel friction surfaces; one a block, the other a wheel. Both are prepared to a surface roughness (Ra) of 3.2–4.0 µm by grit blasting. The applied frictional stimulus is varied by altering the speed of rotation and, normally, using a fixed applied pressure of 0.275 MPa. The rotational velocity for a 50% probability of ignition (V_{50}) is found for a material by a Bruceton method using fresh sample and clean surface for each test. This is compared with the V_{50} for "standard RDX" and a figure of friction (FoF) found as:

$$\text{FoF} = 3.0 \times \frac{V_{50\ \text{sample}}}{V_{50\ \text{RDX}}}$$

Any material with FoF of 3 or less is considered too sensitive to transport in the form tested.

The metal surfaces can be resurfaced by grit blasting the surfaces. The wear on the wheel needs to be considered in the assessment of FoF. Over time, the reduction in diameter will effect the rotational velocity. The test method makes allowance for this and applies limits beyond which the wheels require replacement.

2.2.3 Friction Sensitivity Test

The friction sensitivity test applies a pressure between the ends of two roller bearings with 20 mg of sample between and a pendulum strikes a pin to provide the motion. As the retaining pressure increases there is a corresponding increase in the angle through which the pendulum falls prior to striking. A lower friction limit is found. This is the maximum pressure between the roller bearings that does not give any ignitions in a series of 25 tests. Ignitions are taken as an audible effect, flash or burn trace on the roller bearing surface.

Any material with a lower friction limit of less than 200 MPa is considered too sensitive for transport in the form tested.

2.2.4 ABL Friction Test

The friction surfaces in the ABL friction test are a stationary steel wheel and a sliding steel anvil. Sample is spread on the anvil to form a track, the wheel is then lowered and a force applied. Motion (0.9 m s^{-1}) is generated by releasing a pendulum that hits the anvil. The highest compressive force that gives no positive results in 20 trials is found, this is known as the "Threshold of Initiation" (TIL). Any material that produces a TIL greater than that of PETN (184 N) is deemed to be fit for transport (i.e., any material with a TIL of ≤184 N is considered too sensitive for transport in the form tested).

2.2.5 Torpedo Friction Test

A different approach is used in the Torpedo Friction Test.[14] The sample is placed on an anvil and struck a glancing blow from sliding a metal torpedo down an inclined V-guide. Typically an angle of 80° is used and the height to produce an initiation is found. The head of the torpedo and the anvil can be varied to investigate the friction sensitiveness of the material with the materials that could be used in, for example, production machinery.

2.2.6 Closed Friction Test

Chapman[15] is developing a closed friction test. Current standard tests are essentially "open tests" in as much as the gasses produced are free to escape from the apparatus. This test is designed to identify gas release from insensitive materials or where determining a positive result by the conventional flash or bang is difficult. This test houses the friction plates within a brass enclosure. A force is applied pneumatically between the two plates and motion applied by using a drop weight. The enclosure is connected to a manometer to measure gas volume change as used in the Rotter test. This apparatus is currently at the proving stage.

2.3 Electrostatic Tests

There are no UN transport classification tests for electrostatic sensitiveness. Different centres have developed different tests, all based on passing an electrical discharge through the material under test. The charge is stored in a capacitor of known value charged to a known high voltage. Then the energy of the discharge, assuming no loss, is:

$$E = \tfrac{1}{2}CV^2$$

where E is the energy in Joules, C is the capacitance, and V is the voltage.

The electrode arrangements are the main difference between one test and another. These vary from two flat surfaces as electrodes, to one flat electrode and the other selected from a range including the point of a needle and a defined curved surface. The shape of the electrode will affect the resulting energy required to initiate the pyrotechnic material.

One such system is described in the *Encyclopaedia of Explosives and other Related Items*[16] where a charged capacitor is discharged through a sample using a "phonograph" needle. The other electrode is a steel plate. Using this system Blackpowder [passing through a 100-mesh (150-μm) sieve] was reported to not produce ignitions up to 12.5 J while magnesium powder varied from 0.007 to 12.5 J, presumably depending on the particle size. A material producing a result of no ignitions up to 12.5 J in this apparatus would be considered to be relatively insensitive to electrostatic discharge.

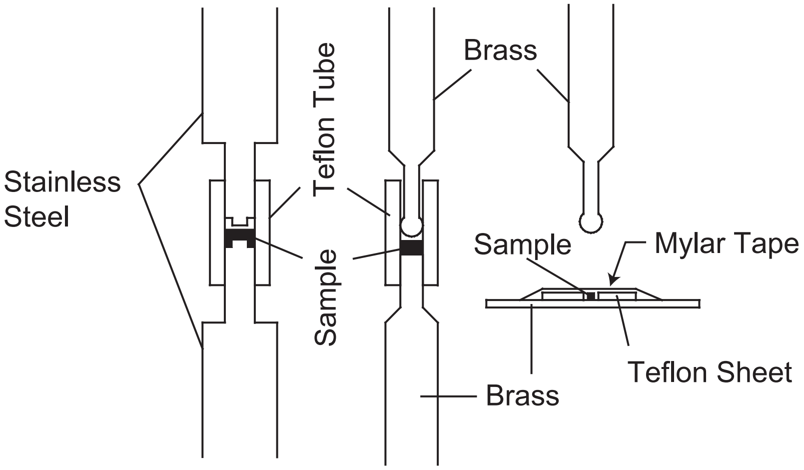

Figure 3. Schematic representation of the electrodes used in Matsuzawa's work.

At the other extreme the apparatus described in the Sensitiveness Collaboration Committee publications[2] employs two copper foils as the electrodes separated by a 3.175 mm (1/8 inch) polythene strip. A series of capacitors are arranged to produce discharge energies of: 0.045, 0.45, and 4.5 J. Materials requiring an energy greater than 4.5 J are regarded as "insensitive", those from 4.5 to 0.45 J as "comparatively insensitive", 0.45 to 0.001 J as "sensitive" and any composition requiring less than 0.001 J is regarded as "very sensitive".

These classifications were applied by Matsuzawa et al.[17] to a range of fireworks compositions tested using two different "Electrostatic Sensitivity Testing Apparatus" and a selection of electrodes. Both systems consisted of a high voltage source, capacitor and electrodes to form the gap for the test material. The main difference was the use of a relay in one and a pendulum switch in the other. Two closed electrode configurations were used. In one electrode system two stainless steel electrodes were sheathed within a 4 mm diameter Teflon tube. The faces of the stainless steel were turned down below the 4 mm diameter and sanded to give a flat surface with rounded edge. A gap of 1 mm was employed. The alternative closed electrode system used brass electrodes set within a 2 mm diameter Teflon tube. In this case there was one flat electrode and a 2 mm diameter spherical electrode. The final electrode system is open and consists of a brass plate as one electrode and a spherical brass electrode (3 mm diameter) as the other. This has the sample in a hole in a Teflon sheet held using Mylar tape. The electrode systems are shown in Figure 3.

2.4 Ad Hoc Test Methods

2.4.1 Portable Impact Tester

The BAM impact test criterion for transport is a limiting load of 2 J or greater. This is at the lower end of the capability of the machine to measure and is produced by a 1 kg mass falling 20 cm. The machine uses three different masses and various drop heights. However, if it is only a pass/fail test that is required, then a 2 J drop can be readily achieved without the complication of the full sized apparatus. Such a device was developed by Chapman[15] for use in the field to assess impact sensitiveness of materials that may, for example, have been affected by a fire prior to transport for full test (i.e., they were of uncertain sensitiveness and could have posed a hazard in transport).

To ease testing, the use of standard BAM consumables (collars and roller bearings) and parts of the full scale BAM apparatus were used. A fixed height drop of 20 cm and a 1 kg mass are used to generate the 2 J drop energy. A Perspex tube, which also provides part of the protection for an operator, guides the weight onto the BAM consumables containing the test sample. The methodology used is that of the full sized BAM test (i.e., up to six drops at 2 J). Any material that does not give an initiation would be assumed to be suitable for transport in the form tested.

2.4.2 Mallet Friction

A corresponding (semi-portable) test for friction is provided in the mallet friction test. This uses a series of anvils and mallets to assess the response of an explosive (pyrotechnic) to friction. The test, additionally, assesses the response to different combinations of friction surface, the full list of surface combinations are: steel on steel, nylon on steel, wood on softwood, wood on hardwood, wood on Yorkstone. The Yorkstone anvil, for example, is said to simulate the effect of powdered pyrotechnic on a concrete floor. The steel anvil and mallet are representing the situation in processing machinery where there could be steel to steel rubbing if the mechanism is not set correctly.

To carry out the test the powdered material is spread in a thin strip on one of the anvils and struck with an appropriate mallet. The blow is required to be glancing to impart rubbing friction stimulation rather than a direct blow that would be mainly impact. The test will to an extent be operator dependent due to the need to produce the glancing blow with minimum impact contribution. A series of ten strikes are used. Any strip of sample can be struck up to five times. Results from this test are included in Table 6 later in this chapter.

2.4.3 Hammer Test

Ofca[18] uses an ad hoc test to give a subjective "feel" of the sensitiveness of pyrotechnic compositions. In the "hammer test" small portions of pyrotechnic are placed on a steel plate and hit with the ball end of a steel ball-peen hammer. The pyrotechnic is hit with increasing force until initiation occurs. This will give an indication of impact sensitiveness.

A similar friction test uses the flat of the hammer head. Again small portions of the pyrotechnic are placed on the steel plate and this time the hammer is gently placed on the sample and pushed down while the hammer shaft is moved to rotate the head. By increasing the applied force an indication of the friction sensitiveness is made.

While both methods are uncalibrated and probably cannot be cross-correlated with other methods, the simplicity of the test does have an attraction for amateur pyrotechnists.

2.5 Non-Ambient Test Methods

Current sensitiveness methods are performed at ambient temperature. Many processing operations may well result in the material being heated either deliberately or more likely due to work being performed on the material. The UK Health and Safety Executive has funded work involving the development of elevated temperature mechanical sensitiveness test units.

2.5.1 Elevated Temperature Impact

Jarman and Formby[19] reported the development of an elevated temperature impact sensitiveness test machine. This had elements of both the BAM and Rotter machines. Both BAM or Rotter consumables could be used to hold the sample. The consumables, with explosives, were then placed into a housing very similar to that of the Rotter machine with heating elements incorporated. The sample was allowed to attain the test temperature before impact testing. As the housing produced a closed system it was possible to use the gas generated as evidence of the composition having ignited.

Results[20] obtained indicated that, for explosives that do not undergo a phase change (melting), median drop height (H_{50}) reduced with temperature. Interestingly, where TNT was a constituent, the material became less sensitive above the TNT melting temperature. No pyrotechnic materials were tested.

2.5.2 Elevated Temperature Friction

In a similar study the effect of temperature on friction sensitiveness was investigated by Miles et al.[21,22] The apparatus developed was similar to a BAM system in that it used a lever arm to provide the frictional load to the sample. The friction surfaces were an adhered ground glass on Perspex plate and a roughened metal wheel. Motion was provided by a pneumatic piston that accelerated a mass on the end of the actuator, this after accelerating, struck a free moving trolley loaded with the friction plate and sample.

Results[23] suggest that the explosives, propellants and pyrotechnic tested increase sensitiveness with increased temperature. Red star (strontium nitrate in a urea-formaldehyde binder) was reported as having a reduced L_{50} at 50 °C compared with the ambient result. At 50 °C, the formulation was initiated with a probability greater than 50% at the lowest available load, indicating that it had become extremely sensitive compared with a result of a 1 kg load at ambient.

While little work has been carried out on pyrotechnics, some general principles can be identified from the available information. It is likely that most pyrotechnic compositions would become more sensitive to mechanical stimulus as the temperature increases. However, there may well be cases where a binder or other additive softens or melts as the temperature increases. Such materials may well have a discontinuity in their sensitiveness vs. temperature graph, and there could be a decrease in sensitiveness at or about this temperature. Further work would be required to identify such materials.

3 Sensitiveness Test Result Treatment

All sensitiveness tests depend on the reaction of a set of samples to a series of energy inputs. Each individual sample is subjected to a given input level and as a result it will or will not initiate. Test methods then determine a level of response that is deemed to be acceptable. This can be a level at which there are no initiations in a given set, or some level of probability (e.g., 1 in 6 or 50%). Generally, these levels are set against criteria developed over many years of experience and often use comparisons to a material (e.g., RDX) that is accepted as a standard.

3.1 Limiting Values

Limiting values are used in the BAM Fallhammer, 30 kg Fallhammer and the impact sensitivity test. Of these the BAM Fallhammer test sets a level of one ignition in a set of six with the next level of stimulus giving no events in a set of six. The other two limiting values tests are no ignitions in three sets and no ignitions in 25 sets, respectively. There is no published data for pyrotechnic compositions examined using all three tests; however, results for the explosive RDX have been reported. Dry RDX is deemed fit for transport in the BAM Fallhammer test, but not in the 30 kg Fallhammer or impact sensitivity test.

Similarly, in the friction tests there are limiting loads. The BAM test uses a one in six limit with the next level giving no ignitions. The impact sensitivity test requires no ignitions in 25. In both tests, dry RDX is deemed fit for transport.

3.2 Bruceton Method

The Bruceton method provides a means of investigating the 50% probability of an ignition. A starting stimulus is obtained in a short pretest, which indicates levels of stimulus that give both ignition and non-ignition. Each sample then receives a stimulus depending on the previous outcome. If the previous sample was ignited, then the stimulus level moves down a step, and if no ignition was obtained, then the stimulus level moves up a step. In this way the testing should be on or about the 50% probability of initiation of the material. The Bureau of Explosives, Rotter and the modified type 12 impact test all use a Bruceton method. Using this method, dry RDX is deemed unfit for transport.

The Bruceton method is employed in the rotary friction test. Dry RDX is deemed fit for transport on the basis of this test.

3.3 Probit Analysis

Tests where there are two possible outcomes (e.g., an explosion or not) or in the case of a biological example, a fatality or not, the response to a stimulus generally follows a sigmoid curve when the probability of the response is plotted against the level of stimulus. Probit analysis[24] transforms this response curve into a straight line allowing assessment over the whole probability range from a limited set of stimulus levels. Such an approach is commonly

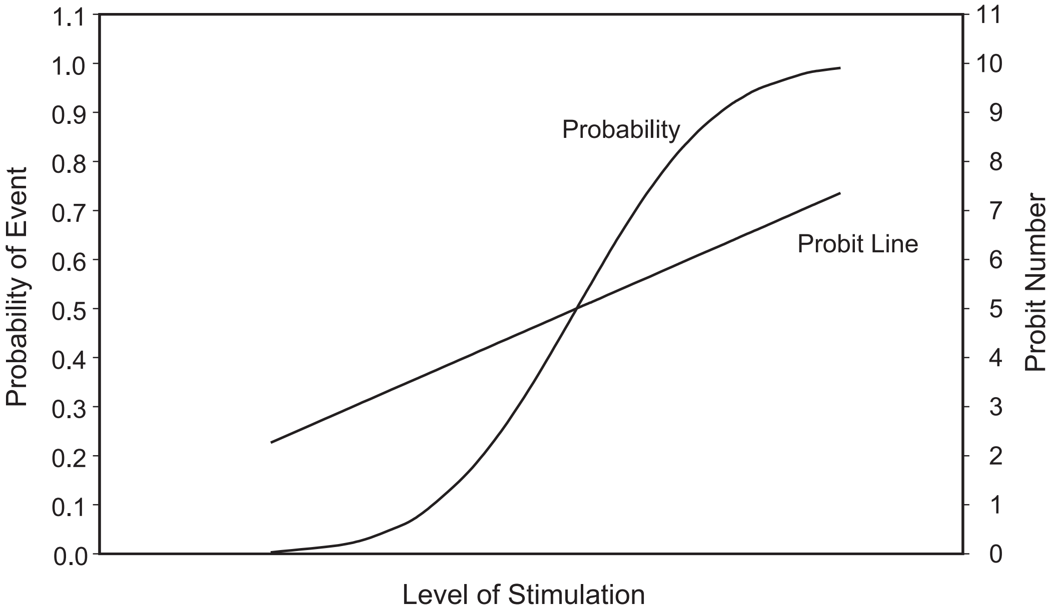

Figure 4. General response curve for probability of an event against stimulation level.

used in estimating the LD_{50} levels for insecticides and "safe" levels for therapeutic drugs. Figure 4 illustrates the general shape of a sigmoid response curve and the transformed data that have been converted to a straight probit line.

When applied to an explosive property, the data collected allows the probability of explosion at any level of stimulation to be calculated. Other methods tend to find the stimulation required for a single (fixed) probability (e.g., the 50% level by the Bruceton method). Probably more importantly, the use of a Probit analysis allows estimation of the stimulation level required for low (accident type) probability, which none of the other methods provide. For example, two compositions may have the same stimulation level for a 50% probability of initiation. But, one may have a greater probability of initiation with a low stimulation level. This is found from the gradient of the Probit line.

4 Comparison of Test Methods

There are a few sources of comparative data for different test methods. The UN "Orange Book" gives a limited number of test results for each of the described tests. Finding a sample that is common to all tests is not easy, particularly if pyrotechnics are of interest; explosives are a little easier. This is probably due to the interest in sensitiveness of military compositions.

4.1 UN Orange Book Comparisons

Each of the tests described in the UN *Recommendations on the Transport of Dangerous Goods Manual of Tests and Criteria* (UN Orange Book)[7] has a set of specimen results. Unfortunately for those working with pyrotechnics there are very few results quoted for such materials. The bulk of the results are for explosives and energetic materials (i.e. materials that have marginal explosive properties but are not intended as explosives). The only material common to all impact tests is RDX, which interestingly is very close to the borderline on all tests and is reported as acceptable for transport in 2 of the tests but not in the other 3. Table 2 summarises the results for RDX.

A similar problem is encountered with the friction tests in the UN Manual, in that the materials for which sensitiveness values are quoted are explosives. However, a larger number of materials appear in the three lists. TNT (a fairly insensitive explosive) RDX, and lead azide (a primary explosive) are all found. Table 3 summarises the data from the UN Orange book.

Table 2. Comparative Results, UN Impact Testing of RDX.

UN Test for Impact	Test Result	UN test designation
BAM Fallhammer	5 J (limiting impact energy)	–
Rotter	80 (figure of insensitiveness)	+
30 kg Fallhammer	1.0–2.0 m (limiting height)	–
Modified No. 12 Impact Tool	38 cm (median height)	+
Impact Sensitivity Test	70 mm (lower limit in assembly 2)	+
+ indicates that a material is too dangerous for transport in the form in which it was tested.		

Under all three tests lead azide is deemed to be too sensitive for transport in the form in which it was tested while the other two explosives are not.

4.2 *Encyclopedia of Explosives* Comparisons

The *Encyclopedia of Explosives* gives comparative data for a series of explosives using the Type 12 Impact Tool, the Bureau of Mines Impact Apparatus and the Picattiny Arsenal apparatus. No pyrotechnic is reported. Interestingly, the study shows that the same equipment used in different laboratories produces different results. There are results from three apparatus measuring H_{50} for RDX. The Type 12 Impact Tool produced H_{50} of 22 and 24 cm at different centres, 79 cm was reported using the Bureau of Mines Impact Apparatus. Similar data for the Rotter Impact test indicated H_{50} to be 98 cm for military grade RDX and 104 cm for “Standard RDX”. Using the Picatinny Arsenal Impact Test Apparatus, drop heights of 32 cm and 8 inches (approximately 20 cm) were reported for 10% initiations (more correctly at least one in ten initiations with no initiation at 2.5 cm lower drop height). This clearly indicates that the different test apparatus apply a different proportion of the impact energy to the sample but also that different apparatus of the same type may well also perform differently.

4.3 Comparative Studies

Bowes[25] has reported comparative testing for both impact and friction sensitiveness of pyrotechnic compositions using a series of the test methods. Unfortunately no composition details are presented. Impact comparison is made between the Bureau of Explosives Apparatus (number of ignitions in ten from 102 mm) and the Modified Type 12 Impact tool (H_{50}) and BAM impact (limiting impact energy) showed that there was a general agreement in ranking of the explosives between the different tests. A composition found to be sensitive in one test was, generally, sensitive in the others. Comparison of the Torpedo Friction Test (H_{50}) and the BAM Friction Apparatus (limiting load) also showed similar general agreement between the

Table 3. Comparative Results, UN Friction Testing.

Material	UN Test for Friction	Test Result	UN Test Designation
Lead azide	BAM	10 N (limiting load)	+
	Rotary Friction	20 (figure of friction)	+
	Impact Friction Test	30 MPa (lower limit)	+
RDX	BAM	120 N (limiting load)	–
	Rotary Friction	3.4 (figure of friction)	–
	Impact Friction Test	200 MPa (lower limit)	–
TNT	BAM	360 N (limiting load)	–
	Rotary Friction	5.8 (figure of friction)	–
	Impact Friction Test	600 MPa (lower limit)	–
+ indicates that a material is too dangerous for transport in the form in which it was tested.			

Table 4. Comparison Results for BAM and Rotter Tests from Biers et al.

Composition	BAM consumable in		Rotter consumable in	
	BAM (LIE J)	Rotter (LIE J)	BAM (LIE J)	Rotter (MIE J)
Blackpowder (KNO_3 75%, Charcoal 15% Sulfur 10%)	20	20	>50	82.7
Mg-Al alloy, mixed nitrates, binder	25	20	40	34.4
Mg-Al alloy, oxidiser, binder	>50	>50	50	29.2

Table 5. Apparatus Comparison from Biers.

Composition	Fallhammer 1	Fallhammer 2	Fallhammer 3	Fallhammer 4
Waterfall	3.0	3.0	4.0	5.0
Air bomb	25.0	15.0	15.0	20.0
Whistle	7.5	7.5	7.5	10
Flash	>50.0	>50.0	4.0	10.0

tests. Individual compositions could, however, show an anomalous result on one method compared to the others.

Biers et al.[26] undertook a study to investigate the differences in the BAM and Rotter impact tests. Both apparatus were used with both sets of consumables to give a matrix of 4 possible test conditions, BAM consumables on the BAM and Rotter apparatus and Rotter consumables on both. Limiting impact energies (LIE) are reported in three cases, and the median impact energy (MIE) (derived from H_{50}) was reported for the Rotter consumables on the Rotter apparatus. Three pyrotechnic compositions were included in the study and the results are reproduced in Table 4.

Further work[27] comparing the impact sensitiveness values obtained by different operators using BAM Impact apparatus at different centres included four fireworks compositions. No formulations were given. Table 5 lists the results.

In all the tests, except those with flash composition, the results obtained are within 2 “BAM steps”. Taking the air bomb composition as an example, the consecutive impact energies tested are 15, 20 and 25 J. Operating at one ignition in six, it would be expected that there would be some statistical variation in the result obtained due to the limited number of samples tested. The results with flash composition may well reflect some other extraneous influence such as moisture content, which could be dependent on the ambient conditions such as relative humidity.

Table 6. Test Comparison from Mullenger.

Composition	Figure of Insensitiveness (FoI)	Rotter Median Impact Energy (MIE) (E_{50}, J)	BAM Limiting Impact Energy (LIE) (J)
Blackpowder (KNO_3 75%, C 15%, S 10%)	122	82.7	25
Bi_2O_3 / B / viton	27	18.5	>50
Mg-Al alloy / oxidiser / binder	43	29.2	>50
Mg-Al alloy / mixed nitrates / binder	51	34.4	5
Mg / $MgCO_3$ / PTFE	177	88.6	>50

Table 7. Test Comparison from Wharton and Harding.

Material	Figure of Friction (FoF)	BAM Limiting Load (N)	Mallet Friction Test				
			Steel on Steel	Nylon on Steel	Wood on Softwood	Wood on Hardwood	Wood on Yorkstone
LDNR	<0.7	<5	100%	50%	100%	100%	100%
PETN	2.4	73	50%	0%	0%	0%	0%
HMX	2.5	147	50%	0%	0%	0%	0%
RDX	3	173	50%	0%	0%	0%	0%
Tetryl	6.3	>360	0%	0%	0%	0%	0%
RDX / TNT	>8.2	>360	0%	0%	0%	0%	0%
TNT	>8.2	>360	0%	0%	0%	0%	0%

Mullenger[28] reported a comparative study of impact sensitiveness performed on the Rotter and BAM apparatus. Of the thirteen materials examined five were pyrotechnic compositions. Mullenger's results are given in Table 6.

The impact results offer an insight into the differences between the two impact apparatus. Three pyrotechnic material's display little or no sensitivity to impact in the BAM test. Of these only the Mg/$MgCO_3$/PTFE is also insensitive in the Rotter apparatus. The Rotter apparatus allows material flow within the sample consumables while the BAM does not. Hence, the BAM results will be little influenced by friction sensitiveness while the Rotter results may well reflect the materials friction sensitiveness due to the plastic deformation and flow of the sample under impact. The BAM results are often regarded as "pure impact", while those from the Rotter apparatus are regarded as having an additional contribution from friction.

Wharton and Harding[29] reported a comparison of three friction sensitiveness test methods; BAM friction apparatus, Rotary friction apparatus and the mallet friction test. All the materials compared were explosives, and no pyrotechnic materials were included in the work. However, the work does provide some useful information on the different ways the three test methods rank explosives. The results are summarized in Table 7.

Clearly the three tests have differing abilities to discriminate between explosives. The Mallet friction test appears to have the least discrimination, but does have the advantage of a simple test apparatus and the ability to investigate differing friction surfaces in the standard test configuration. The BAM and Rotary Friction apparatus generate a similar ranking for explosives that are "on scale". The Rotary Friction apparatus can assess less sensitive explosives.

A relationship between Rotary Friction FoF and BAM limiting load for high explosives was reported by Wharton and Chapman.[30] In this work, the relationship derived was

$$\text{Limiting load} = 55 \times \text{Figure of Friction}$$

Unfortunately, no pyrotechnic materials were included in the study. It is possible that they will respond differently, hence the relationship may not hold.

5 Use of Sensitiveness Methods

There are many "official" (national or international) uses for sensitiveness data. All have impact on the commercial use of sensitive materials. This can range from requirements on packaging for storage and/or transport, restrictions on movement, to a total ban on use in some areas.

5.1 Transport (UN Orange Book)

The United Nations scheme for transport is far reaching in its investigation of hazardous properties; sensitiveness is a small part of this scheme. Series 3 tests (including the sensitiveness tests) are used to assess if intentional explosives (materials made for their explosive properties as opposed to unintentional explosives, which were made for some other purpose but are found to have explosive properties) or materials that have undergone UN Series 1 and

UN Series 2 tests and been found to have explosive properties are suitable for transport in the form tested. Most pyrotechnic materials would, by definition, be explosive and start their testing at Series 3.

Materials "failing" the sensitiveness test (i.e., are more sensitive than the limit set in the test employed) would not necessarily be barred from international transport but would require further testing when packaged to ascertain the hazard posed. After a suitable hazard division has been allocated, the materials can be transported. Most fireworks are currently transported with a 1.4G hazard classification. However, fireworks may fall into 1.1G, 1.2G, 1.3G 1.4G 1.4S and possibly 1.5G. As the number increases, the perceived hazard diminishes. A 1.1G firework would mass detonate while the effects of 1.4S fireworks would be expected to be contained within the packaging. Fireworks such as party poppers could well meet the requirements of 1.4S. The full classification is determined by response in the Series 6 tests [6(a) single package test, 6(b) stack test and 6(c) external fire (bonfire) test] not the response in the Series 3 sensitiveness tests.

5.2 Notification of New Substances

In the European Union (EU) there is a requirement[31] for materials to have hazard testing prior to large-scale supply into the market. This includes sensitiveness measurement for materials with explosive properties.

5.3 Placing Explosives on the European Market[32] (CE Marking)

Sensitiveness requirements are set for explosives that are placed on the market in the European Union. Pyrotechnic articles (fireworks) are outside of the scope of this provision. Current sensitiveness requirements for explosive are similar (but not identical for all classes of explosive) to those for transport under the UN scheme.

5.4 Major Hazard Safety Control Systems (COMAH)

The Control of Major Accident Hazards Regulations 1999 (COMAH) requires sites manufacturing and storing hazardous materials (explosives, toxics, oxidisers, etc.) to provide the authorities with a COMAH safety case. The level of detail depends on the quantities and level of risk. Highly sensitive explosives, for example, would trigger the requirement for the safety case at a lower inventory level than for low sensitive materials.

6.0 Sensitiveness Results for Pyrotechnic Compositions

6.1 Impact Sensitiveness Results

Probably the widest range of fireworks compositions investigated were those reported by Shimizu[33] where he used a "Sakashita drop hammer" with either a 2 or 5 kg hammer to rank the sensitiveness of fireworks compositions. The hammer was dropped onto a pellet of

Table 8. Impact Sensitiveness of Pyrotechnic Compositions from Shimizu.

Composition	Height for 10 No Explosions (cm)
Safety match	5
$KClO_3$(62.5) / As_2S_2(37.5)	6–13
$KClO_3$ / S various mixes	15
Red star	25
Green star	25
Whistle composition, $KClO_3$(75) / gallic acid (25)	37
Flash and thunder, $KClO_4$ (51.3) / Al (23) / S(15.4) / Sb_2S_3(10.3)	37
Blue star	37
Blackpowder	50

Table 9. Sensitiveness of Sulfur-Containing Fireworks Compositions from Chapman et al.

Component	Composition (% by mass)					
	Rocket	Gerb	Golden Streamers	Tourbillion	Flash-cracker	Pin-wheel
Potassium nitrate	68	57	53	36	—	60
Potassium perchlorate	—	—	—	—	50	—
Charcoal (30–100 mesh)	21	10	3	9	—	20
Sulfur	11	10	14	9	25	10
Aluminium (200 mesh)	—	—	—	—	25	—
Meal powder	—	—	—	32	—	10
Iron filings (fine, untreated)	—	23	—	14	—	—
Dextrin	—	—	3	—	—	—
Sodium oxalate	—	—	27	—	—	—
Sensitiveness (Limiting Impact Energy J)	20	20	40	25	7.5	30

pyrotechnic composition held between thin tin foil plates. Heights that produced no explosions in 10 and 50 drops (another method of quantifying the sensitiveness) were found. In his table of impact sensitiveness in the drop hammer test, compositions are ranked from most sensitive to least. The most sensitive compositions are those containing potassium chlorate as oxidiser. Of the potassium chlorate compositions those with arsenic sulphide and sulfur proved to be the most sensitive materials tested. These results are listed in Table 8.

Chapman et al.[34] have reported sensitiveness data for fireworks compositions containing sulfur, prepared from compositions taken from Weingart's book.[35] Table 9 lists the compositions and their respective impact sensitiveness measured using the BAM impact machine. These compositions were also modified by the addition of potassium chlorate and sensitiveness remeasured. In most cases the sensitiveness was increased, this was particularly marked with the compositions containing iron.

A similar investigation was undertaken on chlorate star compositions. Table 10 lists the compositions and sensitiveness data. Again modifying the material to form sulfur/chlorate-containing mixes resulted in increased sensitiveness (lower limiting load).

Table 10. Sensitiveness of Chlorate-Containing Fireworks Star Compositions from Chapman et al.

Component	Composition (% by Mass)	
	Red Star	Green Star
Strontium nitrate	38.7	—
Barium nitrate	—	38.7
Potassium chlorate	38.7	38.7
Charcoal	12.9	12.9
Dextrin	3.2	3.2
Shellac	6.5	6.5
Sensitiveness (Limiting Impact Energy J)	30	50

Impact sensitiveness of some potassium nitrate-containing whistle compositions were studied by Li et al.[36] using the Kast impact apparatus. A 5 kg hammer and 25-trial Bruceton determination was used in each case to measure the height required for a 50% probability of initiation of the mixtures. Table 11 lists the results.

Table 11. Impact Sensitiveness of Whistle Mixtures from Li et al.

Fuel	H_{50} (cm)
Potassium hydrogen phthalate	74.3
Sodium benzoate	69.5
Sodium salicylate	69.8

Table 12. Impact Sensitiveness of Chinese Fireworks Composition from Qin Daochao.

Sample	Number of samples having Probability				
	0%	100%	0–50 %	50–80%	80–100%
Red star	4	0	7	1	1
Green star	50	0	2	1	0
Yellow star	2	0	5	1	0
Purple star	0	0	2	0	0
Whistle star	2	0	4	0	0
Other star	7	0	4	1	2
Gunpowder	13	0	40	10	3

One of the problems encountered in assessing the results obtained by the various workers is that of treatment of the results. Some use a limiting value, one in six or one in ten while others adopt the military specification of the 50% probability. Any set of results by a given method may not necessarily correspond to a set using a different method of handling the data, even if the same apparatus is used.

Testing of Chinese fireworks compositions has been reported by Qin Daochao.[37] The method adopted appears to be that of dropping a fixed mass from a fixed height and assessing the proportion of positive results from a set (unspecified size) of test samples. Star compositions (unspecified) are reported with gunpowder (Blackpowder) as a comparison.

While full experimental details are not provided in the paper, it appears that a drop energy of approximately 25 J was used in testing. All the stars tested appear to be less sensitive to impact than Blackpowder. A summary of the results appears in Table 12.

6.2 Friction Sensitiveness Results

As with the impact testing, Shimizu[32] has reported friction sensitiveness results for a wide range of pyrotechnic compositions. This work used the "Yamada friction instrument". This apparatus uses carborundum (corundum) surfaces to provide the friction, a spring to apply the force between the plates and a pendulum to provide the motion. The pressure applied by the spring is varied and this provides a method of determining the values that result in no fires in either 10 or 50 trials, each with fresh sample. A selection of Shimizu's results is tabulated in Table 13.

Table 13. Friction Sensitiveness of Pyrotechnic Compositions from Shimizu.

Composition	Pressure for 10 No Explosions (kg)
Safety match	10
$KClO_3$ (62.5) / As_2S_2 (37.5)	1.88
$KClO_3$ / S various mixes	7.5
Red star	50
Green star	50
Whistle composition, $KClO_3$ (75) / Gallic acid (25)	25
Flash and thunder, $KClO_4$ (51.3) / Al (23) / S (15.4) / Sb_2S_3 (10.3)	62.5
Blue star	75

The compositions containing potassium chlorate were again found to be the more sensitive. There is not necessarily a correlation between impact and friction sensitiveness and there are

Table 14. Friction Sensitiveness of Some Fireworks Compositions from Chapman et al.

Composition	Limiting Load (N)
Rocket	>360
Gerb	>360
Golden Streamers	>360
Tourbillion	>360
Flash-cracker	40
Pinwheel	>360
Red star	360
Green star	240

Table 15. Electrostatic Sensitiveness from Matasuzwa.

Composition Name	Formulation		MIE on 1	MIE on 2
Cascade 1	$KClO_3$ Al (coarse flake) Al (fine flake)	55.0 6.0 9.0	20.7	—
Cascade 2	As above + Sulfur	+ 7.0	4.5	—
Cascade 3	$KClO_3$ $Ba(NO_3)_2$ Al (coarse flake) Al (coarse) Al (fine flake) S	37.0 7.0 12.0 27.0 10.0 7.0	15.2	—
Blackpowder (mealed)	KNO_3 Charcoal S	74.0 16.0 10.0	2.0	1.03
Blackpowder (fine grain)	KNO_3 Charcoal S	74.0 16.0 10.0	2.0	—
Burst charge 1	$KClO_4$ KNO_3 Hemp coal Rice starch	56.2 18.8 22.5 2.5	2.0	—
Burst charge 2	$KClO_4$ KNO_3 $Ba(NO_3)_2$ Hemp coal Rice starch	54.9 16.5 2.7 22.0 3.9	2.0	—
Burst charge 3	KNO_3 Hemp coal S Rice starch	73.5 14.7 7.4 4.4	1.1	1.03
Thunder 1	$KClO_3$ Al (fine flake) S	71.4 21.4 7.2	0.21	0.21
Thunder 2	$KClO_4$ Al (fine flake) S	71.4 21.4 7.2	0.46	0.21
Yellow star		—	2.0	—
Violet star		—	2.0	1.03
Silver star		—	1.1	0.52

compositions that were relatively highly sensitive to impact that are much less sensitive to friction and *vice versa*.

In work by Chapman et al.[33] the series of compositions that were investigated for impact sensitiveness were also tested for friction sensitiveness. Table 14 gives the values obtained, the compositions are fully described in Tables 9 and 10. As with the impact study, the formation of sulfur/chlorate mixtures reduced the limiting loads, sometimes considerably.

6.3 Electrostatic Sensitiveness Results

Matasuzawa et al.[16] used two test apparatuses in investigating fireworks compositions. The materials tested are listed with their compositions in Table 15. The two electrostatic test devices were, 1, the Hosoyo apparatus and,

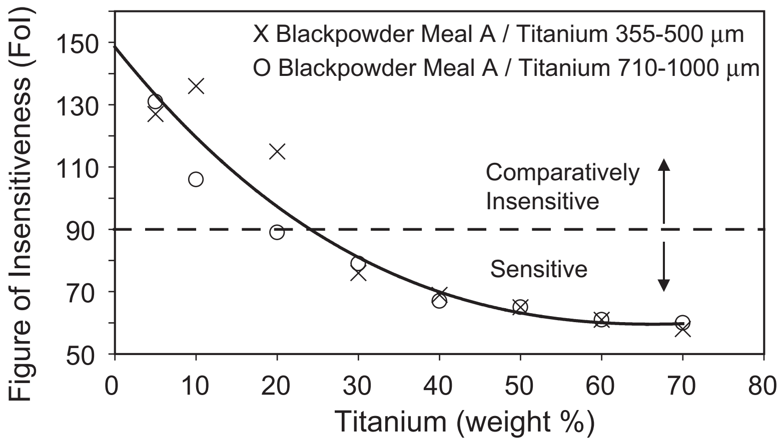

Figure 5. Impact sensitiveness of titanium-Blackpowder mixtures from Wharton et al.

2, the Chegoku Kayaku apparatus. Both were used to measure a minimum ignition energy (MIE). Results are given in Table 15. The most sensitive samples contained sulfur with potassium chlorate or perchlorate. However, with a large proportion of aluminium providing a conducting path (cascade 3) the composition was the least sensitive.

7 Sensitiveness Case Studies

7.1 Titanium-Blackpowder Gerbs

Titanium-Blackpowder gerbs are often used as theatrical pyrotechnics for shows and commonly contain 20–30% titanium in the mixture. They are usually made by pressing the composition into tubes. Ignitions have been reported during the pressing, some have lead to serious injury. Following one such incident the mechanical sensitiveness of the mixtures was investigated.[38]

Titanium flake used in the manufacture of the display gerbs was sieved to find the particle size distribution. The sieve fractions at the two extremes were used in the investigation. Hence, the effect on friction and impact sensitiveness of 355–500 and 710–1000 µm titanium mixtures with Blackpowder was examined using Rotary Friction and Rotter Impact apparatus. Figure 5 illustrates the change of impact sensitiveness, measured as FoI, for titanium-Blackpowder mixtures. Impact sensitiveness was found to increase throughout the range investigated with compositions containing greater than 25% titanium found to be in the sensitive category as defined by the SCC.[2] The increase in the amount of titanium is likely to have two effects:

1) to increase the number of "hot-spots" generated, and
2) to provide a greater heat sink to adsorb the heat generated.

It is likely that hot-spot generation increase makes the composition more sensitive to impact.

With the friction results, shown in Figure 6, it appears that the two effects (generation of hot spots and the heat sink effect) are both affecting the outcome. Initially, the presence of the hard titanium particles is increasing sensitiveness, up to about 30% titanium in the mixture. Beyond that the heat sink effect is removing heat and making the material less sensitive. The overall effect being that a mixture between 20 and 30% titanium is particularly sensitive to friction and is approaching the levels of sensitiveness regarded as very sensitive by the SCC.[2] Thus the mixture that ignited when being pressed had an optimal sensitiveness to accidental ignition.

Similar findings were reported by Bazaki and Kubota[39] when investigating the effect of metal-containing catalysts in ammonium perchlorate propellants and by Wharton and Royle[40] in work on aluminised ammonium nitrate/fuel oil explosives.

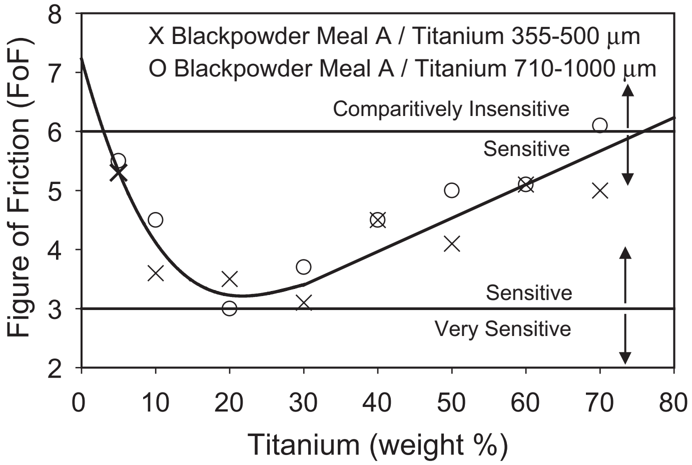

Figure 6. Friction sensitiveness of titanium-Blackpowder mixtures from Wharton et al.

7.2 Peterborough Explosion

An explosion occurred at Peterborough UK in March 1989 when a mixed load of 800 kg of explosives was being transported. The resulting explosion caused one fatality, over one hundred serious injuries and extensive damage to surrounding buildings. The official investigation[41] revealed that the primary cause of the explosion was initiation of the explosives following the frictional ignition of pyrotechnic composition.

The load consisted of 725 kg cartridged explosives, 62.5 kg cast primers, 15 kg of detonators and 12400 electric fuse heads (electric matches), 2400 of which were cerium fuseheads in the form of "combs". The remainder were Vulcan fuseheads. Revised transport regulations after the incident prevent such loads being carried without proper separation of the materials.

Examination of packages used to carry the cerium fuseheads indicated that the tinned steel boxes contained brown deposits. Additionally, the boxes were poorly constructed with flux and solder protruding from the inner surface. Small gaps were also found where the folded metal had not been joined correctly. Loose cerium fusehead composition that had become detached during transport was found in boxes that had previously been used for the carriage of these items.

A series of tests were carried out on the materials involved in the incident. BAM impact and Rotary Friction tests were used to measure the mechanical sensitiveness. Both fusehead compositions were found to be extremely sensitive to friction but only moderately sensitive to impact. The materials were of such sensitiveness to friction that V_{50} could not be measured using the normally applied pressure between the friction surfaces. The applied pressure was reduced in the Rotary friction apparatus to ascertain V_{50} values and hence a Figure of Friction for the materials. Table 16 lists the mechanical sensitiveness results, RDX values are provided for comparison.

Table 16. Mechanical Sensitiveness of Fusehead Materials.

Material	Limiting Impact Energy (J)	Figure of Friction	
		UN 3(b)(ii)	Reduced Pressure Test
Cerium fusehead composition	4.0	<0.7	0.3
Vulcan fusehead composition	3.0	<0.7	0.4
RDX	7.5	3.0	—

Table 17. Sensitiveness of Potassium Chlorate/Thiourea Mixtures from Wharton and Barratt.

Mixture			
Thiourea (%)	Potassium chlorate (%)	Impact (FoI)	Friction (FoF)
15	85	23	0.3
20	80	Too sensitive	0.4
25	75	Too sensitive	0.4

Further work on impact sensitiveness indicated that the presence of rust with the fusehead composition reduced the limiting impact energy to <0.1 J rendering it extremely sensitive to impact in the rusty metal boxes.

A series of drop tests were performed on boxed fuseheads and some ignitions were obtained at 1.2 and 3 m. Samples taken from boxes where ignition had not occurred indicated that loose composition was generated. This also occurred in vibration tests on the packaged fuseheads in transport simulations. Additionally, damage to the fuseheads, which detached part of the protective coating, was observed.

Tests in an explosives transport vehicle identical to that involved in the incident indicated that an ignition of the fuseheads was sufficient to detach the locked roller shutter door and produce a tongue of flame similar to that reported by the driver of the vehicle involved in the incident.

The findings of the technical investigation concluded that the initial cause of the explosion was either a friction or impact event. The materials in the metal boxes were extremely sensitive to both. On balance, it was thought that friction was the more likely stimulus. This initial local fire caused by the fuseheads then propagated to combustible packaging and finally to the detonators, primers and explosives, which in turn detonated after some 12 minutes.

7.3 Potassium Chlorate-Thiourea Mixtures

Potassium chlorate-thiourea mixtures have been used in the production of pyrotechnic smokes. The mixture alone produces white smoke, while coloured smokes are produced by the addition of dye. After an explosion in a grinder that had been used to grind potassium chlorate followed by urea, Wharton and Barratt[42] investigated the sensitiveness and thermal properties of such mixtures.

Mixtures containing 15, 20 and 25% thiourea in potassium chlorate were subjected to mechanical sensitiveness testing using the Rotter impact and Rotary friction tests. The mixtures proved to be too sensitive for the Rotary friction to be operated using normal applied pressure of 40 psi (276 kPa) and a reduced loading pressure of 5 psi (34 kPa) was used to ascertain the Figure of Friction. Mixtures with 20 and 25% thiourea were too sensitive for their Figure of Insensitiveness to be measured. Table 17 reports Wharton and Barratt's measurements.

The individual materials were found to be insensitive or comparatively insensitive to both impact and friction, potassium chlorate having a measurable Figure of Friction of 4.1, all other measurements being "off-scale". Once initiated, the mixtures were found to be highly exothermic leading to rapid decomposition of the mixture.

Wharton and Barratt concluded that the mixtures were very sensitive and that minimal mechanical stimulation would be required to accidentally initiate the mixture. This was attributed to the low Tammann temperature[43] of the potassium chlorate, which allows considerable diffusion of fuel materials into the crystal lattice. Similar findings are cited as being the main cause of sulfur-potassium chlorate sensitiveness.[44]

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Hazardous Chemical Combinations: A Discussion

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ABSTRACT

All pyrotechnic compositions present some hazard due to their ability to produce energy. However, some compositions pose an added hazard because of the combination of incompatible materials. The use of such compositions may result in more frequent accidental ignitions during processing or spontaneous ignitions during storage. Other compositions pose an added hazard because of their ability to produce especially large amounts of energy with rapid reaction rates. The use of such compositions is likely to result in especially powerful explosions in the event of an accidental ignition.

This article attempts an organized examination of some combinations of commonly used pyrotechnic chemicals that are believed to have significantly increased hazard potentials.

Keywords: accidental ignition, spontaneous ignition, hazardous combinations, chemicals, compatibility, incompatibility

Introduction

By their very nature, all pyrotechnic compositions could be considered hazardous because of their potential for producing energy (occasionally at inopportune times). However, some combinations of materials present a special hazard, either because of an added potential for unintentional ignition or because of the potential for producing a powerful explosion upon ignition. Note that there are other hazards, such as health hazards, which may be associated with certain chemical combinations; however, that is beyond the scope of the present article.

A pyrotechnic chemical reaction characteristically produces heat energy. This so called "Heat of Reaction" may be useful directly as thermal energy, or more usually as light, sound, or kinetic energy to achieve a desired effect. However, a pyrochemical reaction must not begin to proceed as soon as the pyrotechnic composition is mixed, for then the composition could not be safely prepared. Such spontaneity is prevented by another characteristic of pyrotechnic compositions, a so-called "Activation Energy" barrier.

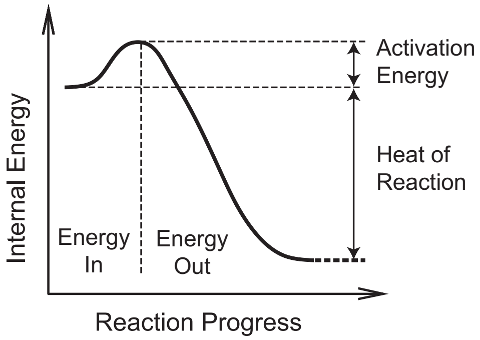

Figure 1. An illustration of the internal energy relationships in a pyrochemical reaction.

The internal energy associated with a pyrochemical reaction is depicted in Figure 1. Note that initially as the reaction begins, the internal energy of the system increases. This corresponds to the ignition process, when the composition is being supplied energy, such as by an externally applied flame. This requirement, to first input activation energy to the composition, is what prevents its spontaneous ignition. If the activa-

Table 1. Some Hazardous Chemical Combinations Encountered in Pyrotechnics.

Species		Chlorates	Perchlorates	Aluminum	Magnesium	Zinc
Chlorate	ClO_3^-	0	—	X	X	X
Perchlorate	ClO_4^-	—	0	?	?	—
Aluminum	Al	X	?	0	—	—
Magnesium	Mg	X	?	—	0	—
Zinc	Zn	X	—	—	—	0
Acids	H^+	X	—	—	X	X
Ammonium	NH_4^+	X	—	—	X	X
Water	H_2O	—	—	?	X	?
Copper(II)	Cu^{2+}	?	—	?	X	X
Sulfur	S	X	X	—	X	X
Sulfide	S^{2-}	X	X	—	—	—

X = Generally a significantly hazardous combination.
? = Can be significantly hazardous depending on circumstances.
— = Ordinarily, little if any added hazard.
0 = Place filler.

tion energy barrier is high, much energy is required for ignition and accidental ignitions will be unlikely. If the activation energy barrier is low, less energy is required for ignition. When this is the case, accidental ignition will be more likely because a relatively small amount of mechanical, thermal or electrostatic energy can cause ignition of the composition. After ignition has been accomplished, internal energy falls as energy is released from the composition. (See reference 1 for more complete discussions of activation energy and heat of reaction.)

Over the years, pyrotechnists have tested many substances that seemed promising for use in fireworks. It turned out that some of these, such as potassium permanganate and phosphorus, have such low activation energies in pyrotechnic compositions that they invariably create a significant hazard. Because their unsafe nature in compositions is ubiquitous, it is easy to eliminate such substances from use. A much more difficult problem is the particular combinations of materials that lead to a low activation energy, even though the same materials in other combinations do not pose that hazard. Many of these hazardous chemical combinations are mentioned in the pyrotechnic literature (e.g., reference 2) but usually without complete explanatory comments. This paper attempts to present somewhat more complete information and explanations. However, this task is often complicated by the lack of solid experimental data reported in the literature. As a result, in some cases the authors will only be able to offer conjecture and anecdotal evidence. While this is not ideal, until more studies are conducted and reported, it is the best that can be done, and it is preferable to not providing any information for these combinations.

Some chemical combinations in pyrotechnic mixtures that can be particularly hazardous are listed in Table 1. However, it is important to note that the list is not all-inclusive. Further, on occasion, because of mitigating factors, some listed combinations may not present a high degree of hazard. To better understand why particular combinations of materials can present an increased hazard, each column in Table 1 will be discussed in turn.

Chlorates

Chlorates have the lowest activation energy towards decomposition of any class of oxidizers commonly used in fireworks. Consequently, mixtures containing chlorates tend to be sensitive to all types of accidental ignition. This is

Table 2. A Comparison of Ignition Temperatures for Some Common Oxidizers in Stoichiometric Combination with Various Fuels.[3a]

Oxidizer	Ignition Temperature (°C)				
	Sulfur	Lactose	Charcoal	Magnesium	Aluminum
Potassium chlorate	220	195	335	540	785
Potassium perchlorate	560	315	460	460	765
Potassium nitrate	440	390	415	565	890

[Note that °F = 32 + (9/5) °C.]

evidenced by the especially low ignition temperatures of binary mixtures of potassium chlorate and fuels with low melting point or low decomposition temperature (e.g., see sulfur and lactose in Table 2). One should pay close attention to the materials a chlorate is being mixed with, to be sure that the hazard is not thereby exacerbated. However, by no means is it intended to imply that all chlorate compositions are dangerously unsafe.

With Aluminum:

Aluminum has a highly cohesive and nonporous oxide coating that must be disrupted in order for a reaction with oxidizers to take place. This feature tends to raise the activation energy for ignition, compared with many other pyrotechnic fuels, see again Table 2. However, when assessing degree of hazard, it is necessary to consider both the probability and the consequence of a potential accident.[4] In this case, the binary mixture of potassium chlorate with a fine particle size aluminum is a classic flash powder, and it has a relatively small critical mass for an unconfined explosion. Therefore, the consequences of such a mixture undergoing accidental ignition are likely to be significantly more severe than for an equivalently small amount of a standard chlorate colored star composition. The mixture is more dangerous because of the consequence, rather than a greater probability of an accident. Indeed, the probability of accidental ignition is probably less for aluminum than with common chlorate star compositions (except perhaps when the metal powder is so fine that the mixture becomes especially electrostatically sensitive).

The common solution to a hazard of this type, where the consequence is particularly severe, is to attempt to reduce the probability of an accidental ignition by raising the activation energy barrier. Usually this is accomplished by using potassium perchlorate in place of potassium chlorate. One can go further in this direction and raise the activation energy more by using barium nitrate as the oxidizer. However, one should beware of thinking that higher activation energy automatically means “safer”. It also means more difficult ignition and a greater potential for ignition failure (i.e., duds are more likely). Obviously, duds are a safety hazard just as is accidental ignition. In addition, the use of nitrate with aluminum can lead to other problems in the presence of water, as discussed below.

Conventional wisdom for flash powders would suggest using the above approach (i.e., substituting potassium perchlorate or barium nitrate for potassium chlorate). It is certainly possible that such a substitution will indeed make the resulting flash powder more resistant to accidental ignition. Unfortunately, published sensitiveness data does not fully support that. Look again at Table 2; the ignition temperature for potassium nitrate (presumably similar for barium nitrate) and aluminum is the highest of the three oxidizers. However, it is the mixture with potassium perchlorate, and not that with potassium chlorate, that has the lowest ignition temperature.

Since these ignition temperature data are inconsistent with conventional wisdom, it is worth considering whether ignition temperature is the best indicator of the sensitiveness of mixtures, or even that the published data may be in error. Table 3 presents impact sensitiveness data for the same three oxidizers. Of the mix-

Table 3. A Comparison of Impact Sensitiveness for Some Common Oxidizers in Stoichiometric Combination with Various Fuels.[3b]

Oxidizer	Impact Sensitiveness (kg·m/cm^2)				
	Sulfur	Lactose	Charcoal	Magnesium	Aluminum
Potassium chlorate	1.1	1.8	3.2	4.5	4.5
Potassium perchlorate	1.2	2.9	4.2	4.4	5.0
Potassium nitrate	3.6	5.0	5.0	4.6	5.0

tures with aluminum, potassium chlorate is most sensitive; however, it is roughly equivalent to that for mixtures with either potassium perchlorate or potassium nitrate. Based on the data in Tables 2 and 3, it is not clear that improved safety results from substituting potassium perchlorate for potassium chlorate in two-component mixes with aluminum.

If it is true, that substituting potassium perchlorate for potassium chlorate does not significantly decrease the sensitiveness of binary mixes with aluminum, then one is left to ponder why conventional wisdom suggests that it does. Could it be a result of experience with flash powders that are not simple binary mixtures, but rather with mixtures including sulfur or antimony sulfide? Tables 2 and 3 do not include data for antimony sulfide but do have data for mixtures with sulfur. The impact sensitiveness data suggests that a sulfur-containing chlorate flash powder would be a little (but not much) more impact sensitive than that with potassium perchlorate. However, the ignition temperature data suggests that the chlorate flash powder would be considerably more sensitive.

The foregoing discussion is far from definitive in answering the question of relative flash powder sensitiveness. However, it is obvious, for safety, that sulfur (and almost certainly antimony sulfide) should not be present in flash powder using either potassium chlorate or perchlorate. In addition, in the absence of more data (e.g., friction and electrostatic sensitiveness), it would be prudent to abide with conventional wisdom regarding the preference for choosing potassium perchlorate or barium nitrate over potassium chlorate.

With Magnesium and Zinc:

Like aluminum, magnesium and zinc form energetic mixtures with chlorates, and similar considerations apply. However, because of the lack of a cohesive oxide coating on these metals, the activation energy for their ignition is significantly lower than it is for aluminum. The combination of both the fuel and oxidizer contributing to low activation energy provides these mixtures the potential to be particularly dangerous.

With Acids:

The predecessor of the modern match was a wooden splint tipped with a chlorate pyrotechnic composition. This was ignited by allowing the composition to come in contact with concentrated sulfuric acid[5] (which was sometimes absorbed on asbestos wool for relative safety). Use outside the home obliged one to carry a vial of sulfuric acid in one's pocket! Also, Alfred Nobel apparently invented a mine for use in naval warfare based on this principle. A ship hitting the mine would break a glass tube of sulfuric acid, which then triggered the potassium chlorate and sugar igniter.

The high ignition sensitiveness of chlorate compositions in the presence of acids is thought to involve the formation of chloric acid.[6,7]

$$KClO_3 + H^+ \rightarrow HClO_3 + K^+ \qquad (1)$$

Ignition may occur because chloric acid is capable of spontaneous ignition of organic fuels, or through its decomposition into highly reactive and unstable chlorine dioxide.[8–10]

One can therefore appreciate the necessity for keeping acidic materials away from chlorate compositions. However, if the acid is sufficiently weak, such as stearic acid, it is probably incapable of displacing sufficient chloric acid from the chlorate to induce spontaneous ignition. Moreover, the greasy nature of stearic acid helps lubricate the composition, thereby reducing its friction sensitiveness.

With Ammonium Salts:

Ammonium ions are capable of acting as an acid (proton donor).

$$NH_4^+ \rightarrow NH_3 + H^+ \qquad (2)$$

Accordingly, most ammonium salts, such as ammonium perchlorate, are acidic in aqueous solution and potentially lead to the problems discussed above.

In addition, a mixture of a chlorate oxidizer and an ammonium salt may form ammonium chlorate through a double decomposition reaction.[11]

$$NH_4^+ + ClO_3^- \rightarrow NH_4ClO_3 \qquad (3)$$

This is problematic because ammonium chlorate is a substance that explosively decomposes at 102 °C and is probably capable of undergoing a true detonation.[9,12a]

With Copper(II) [Cupric] Salts:

Like the ammonium ion, the cupric ion (Cu^{2+}) has an acidic reaction in aqueous solution. In addition, in common with other transition metals, copper ions catalyze the decomposition of some oxidizers by lowering their activation energy. For these reasons soluble copper(II) salts with an acidic reaction, such as the sulfate, should not be used with chlorates. In practice, experience has shown that such potential problems can be overcome by using a copper(II) compound that is insoluble and/or has a counter anion with a basic reaction (e.g., carbonate, oxide, etc.). Note also that copper(I) [cuprous] salts (Cu^+) do not have an acidic reaction and therefore engender a relatively minor increase in sensitiveness, unless they contain sulfur, such as copper(I) thiocyanate (CuCNS).

With Sulfur:

The combination of sulfur with chlorates is historically the most famous cause of accidental ignitions in pyrotechnics due to "incompatible" chemicals.[13,14] Such mixtures have long since been banned in some countries (e.g., England). One possible mechanism for the high sensitiveness of such mixtures may begin with the formation of polythionic acids on the surface of sulfur grains, and ultimately producing sulfuric acid[6,7] (see comments above about acids). To some extent, during mechanical action sulfur reacts with oxygen in the air to form sulfur dioxide.[13] It is thought that a chain reaction involving the gases sulfur dioxide and chlorine dioxide may be implicated in cases of spontaneous ignition of potassium chlorate and sulfur mixtures.[6,7]

$$2\,KClO_3 + SO_2 \rightarrow K_2SO_4 + 2\,ClO_2 \qquad (4)$$

$$4\,S + 2\,ClO_2 \rightarrow 2\,SO_2 + S_2Cl_2 \qquad (5)$$

It can be seen from the equations that one molecule of sulfur dioxide ends up generating two molecules of sulfur dioxide, and the cycle potentially repeats at twice the rate; and so forth until the ignition temperature may be reached. Further, sunlight is thought to exacerbate this problem as well as the use of sublimed sulfur (flowers of sulfur) rather than sulfur flour.[7,16]

It is probable that the bad reputation this mixture acquired in the past was due, in part, to impurities in the materials formerly available.[17] For example, the presence of chlorite in the chlorate, or various sulfur acids in the sulfur, could serve to initiate the chain reaction. Notwithstanding this proviso, it is clear that even with pure materials the sensitiveness of a chlorate and sulfur mixture to friction and impact is too high to justify its use.[18]

With Sulfides:

Similar considerations apply to mixtures of chlorates with sulfides as for mixtures with sulfur described above. For example, the mixture of arsenic sulfide with potassium chlorate is even more impact sensitive than the mixture of sulfur with potassium chlorate.[3c] However, different sulfides may vary in the degree and type of hazard involved. While the sulfides of antimony and copper were those most commonly used with chlorates in the past, it would be wise to assume that any sulfide so used represents a significant hazard.

Perchlorates

Perchlorates produce substantially less energy upon their decomposition than do chlorates, see Table 4. Therefore, it can be inferred that any given material is likely to form a "safer" mixture with a perchlorate than with a chlorate. (However, note that ammonium perchlorate is incompatible with many materials because of the ammonium ion.) Perhaps equally important is the observation that, in perchlorate compositions, additives are sometimes specifically used to restore the favorable burning properties present in the corresponding chlorate composition. While it has not been well researched, there is the potential for these additives to increase the hazard, possibly approaching that of the chlorate composition. Thus, one can by no means make a valid generalization, "perchlorate compositions are safer than chlorate compositions". Much of the advantage of perchlorates lies with less stringent compatibility considerations, rather than its inherent safety.

Table 4. Decomposition Energies for Some Common Oxidizers.[3d]

Oxidizer	Product	Decomposition Energy (kcal/mole)
Fe_3O_4	Fe	+266
KNO_3	K_2O	+151
$Ba(NO_3)_2$	BaO	+104
$Sr(NO_3)_2$	SrO	+89
$KClO_4$	KCl	−1.2
$KClO_3$	KCl	−10

Note that the sign convention is that negative values correspond to exothermic decompositions.

With Aluminum:

The combination of potassium perchlorate with aluminum has quite a large activation energy and generally causes no problem. However, when the aluminum is a very fine powder, such as in the context of a flash powder, the consequence of accidental ignition is so devastating that such mixtures should be handled with extreme caution and avoided when possible. Mixtures containing relatively small percentages of potassium perchlorate or fine aluminum tend not to be a problem.

With Magnesium:

As with aluminum, there is generally no direct problem with the combination of potassium perchlorate and magnesium. However, as will be discussed below, the presence of water with this mixture is problematic. Further, with fine magnesium powder, the combination of lower activation energy and high energy output do make for a substantial hazard. Small percentages of either potassium perchlorate or fine magnesium in these mixtures do not seem to pose a problem.

Substances Hazardous with Chlorates but not with Perchlorates:

Zinc is not a particular hazard with perchlorates because, despite zinc having a lower activation energy than aluminum, it is not a sufficiently high energy fuel to form a dangerous flash powder with these oxidizers (see Table 5). It is important to note, however, the combination of zinc with ammonium perchlorate is exceptionally hazardous because of its incompatibility with the ammonium ion (discussed below).

Acids (typically encountered in pyrotechnics), ammonium salts, or copper(II) salts present little or no problem with perchlorates for two reasons. First, perchloric acid is a significantly stronger acid than chloric acid and so is less susceptible to displacement from its salts. Second, perchloric acid is a stable acid, in marked contrast with chloric acid, which spontaneously decomposes at 40 °C (104 °F).[12b]

With Sulfur:

The combination of sulfur with a perchlorate is generally believed to be substantially less hazardous than the combination with a chlorate. However, with respect to impact sensitiveness (see Table 3), the difference is barely worth mentioning. It has been speculated that to some extent the bad reputation of sulfur and chlorate mixes came about because earlier supplies of materials were contaminated.[17] If this was the case, that might explain the wisdom about perchlorate and sulfur mixtures being substantially less hazardous. That may have been true at one time but not for high purity materials.

Nonetheless, potassium perchlorate and sulfur mixes do have a low activation energy barrier, are quite sensitive to accidental ignition, and must be avoided if possible.

With Sulfides:

Similar considerations apply to mixtures of perchlorates with sulfides as for mixtures with sulfur.

Aluminum

The burning of aluminum metal produces the greatest amount of energy of the fuels in common use in fireworks, see Table 5. Nonetheless, aluminum can be one of the safest high energy metal fuels because of the cohesive and non-porous oxide coating, which engenders a high activation energy barrier for both combustion (see Tables 2 and 3) and corrosion. However, there are certain circumstances in which the oxide coating may be disrupted, potentially creating a hazard.

Table 5. Heats of Reaction for the Complete Combustion of Various Fuels.[19,20]

Fuel	Heat of Reaction (kcal/mole) [a,b]
Aluminum	–200
Titanium	–225
Silicon	–216
Magnesium	–144
Shellac	–131[c]
Stearic acid	–151[c]
Lactose	–113[c]
Carbon[d]	–94
Zinc	–84
Sulfur	–71

a) Unless otherwise noted, this is per mole of fuel.

b) Note that negative values correspond to exothermic reactions.

c) This value is per mole of carbon in the compound.

d) Carbon is in the form of graphite.

With Water:

Water is widely used to activate binders of pyrotechnic compositions and must therefore be considered a temporary ingredient of such compositions. Any active metal has the capability for a reaction with water to produce hydrogen gas. One example is the simple mixture of aluminum metal powder and pure water.

$$2\,Al + 6\,H_2O \rightarrow 2\,Al(OH)_3 + 3\,H_2 \qquad (6)$$

Because this is an exothermic reaction, there is the potential for generating sufficient heat to reach the ignition temperature of a pyrotechnic composition. (Even if the ignition temperature is not reached, the metal can corrode and the pyrotechnic composition can become useless.) In Figure 2, note the relatively sudden onset of the exothermic reaction after a prolonged latency (see Table 6 for experiment conditions).

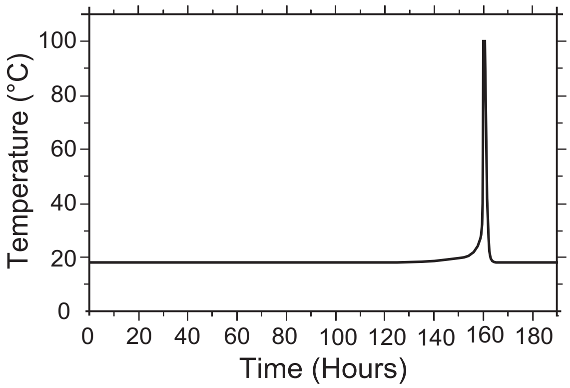

Figure 2. An example of an aluminum and water exothermic reaction.[21] [See Table 6 for Experiment Conditions.]

The water reactivity of aluminum rises in particular with nitrate compositions, wherein the following exothermic decomposition can take place:

$$6\,KNO_3 + 16\,Al + 9\,H_2O \rightarrow 6\,KAlO_2 + 6\,NH_3 + 5\,Al_2O_3 \qquad (7)$$

Aluminum oxide is amphoteric, meaning that not only can it dissolve in acids to form aluminum salts, but it can also dissolve in alkalis to form aluminates (such as the potassium aluminate formed in the reaction above). Consequently, the alkaline nature of the ammonia

Table 6. Aluminum and Water Reactivity Data at 18 °C (64 °F) unless otherwise stated. [21]

Conditions for Test[a]	Exotherm Time(b) (hours)
Aluminum, 2 g Distilled water, 2 g	159
Aluminum, 1 g Potassium nitrate, 1 g Distilled water, 2 g	10
Aluminum, 1 g Potassium nitrate, 1 g Boric Acid, 0.04 g Distilled water, 2 g	>500
Aluminum, 1 g Copper(II) oxide, 1 g Distilled water, 2 g	15
Aluminum, 2 g Distilled water, 2 g Temperature 43 ℃ (109 ℉)	1

(a) Aluminum was always Alcoa S-10, 12μ atomized.

(b) Average time to exotherm for three tests. (See Figure 2.)

produced in this reaction (equation 7) can enable it to dissolve not only some of the aluminum oxide produced in the reaction, but also some of the oxide coating of the aluminum. The aluminum so activated can then go on to react directly with water, generating more heat. Another series of tests similar to that shown in Figure 2 was performed; however, half of the aluminum was replaced with potassium nitrate (see Table 6). In this case, a slightly higher temperature was reached as the water was consumed, and the reaction peaked after only 10 hours. At least one plant explosion, is believed to have been caused by such an aluminum, nitrate, and water reaction, when it occurred in 12 kg (26 lb) of a pyrotechnic mixture left partially submerged in water.[22]

In practice, many of these water and aluminum reactions do not appear to be a serious problem when atomized or coarse flake aluminum is used. Presumably, this is because the wetted compositions are cut or rolled into relatively small stars, from which heat readily escapes. Also the amount of water present is relatively small and drying is fairly fast.

If for some reason it is desired to use fine aluminum with a nitrate present, or if the anticipated drying time will be prolonged, a small amount of boric acid can be added to counteract the incipient alkalinity and prevent decomposition. This is partly because the protective oxide coating of aluminum is much more resistant to mild acids than it is to alkali. Moreover, aluminum borate, formed[23] on the surface of the aluminum, is very insoluble and therefore improves the protection offered by the oxide coating. For example, when as little as 0.2% boric acid was added to an aluminum and potassium nitrate mixture, no detectable reaction with water occurred even after 500 hours, see Table 6. (Note that using 0.5% boric acid would provide a more reliable safety margin.)

With Copper(II) [Cupric] Salts:

A metal will react with the salt of a more electronegative (less reactive) metal in what is called a displacement reaction. Such a reaction is exothermic and has the potential of producing enough heat to raise a pyrotechnic composition to its ignition temperature. A classic example of this is the silver nitrate and magnesium flash powder that is initiated by a mist of water droplets:[8]

$$\mathrm{Mg} + 2\ \mathrm{AgNO_3} \rightarrow \mathrm{Mg(NO_3)_2} + 2\ \mathrm{Ag} \qquad \text{Displacement Reaction} \tag{8}$$

$$6\ \mathrm{Mg} + 2\ \mathrm{AgNO_3} \rightarrow 6\ \mathrm{MgO} + 2\ \mathrm{Ag} + \mathrm{N_2} \qquad \text{Flash Reaction} \tag{9}$$

The activation energy of the displacement reaction is lowered so much by the presence of water that the reaction proceeds at ambient temperature, generating sufficient heat to initiate the pyrotechnic flash reaction.

Displacement reactions can occur with copper salts and aluminum, but in practice, this is seldom a problem because of the large activation energy engendered by the oxide layer on aluminum. However, problems can arise when the copper salt is significantly soluble. Although most copper salts used in pyrotechnics are not very soluble, it should be borne in mind that the presence of ammonia substantially enhances the solubility of the copper salts.[24] Consequently, situations with the potential for generating ammonia, such as described in the previous section (equation 7), can be exacerbated by the presence of a copper compound.

As part of the testing of aluminum's reactivity with water (Table 6), a series of tests were conducted wherein a mixture of atomized aluminum and copper(II) oxide were used. Despite the low solubility of copper(II) oxide, a reaction similar to that shown in Figure 2 occurred. The time interval before the peak (exotherm) was 15 hours, nearly as fast as it occurred when testing aluminum with potassium nitrate.

Magnesium

The activation energy for the reaction of magnesium is substantially less than for aluminum. As a result, the associated chemical reactivity problems are generally similar in kind but much greater in degree.

With Acids:

Magnesium is extraordinarily reactive toward acids, thus even mild acids, such as boric acid, must be avoided.

$$Mg + 2\,H^+ \rightarrow Mg^{2+} + H_2 \qquad (10)$$

With Ammonium Salts:

The ammonium ion is sufficiently acidic to react with magnesium:

$$Mg + 2\,NH_4^+ \rightarrow Mg^{2+} + 2\,NH_3 + H_2 \qquad (11)$$

The only effective way of preventing this reaction is by conversion coating the metal. Traditionally, the only effective coating was obtained by treatment with a dichromate.[25,26] This, however, may be considered an extreme solution because of the carcinogenicity of dichromates. Recently, a conversion coating that may be superior to that of dichromate was reported.[27] That coating is based on treatment with a low toxicity ammonium metamolybdate and ammonium dihydrogen phosphate solution.

With Water:

The reactivity of magnesium with water is so great that aqueous binding is generally considered to be incompatible with the presence of magnesium. In fact, reactions occur with unprotected magnesium and many (most?) salts in the wet state. For example, Shimizu[25] reports that active or violent reactions occur between magnesium and the wet salts listed in Table 7.

Table 7. Some Wet Salts Invoking Active or Violent Reactions with Magnesium.[25]

Barium nitrate	Potassium chlorate
Potassium nitrate	Potassium perchlorate
Sodium oxalate	Sodium chloride
Sodium bicarbonate	Sodium carbonate
Strontium nitrate	

With Copper Salts:

The reactivity of magnesium with copper salts (both cupric and cuprous) is so great that such mixtures are generally considered to be incompatible. This is because of an exothermic displacement reaction.

$$Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu \qquad (12)$$

Copper metal or copper(II) oxide should be used when combinations with magnesium are desired. Copper metal works because both it and magnesium metal are in the same oxidation state, zero or neutral, thus displacement is not possible. However, because of magnesium's intrinsic water reactivity and because copper and magnesium metals form an electrochemical couple, non-aqueous binding is essential. When drying times are fairly short, copper(II) oxide seems to be acceptable because of its low solubility. However, there may be problems similar to that when mixed with aluminum (see above and Table 6).

With Sulfur:

Sulfur can act as an oxidizer for active metal fuels. A metal associated with low activation energies, such as magnesium, can react spontaneously with sulfur leading at least to corrosion, and perhaps to ignition under some circumstances. Even aluminum and sulfur mixtures can present a problem under rare circumstances. For example, it has been reported that when a mixture of aluminum and sulfur was ball milled, an explosion resulted.[28] Presumably this was partly the result of physical abrasion removing enough of the protective aluminum oxide layer to lower the activation energy to unsafe levels for ball milling.

Zinc

Despite being a substantially less energetic fuel than magnesium (see again Table 5), zinc also has a somewhat low activation energy barrier, and so generally shares similar compatibility concerns.

With Acids:

Zinc reacts readily with acids, and the combination is best avoided.

$$Zn + 2\,H^{+} \rightarrow Zn^{2+} + H_2 \qquad (13)$$

With Ammonium Salts:

Like magnesium, zinc is incompatible with ammonium salts. The reaction is exacerbated in this case because zinc oxide is dissolved by aqueous ammonia.

$$Zn + 2\,NH_4^{+} \rightarrow Zn^{2+} + 2\,NH_3 + H_2 \qquad (14)$$

$$ZnO + H_2O + 4\,NH_3 \rightarrow [Zn(NH_3)_4]^{2+} + 2\,OH^{-} \qquad (15)$$

Thus, the ammonia formed in the first reaction is able to solubilize the partly protective zinc oxide layer on the zinc particles, thereby accelerating its decomposition. A classic demonstration of spontaneous combustion is a mixture of zinc and ammonium nitrate that is initiated with a drop of water. Under conditions of high humidity, the presence of hygroscopic ammonium nitrate will cause the mixture to spontaneously heat up.

With Water:

In its behavior with water, zinc more closely resembles aluminum than magnesium. Usually there is no problem, even with nitrates present. However, on occasion, such mixtures have been known to heat up. Ammonia, the water reaction product of nitrates and zinc (see equation 7 for a similar reaction) dissolves the protective zinc oxide layer, leading to a self-accelerating reaction.

With zinc metal, because of its acid sensitiveness, anything but a neutral pH composition must be avoided. Thus, in practice, nitrate and zinc mixtures can generally be used with aqueous binding only if there are no acidic or alkaline ingredients present to initiate its decomposition. However, it is well to be aware of this potential problem.

With Copper Salts:

Like magnesium, zinc is incompatible with copper salts due to exothermic displacement reactions as discussed above.

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \qquad (16)$$

With Sulfur:

The mixture of zinc and sulfur is a traditional model rocket fuel.

$$Zn + S \rightarrow ZnS \qquad (17)$$

However, it is not generally recognized that this mixture has a quite low activation energy for ignition and is significantly sensitive to both friction and impact. According to Partington[29] "... the mixture may detonate on percussion." As with magnesium, this combination is best avoided, even though it probably is not capable of a true detonation.[30]

Addendum for Magnalium

In general, the properties of an alloy are somewhat intermediate between those of its constituent metals. However, this is not necessarily the case. For example, the hardness of magnalium (magnesium/aluminum alloy) is significantly greater than that of either of its constituent metals. This relatively greater hardness of magnalium can be expected to pose a greater hazard regarding accidental ignition from friction. Nevertheless, its chemical sensitiveness is more often intermediate than resembling a mixture containing particles of the individual metals.[25] Of particular interest are hazardous combinations that are not exactly predictable from the properties of the constituent metals. (For the purpose of this discussion, magnalium refers specifically to the 50:50 alloy. Other magnalium alloys may be expected to have properties more or less intermediate between this alloy and the major constituent metal.)

With Chlorates and Perchlorates:

It is not expected for there to be a significant deviation from intermediate properties here; namely significantly hazardous with chlorates, less so with perchlorates. (See below for ammonium perchlorate.)

With Acids:

Here again the properties are intermediate. Magnalium is more acid sensitive than aluminum, but less so than magnesium. However, it is still sufficiently acid sensitive so as to preclude its use even with mild acids such as boric acid.[25,31] There are a number of published formulations that combine boric acid with magnalium, or even with magnesium. However, such compositions are almost always used with non-aqueous binding, which minimizes the danger. If similar formulations are developed for use with aqueous binding, the boric acid content should be deleted in the interest of safety.

With Ammonium Salts:

Magnalium is more reactive than aluminum, but less reactive than magnesium, towards moist ammonium perchlorate.[25] Boric acid does not prevent this reactivity and should not be used because of magnalium's reaction with acids. In practice, the problem can be avoided with the use of non-aqueous binding.

With Water:

Magnalium does not usually present any problem with aqueous binding. However, the potential for decomposition exists and it is well to be aware of this possibility when developing formulations. Certain substances seem able to trigger the reactivity of magnalium towards water. Examples are lampblack and alkali metal oxalates.[25,32] The reasons are not obvious and do not necessarily depend on any acidic or alkaline reaction. For example, aqueous lithium oxalate has a pH of 7 (neutral), yet is able to trigger such exothermic decomposition of magnalium.

In general, magnalium is more stable in an alkaline rather than an acidic environment, in contrast with aluminum. Thus, lithium carbonate, with an alkaline reaction, presents no problem with magnalium, although it is incompatible with aluminum.[32]

With Copper Salts:

Copper salts, both copper(I) and copper(II), should be avoided with magnalium unless the counter anion has a basic reaction. Fortunately many of the copper salts used in pyrotechnics, such as the carbonate or benzoate, fall into the latter category and normally present no problem. A danger can arise when conditions allow the production of ammonia, which has the ability to solubilize otherwise poorly soluble copper compounds.[24] Ammonium perchlorate in combination with alkaline materials, such as hexamine, can produce sufficient ammonia to cause a solubilization effect with certain copper salts.[33] Thus, the fourfold combination of ammonium perchlorate, hexamine, copper(II) carbonate, and magnalium is incompatible despite the fact that any of the binary combinations cause no problem.[34] Certain copper compounds, such as copper(II) benzoate, seem to be less problematic for unknown reasons.[34,35]

With Sulfur:

Magnalium does not cause any particular problems with sulfur and resembles aluminum in this respect.

Closing Remarks

The discussion of some particularly hazardous combinations and the listings in Table 1 should not be interpreted too rigidly. They should serve only as guidelines. Some combinations listed as generally hazardous can be used by knowledgeable and skilled pyrotechnists with reasonable safety, provided appropriate precautions are taken. Conversely, the list is not all inclusive, with other hazardous combinations existing.

Knowledge of hazardous combinations has been acquired through more than a century of observations by pyrotechnists. The explanations given in this article should be seen as post facto rationalizations rather than as theoretical predictions. Consequently, formulation development should be guided by cautious experimentation. For example, it is not obvious that titanium is compatible with ammonium salts whereas manganese is not, despite the two metals having almost identical electronegativities.

New star compositions containing active metal fuels should be dampened with water only as a small sample (if at all). Such stars should be checked periodically for the occurrence of an exothermic reaction or other indication of an adverse reaction (e.g., ammonia or hydrogen sulfide odor).

Great care must be taken when working with new formulations, especially if there is any known potential for an adverse reaction. It is always appropriate to start working with very small quantities and to store these materials separate from other pyrotechnic materials and in a manner such that an accidental ignition would be less than disastrous.

Only after small batches have been successfully prepared, should larger batches be attempted. However, it must be recognized that since small batches did not experience adverse reactions, is not a guarantee that problems will not appear when batch sizes are scaled up. Mostly this is because increasing temperature generally has a powerful effect on the rate of chemical reactions. As an example, consider the two experiments with aluminum and water reactions in Table 6. Note that while at 18 °C the reaction peaked only after 159 hours, the same reaction at 43 °C peaked in only 1 hour. When large batches are prepared, any heat produced will generally escape more slowly (i.e., the temperature will rise to higher levels, especially near the middle of containers). This in turn accelerates chemical reaction rates and the rate of heat production. Such a thermal run-away may well lead to a catastrophe for a large batch while a small batch may show no signs of a problem.

In the event an adverse reaction is detected, it may be necessary to take more or less immediate safety measures. If the reaction is mild, the amount of material is small and it is in an isolated location, it may be possible to monitor the situation and hopefully wait it out. Actual ignitions of compositions undergoing adverse reactions are not common; nonetheless, disposal is probably the best way to terminate the potential problem.

The only certain way to eliminate a pyrotechnic hazard is to consume the material, generally by burning. While such disposal may constitute unlicensed hazardous waste disposal, it may also be a safety imperative. Great care must be taken when materials under going adverse reactions are handled or moved, such as in preparation for disposal by burning. Consideration must always be given to the possibility that the material may enflame at any time. (Note that there has been a recent accident with severe burn injuries when a relatively small batch of stars—experiencing an adverse reaction—were being removed from a work area. If the temperature of the composition has risen (as will almost always be the case), combustion of the material will probably be especially violent and could be explosive.

When burning pyrotechnic materials, always be extremely careful. Even under the best of conditions, unexpectedly large or violent output is possible. Some limited guidance on the subject that may be useful can be found in references 36 and 37. In cases where immediate disposal by burning is not possible and when the amount of material is relatively small, it will generally be possible to limit the buildup of heat in the materials by their immersion in a large amount of water. This will preclude the ignition of the material, but often will not terminate the adverse reactions such as the production of flammable (potentially explosive) hydrogen gas. If such treatment is necessary, as soon as possible the pyrotechnic composition should be separated from the water and disposed of by burning. Obviously, the best course of action is studiously to avoid those potentially hazardous combinations that might lead to adverse chemical reactions!

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Assessing the Risks — Suggestions for a Consistent Semi-Quantified Approach

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ABSTRACT

Assessing the risks of an operation, the operation of a whole factory, or the consequences of firing a firework display has become a way of life. Much modern legislation, certainly in the UK, is based less on "prescription" and more on "goal setting", which requires the risk creator to determine the nature of the risk and to allow him to control it adequately. Everyone involved in almost any activity, be it sport, driving, or managing a pyrotechnic production facility, has always assessed the risks—normally in their head and on the job. Modern legislation demands that these informal processes, accurate as they may have been, be documented, monitored and revised as appropriate, partly at least to "prove" in any post-accident enquiry that adequate steps had been taken to identify the particular circumstances that caused the accident. Failing to identify a particular risk is as negligent as failing to control a risk that had been identified.

Keywords: risk assessment, consequence, hazard management

What Does Assessing the Risks Mean?

Assessing the risk is not the same as "doing a risk assessment". The latter term has become devalued. In many cases it simply involves photocopying the last risk assessment! Assessing the risks is a serious task, and although in any operation, for instance a firework display, many factors remain constant, there are always site specific factors that must be addressed.

For instance constant factors may include:

- the range of fireworks used,
- the methods of erecting mortars, and
- the firing system.

Factors that change from site to site, and crucially from event to event include:

- local weather conditions,
- the physical site, for instance, can mortars be dug in, can angle irons be used, or does everything have to be supported by sandbags,
- constraints of the site, for example, where there is plenty of room for varying the firing position, the choice of fireworks may be made knowing that the site can be adapted with knowledge of likely wind conditions during the display—for instance, barges held by tugs may be moved to maximize the fallout area. On the other hand, where the site is fixed, the choice of fireworks may be conservative and dictated by the "worst case" scenario, and
- local hazards (e.g., gas cylinders in the fallout zone).

That is not to say that previous risk assessments are not valuable. Over time, previous risk assessments form a valuable resource, especially where they have been shown—as a result of a "near miss" or real incident—to be lacking. Revision and modification of existing risk assessments in the light of extended experience are probably the most valuable revisions possible.

Assessing the risks does not stop when a risk assessment is written. The process is iterative and risks are not adequately controlled if the process is stopped at any point. Old, out of date risk assessments are almost as useless as no risk

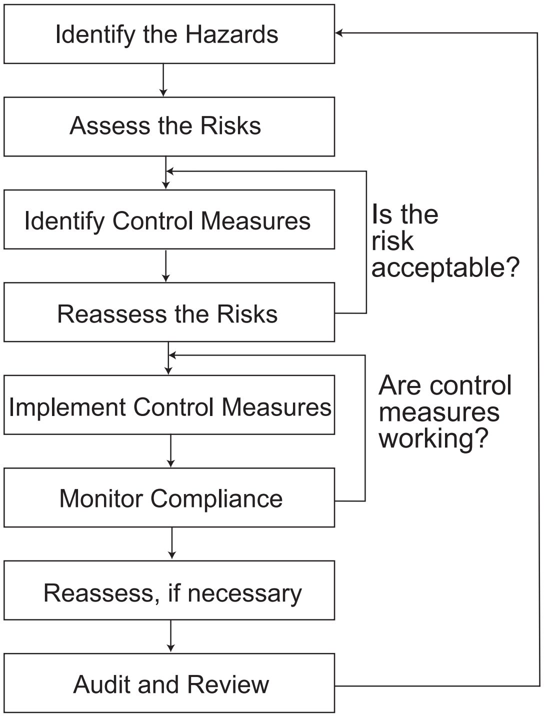


Figure 1. Flow chart for risk assessment.

assessment. Figure 1 presents a generalized flowchart for risk assessment.

Principles of Risk Assessment

Risk assessment is determining the risk posed by an operation. In its most general form the risk of an operation can be described as the product of the consequences of a particular identified incident and the frequency of the particular incident happening. Commonly this is described as

$$\text{Risk} = \text{Hazard } (H) \times \text{Frequency } (F)$$

To determine the overall risk of an operation each identified risk is summed, for a variety of potential occurrences and thus consequences from a particular operation

$$\text{Total Risk} = H_1F_1 + H_2F_2 + H_3F_3 + \ldots + H_nF_n$$

For example, as a result of a fire (from whatever source) in a magazine containing solely 1.4G fireworks, which are packaged and stacked properly, the overall risk is comprised of the factors listed in Table 1.

Risk and Hazard

So what is meant by "Risk" and "Hazard" and why are the two so often confused?

The hazard of an event is the potential consequences of the event—however infrequently that event may occur. It is the intrinsic potential for harm, the consequence of an event. Synonyms for hazard include

- consequence and
- danger (a poor term and one with negative connotations)

The risk arising from that event considers both the intrinsic hazard of the identified event and the frequency of that event occurring. Synonyms for frequency include

- likelihood,
- probability,
- incidence, and
- rate.

Table 1. Overall Risk from a Fire in a Magazine Containing Only 1.4G Fireworks.

Event	Hazard	Frequency
Rapid escalation leading to mass explosion	Building destruction, fragmentation, blast wave, "domino effects" to adjacent magazines	Very low
Projection of firework stars through open door	Burns, thermal effects, ignition of adjacent magazines, etc.	Probable
Smoke plume, deposition of heavy metal salts, etc.	Toxic hazard to fire fighters, environmental aspects, etc.	Probable
Effects confined entirely within magazine	No hazard to outside, however hazard during clean up, etc.	Low

Quantitative vs. Qualitative Risk Assessment

Quantitative Risk Assessment (sometimes referred to as "Quantified Risk Assessment"—but both Quantitative and Qualitative Risk Assessment are also referred to, ambiguously, as QRA) is the process of trying to determine the consequences of an event and the frequency of that event happening using "real" numbers. In this way an estimate of the overall risk may be obtained that is comparable with other risks that workers and the public face during normal activities. For example, in the UK a risk to a specified individual is considered broadly acceptable if it leads to a fatality at a frequency of 1 in 10^{-6} (i.e., about one in a million years). See Figure 2. Fatalities more frequent than this may be acceptable provided they are "As low as is reasonably practical", so called ALARP, or they may be unacceptable. The upper end of the ALARP region in the UK is taken to be about 1×10^{-4} (or about one every ten thousand years) for members of the public. For workers, who may accept a greater level of risk as a consequence of working, the figure is taken to be 1×10^{-3} (or about one every thousand years).

ALARP implies that necessary steps should be taken to reduce the risk, provided that they are "reasonable". Ultimately therefore the measure of ALARP is often based on cost. Sometimes changes could be made that reduce risk slightly, but are cost prohibitive and therefore not practical. On the other hand, some risk control measures may be simple to achieve and also are cost effective.

Quantitative Risk Assessment is a very complicated and rather imprecise science. For instance, to assess the overall risk resulting from an explosion in a brick built magazine, the following facts (and many others) all need to be quantified:

1) Frequency of the event
   a) How often does an ignition occur?
   b) How often does this lead to a mass explosion?

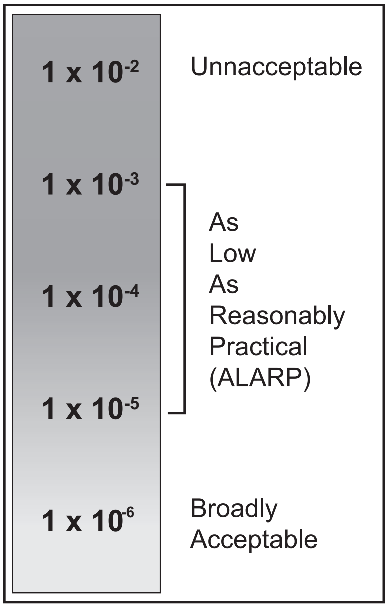


Figure 2. Individual risk.

2) The effect on workers and the public
   a) How far away are potential victims (e.g., do they lie in a debris zone, a blast zone or a fire zone)?
   b) How much time does each potential victim spend at that location?
   c) What is the effect of the incident on people in the open, or within buildings?
3) For people in the open
   a) How much time are they in the open?
   b) What fragments from the explosion are fatal to them?
4) For people in buildings
   a) What is the building construction?
   b) What is the effect of building collapse?
   c) What is the effect of window shatter?
5) What control measures are there
   a) Earth mounding?
   b) Directional effects?

It is obvious that this process is not simple!

Attempts have been made to quantify some of these variables. Merrifield and Moreton[1] conclude that accidents at licensed explosives sites occur at about 1×10^{-4} per building year—in other words, if there are 5000 licensed buildings in the UK, they would expect an unintended ignition about once every other year. Their analysis concentrated on events that led to investigation and thus may actually under-report the frequency of unintentional ignitions. On the other hand, their own figures suggest that post 1974 (the introduction of new general Health and Safety regulations in the UK), the frequency dropped markedly.

Calculating a pure frequency for unintentional ignitions on a firework display site is much more difficult. In many cases a premature ignition may go unrecognized during a display; however, the consequences of such an ignition are usually negligible—providing that the firework continues to function normally. On the other hand, ignitions during rigging and testing have potentially severe consequences, and although the frequency remains low, good risk assessment and consequence control measures are needed to prevent accidents. For instance, responsible firework companies do not test electrical circuits with personnel in the firing area.

The consequences of an incident are also complex to determine. For instance the effect of debris on a person depends on:

- the trajectory of the debris,
- the area they present to debris (for low trajectory debris this is their frontal area, but for high trajectory debris this is their plan area),
- their distance from the explosion, and
- the amount and type of debris produced.

An extensive analysis of models used to predict consequences of an explosion was carried out in the recent review of UK explosives legislation.[2] A comprehensive paper detailing various consequence models available has also been produced by the UK's Advisory Committee on Dangerous Substances.[3] Both papers mainly consider the consequences of high explosive events, whether they are from blast wave or debris. Similar analysis of lower order events, especially those involving fireworks and pyrotechnics, is very rare.

Individual and Societal Risk

Not only does the risk need to be quantified as above, but the risk to two quite separate types of person must be considered. The two types are:

Individual, identified persons—for instance the operator of a particular process or the occupier of a particular dwelling that lies within an area likely to be affected by an incident.

Society as a whole—people passing by a factory on a busy road and the whole population surrounding a particular facility.

The assessment of the risks to these two separate types of person is termed "Individual Risk" and "Societal Risk".

Previously it was stated that the standard for acceptability of individual risk is taken to be 1×10^{-6}. The acceptability of a societal risk is much more complicated. In the most general terms, society's acceptance of a risk is inversely proportional to the number of people who may be affected by the risk. For instance, we all accept, although perhaps we shouldn't, that individuals are killed in road accidents every day of the year. These fatalities rarely make even local news reports; this risk has become a fact of life. However, if, a pile-up kills 10 people, we can be sure that the event will be reported widely in the locality and may even make national news. If hundreds of people are killed, the event will be reported internationally. If children are involved the event will get wider attention for smaller numbers of fatalities.

A plot of cumulative frequency of incidents (F) and number of fatalities (N), the F/N curve (Figure 3), is very reminiscent of the simple plot for individual risk and highlights the same three areas:

- where the risk is unacceptable,
- where risk reduction is required, and
- where the risk is considered negligible.

In practice the calculated societal risks resulting from an incident are normally laid over the acceptability chart above, and the overall acceptability of the risk (or otherwise) determined from where the points lie in relation to the areas above. Calculations may be made on the basis of haz-

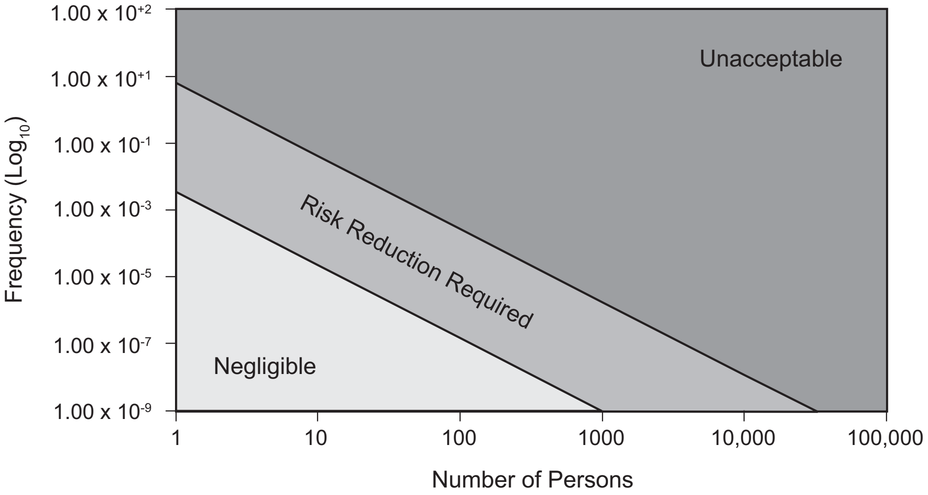


Figure 3. Generalised f/N curve.

ard identification and mathematical modelling of consequence analysis.

This is not to say that we should necessarily equate acceptable societal risk with media perception, but the two run closely hand in hand!

Societal risk should be, but not always is, summed over an entire population—that is, in any one year, any event leading to multiple fatalities should be considered, and therefore the total risk should be calculated across all establishments that may pose that risk. It is unlikely that society would accept multiple incidents over a range of establishments during a relatively short time scale without rightly asking questions as to whether the risks were properly controlled across the entire industry.

Sadly, the public who thus determine the acceptable levels of societal risk are also the people who least understand the nature and mathematics of risk calculations. Indeed the public have little concept of frequency—otherwise why would so may indulge in the lottery!

As a result, most risk assessment is carried out on a qualitative or semi-quantitative basis. The remainder of this paper will concentrate on this approach.

Qualitative Risk Assessment Schemes

There are almost as many qualitative risk assessment schemes as there are people carrying out risk assessments—each may have had its merits, but we are now firmly convinced that a biased 0–10 rating system is the best. See Table 2.

Table 2. Comparison between Some Qualitative Risk Assessment Schemes.

Scheme	Ratings	Comments
Descriptive	Low, Medium, High	Too crude and too few divisions.
Simple 3 tier numeric	1,2,3	As above
Simple 6 tier numeric	1,2,3,4,5,6	Better - but need a “zero” entry
Simple 7 tier numeric with zero	0,1,2,3,4,5,6	Good
Biased 0–10 numeric	0,1,2,3,4,6,8,10	Good, puts greater weight on risks of high consequence or high frequency events

Table 4. Chart Showing the Advantages of a Scheme Based on 0–10 Scale.

Potential Frequency Rating (PFR)

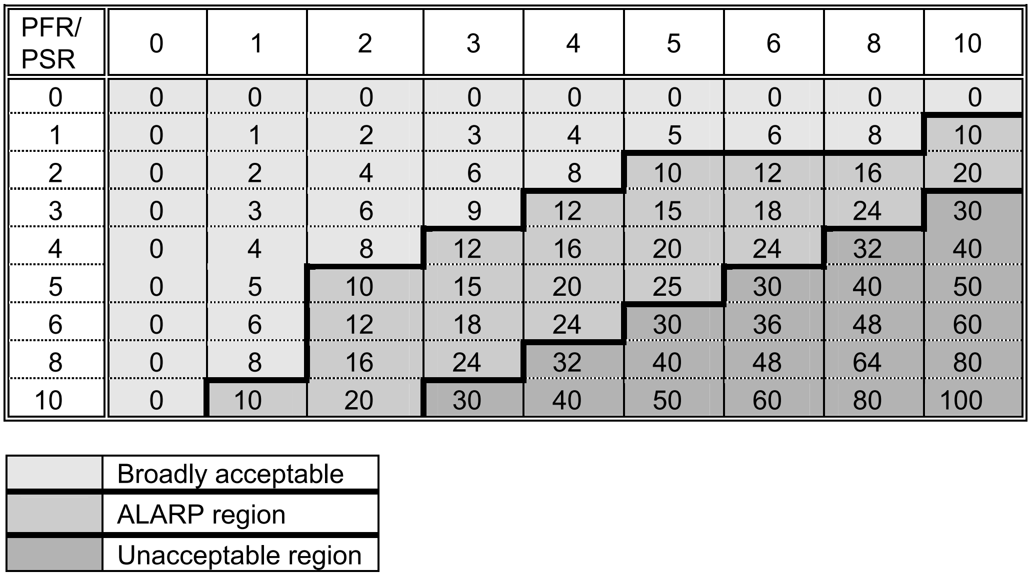
PFR	Description of Frequency	Approximate Frequency (per year)	Example
0	NEVER happens	$F = 0$	Firework debris falling 2 miles upwind
1	Very unlikely to happen	$F < 10^{-7}$	
2	Happens only rarely	$10^{-5} > F > 10^{-7}$	
3	Occasionally happens	$10^{-3} > F > 10^{-5}$	
4	Happens	$10^{-1} > F > 10^{-3}$	Firework fuse fails
6	Frequently happens	$1 > F > 10^{-1}$	
8	Almost always happens	$F > 1$	Lit firework debris landing in firing area
10	ALWAYS happens	$F > 10$	Firework debris landing on ground

Potential Severity Rating (PSR)

PSR	Description of Severity	Example
0	NOTHING of consequence	Ash on hand
1	Single trivial injury	Lit ash on hand causing very minor burn (e.g., from a sparkler)
2	Multiple trivial injuries	
3	Single minor injuries	Ash in eye
4	Multiple minor injuries	
5	Single major injury	Loss of limb
6	Multiple major injuries	
8	Single fatality	Death - immediate or as a result of injury
10	Multiple fatalities	

The advantages of a biased 0–10 scheme as indicated in Table 4 are as follows:

- It includes a zero rating for both frequency and severity. This relates to risks that have no identified consequence or those that simply cannot happen. For example an explosives incident at an explosives factory cannot, by itself, affect a nuclear power station 10 miles away. An explosive incident at the same plant that resulted in release of a toxic gas could, on the other hand, affect the same power station as a result of wind drift and dispersion. Although many regulations (in the UK at least) require only the assessment of "significant risks", it is often better to document and dismiss a risk than not to document it at all!
- Although what follows rating of frequency and severity is just mathematics, the multiplication of the Hazard and Frequency components to evaluate Risk, biasing both ratings at the top end, the highest frequencies and highest consequences, allows risks where more than one group of people are affected to be rated higher than where only one group is affected, and frequently occurring risks to be rated higher than rare occurrences.
- The scheme has enough divisions to allow risks to be rated in a meaningful way and to allow risk control measures to have a real effect on the mathematics of the risk. For instance, a risk that potentially injured many people may be reduced to one that only caused minor injuries to many people once control measures are in place. Both these might be considered "medium" severities in a simple 3 tier scheme, so no risk reduction would be apparent.



PFR/ PSR	0	1	2	3	4	5	6	8	10
0	0	0	0	0	0	0	0	0	0
1	0	1	2	3	4	5	6	8	10
2	0	2	4	6	8	10	12	16	20
3	0	3	6	9	12	15	18	24	30
4	0	4	8	12	16	20	24	32	40
5	0	5	10	15	20	25	30	40	50
6	0	6	12	18	24	30	36	48	60
8	0	8	16	24	32	40	48	64	80
10	0	10	20	30	40	50	60	80	100

░	Broadly acceptable
▒	ALARP region
▓	Unacceptable region

Figure 4. Simple semi-quantified risk assessment.

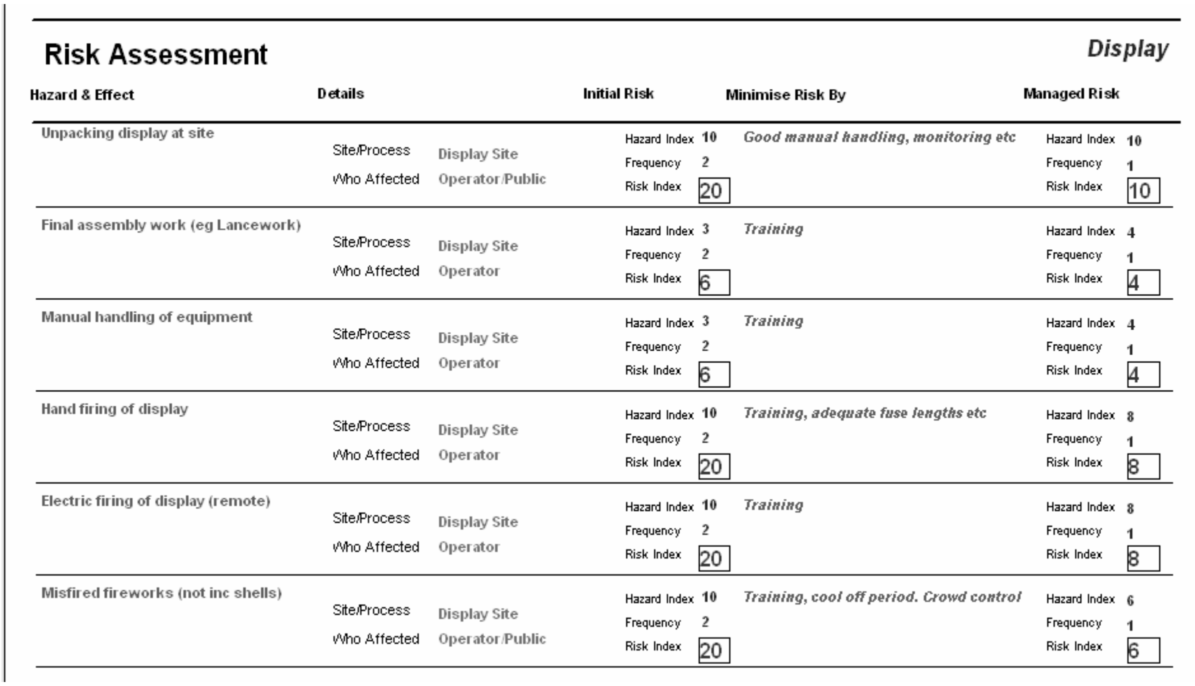
Each potential identified risk should be assessed for both hazard and frequency and then rated for risk. In this way, each risk is related on a scale of 0–100 (Figure 4), and for multiple effects from the same event (e.g., both on-site and off-site fatalities), those events that pose the greatest risk are identified by simple addition. Figure 4 also identifies those areas where the resulting risk may be considered acceptable, often described by regulators as “broadly acceptable”. This term acknowledges that the risk is not completely controlled and—once higher risks have been reduced—this area may merit revisiting to control the risk further. No enforcing authority will ever commit themselves to agreeing that a risk is fully and acceptably controlled and that it always will be. The remaining regions are those where the risk is unacceptable, and the vast majority where the risk is “ALARP”. Again the plot resembles that for individual and societal risks.

In the ALARP band, steps should be taken to reduce the risks, but any such risk reduction measures must be proportionate with the effort required to achieve them, both practically and financially. Ultimately, therefore, risk reduction cannot be separated from cost expenditure. Every firework fired could be entirely safe to the operator if the operator is situated behind a 30 cm thick steel plate 2000 m from the firing area, but this is neither practical nor cost effective.

The challenge to industry is to be consistent in assessing both the hazard and frequency of any event in this simple, semi-quantitative, approach where definitions have been made in terms of, for instance, “happens” and “frequently happens”. The virtue of using an extended 0–10 scale is that, in the light of experience, the frequency or hazard of an event may be reassessed when control measures are in place and the risk reassessed. For instance, shells discharging prematurely from stray sparks where the shell leaders are completely unprotected “happens”. It is not a frequent event, nor is it an infrequent event. Covering each leader with tinfoil and protecting the mouth of each mortar with more tinfoil may reduce this to “happens only rarely”—a reduction in potential frequency rating (PFR) from 4 to 2. Assuming the consequences stay the same, this reduction in PFR reduces the overall risk from *this event* by half.

It is important to realize, however, that measures taken to reduce a particular risk to one set of individuals may actually increase the risk to others. The classic case here is electrical firing of racks of shells. Removing the operator from the firing point reduces the risk to him, but he may be so removed that he is unable to determine that the rack has been disrupted in some way and is now pointing horizontally towards the audience, thus greatly increasing the risk to them! All risk reduction measures must be such

Example 1. Extracts from generalised risk assessment for a UK Firework Competition. Note that each competitor in the competition also has to provide a site specific risk assessment pertinent to the materials they are firing and their methods of rigging.



Risk Assessment *Display*

Hazard & Effect	Details	Initial Risk	Minimise Risk By	Managed Risk
Unpacking display at site	Site/Process Display Site Who Affected Operator/Public	Hazard Index 10 Frequency 2 Risk Index 20	*Good manual handling, monitoring etc*	Hazard Index 10 Frequency 1 Risk Index 10
Final assembly work (eg Lancework)	Site/Process Display Site Who Affected Operator	Hazard Index 3 Frequency 2 Risk Index 6	*Training*	Hazard Index 4 Frequency 1 Risk Index 4
Manual handling of equipment	Site/Process Display Site Who Affected Operator	Hazard Index 3 Frequency 2 Risk Index 6	*Training*	Hazard Index 4 Frequency 1 Risk Index 4
Hand firing of display	Site/Process Display Site Who Affected Operator	Hazard Index 10 Frequency 2 Risk Index 20	*Training, adequate fuse lengths etc*	Hazard Index 8 Frequency 1 Risk Index 8
Electric firing of display (remote)	Site/Process Display Site Who Affected Operator	Hazard Index 10 Frequency 2 Risk Index 20	*Training*	Hazard Index 8 Frequency 1 Risk Index 8
Misfired fireworks (not inc shells)	Site/Process Display Site Who Affected Operator/Public	Hazard Index 10 Frequency 2 Risk Index 20	*Training, cool off period. Crowd control*	Hazard Index 6 Frequency 1 Risk Index 6

that the consequential risks to all parties are examined. The analysis may ultimately conclude that the measure is not effective. In the case of electrical firing of shells in mortar racks the process will present a lower risk overall, only if adequate precautions have been taken to secure the mortar racks from disruption (e.g., adequate sandbagging, stakes, separation of tubes within the rack, etc.).

The Role of Risk Assessment in UK Pyrotechnic Operations

As noted above, UK law has gradually changed from one of "prescription" to one of "goal-setting". This change, brought about in essence by the publication of the Robens Report[4]—a fundamental review of UK Health and Safety legislation—has not been universally welcomed. Small businesses, which are predominant in the pyrotechnics sector—at least in the UK, would generally rather be told what they can and cannot do. Small businesses do not have the resources, time or staff to base their entire operations on even semi-quantified risk assessment. The Manufacture and Storage of Explosives Regulations (due for adoption in early 2004) recognize this and do lay out prescribed "Quantity/Distance" tables relating the permitted quantity allowed to be stored in a building to the "Hazard Type" of the material being stored, the construction of the building, and the proximity of inhabited buildings, major roads, etc.

Which Risks Are the Most Important To Address First?

Which risks are the most important to control effectively? It is tempting to conclude that high frequency risks are the most important, because they are the most easily dealt with. However, these risks should be of low consequence. (If they are high consequence *and* high frequency, then you are in the wrong business.) The most important risks to control are those of high consequence that occur infrequently. The plain truth is, we control these risks poorly. We assume they will not occur, and we don't quite know how to control them anyway.

Examples of both types of event can again be found in the firing of shells.

A high frequency, low hazard incident is the premature ignition of a shell from stray sparks, leading to the shell being ejected from the mortar in its normal manner, exploding normally in the air, and presenting the same risks from functioning as a shell fired deliberately.

A mortar tube that has been disrupted (i.e., displaced or tipped over by the malfunction of an adjacent tube) provides an example of a low frequency, high hazard incident. As described in Example 1, this example also illustrates the need to calculate the risk to both operator and audience. In this case remote electrical firing of the shell would almost certainly lead to lower risk to the operator, but if he is unable to witness the disruption of the mortar, and additional measures have not been put in place to prevent a shell discharging at a low trajectory towards the audience, and he then "presses the button", oblivious to the disruption of the mortar, a significant increase in risk to the audience may result.

Keeping Risks in Perspective

As previously noted, the public has little concept of risk. There is a danger with public information that "a little knowledge is a dangerous thing". The need for scientific education of the public is far beyond the scope of this paper, pressing though it may be, but the following points are important:

- The public (or legislators or event organisers) should not be misled into thinking risks are infinitesimally small when in reality accidents and incidents do occur.
- The public should be not bombarded with overly scientific information that they are unable to understand or to draw conclusions from.
- Information should be presented dispassionately, but concisely.

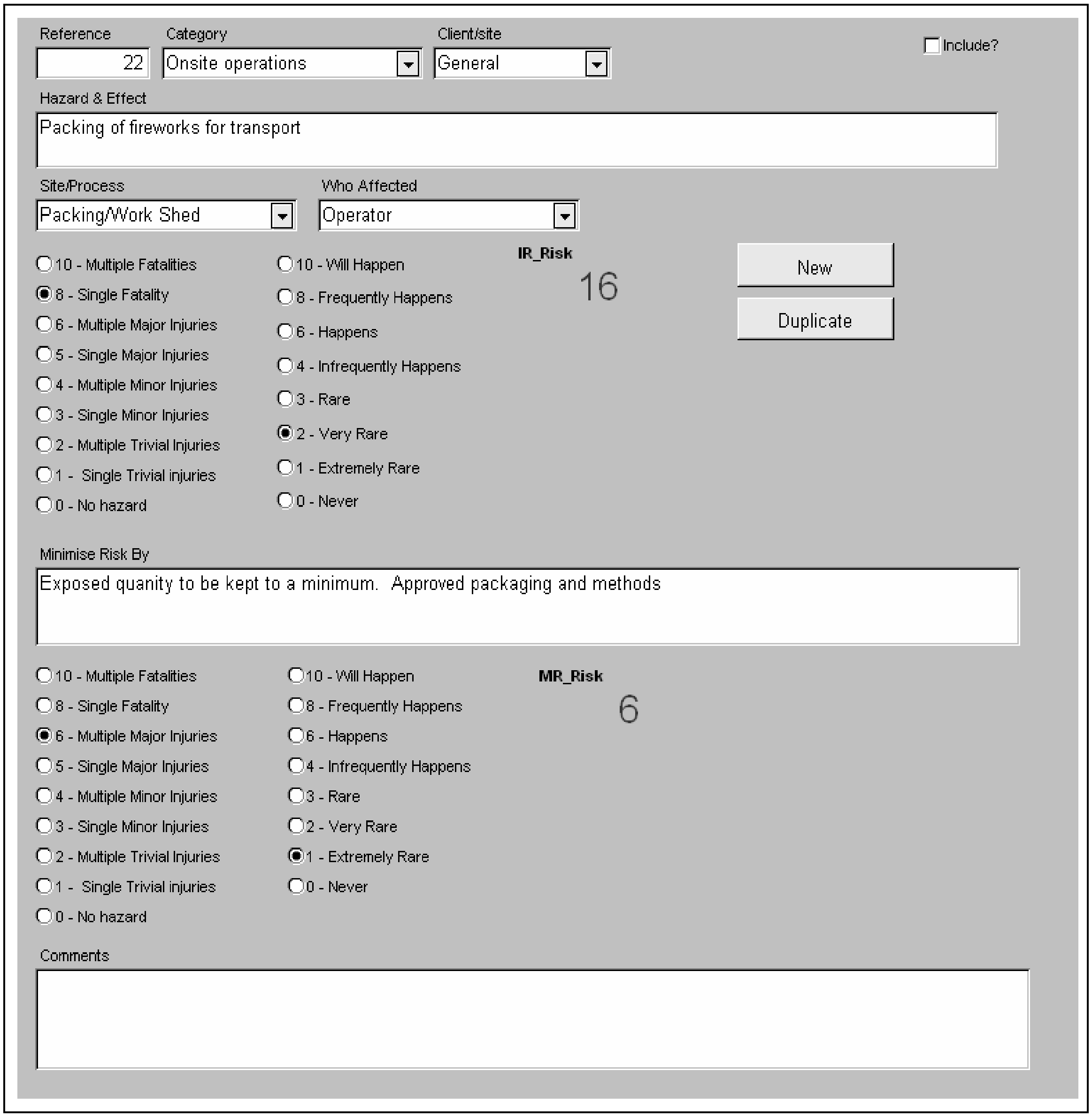
If risks in the ALARP region are controlled, they are infrequent, but the consequences may be relatively severe. This is why these risks are the most difficult to present to the public, and ironically they are the most difficult to control. How many times has the press been full of "We never knew the ... factory was there" or "I didn't know we were living next to a bomb ..."?

It is important to present the information at the appropriate level to the intended audience. Poorly documented risk assessment may be rejected by enforcers, and it is hoped that the methods presented here at least provide a degree of consistency of approach that makes the enforcers' task easier.

Presenting pages of detailed analysis to the public may convince them the operation is so "risky" that it is unacceptable. On the other hand, glib, "dumbed down" statements to the public may actually increase their suspicions and lead to the conclusion that proper risk assessment has not been carried out.

Documenting Risk Assessments

Like Risk Assessment methodology, there are as many ways of documenting the assessment of risks as there are people doing it. Risk assessments range from simple, single page, documents that generally lack detail and do not address all the risks, to multipage documents full of science that fail to highlight the most important risks, and the methods in place to control those risks. Example 1 presents a sample of the documentation we now adopt. Each row (each risk) is rated on the 0–10 system outlined above and details the identified hazards, the recipients of the hazard and the consequences and frequency of the risk occurring. It also details methods to control each identified risk. In essence therefore the column of control measures becomes an operating manual. If each of these measures is in place and is working effectively, then the risks are controlled to an acceptable level. Monitoring of the controls is paramount. The failure to implement a control measure may render a risk unacceptable. Data entry to this database is via a simple screen (Figure 5). Using a database is not, however, merely a means of regurgitating old documents, this would be



Reference: 22

Category: Onsite operations

Client/site: General

☐ Include?

Hazard & Effect: Packing of fireworks for transport

Site/Process: Packing/Work Shed

Who Affected: Operator

○ 10 - Multiple Fatalities	○ 10 - Will Happen	IR_Risk
● 8 - Single Fatality	○ 8 - Frequently Happens	16
○ 6 - Multiple Major Injuries	○ 6 - Happens	
○ 5 - Single Major Injuries	○ 4 - Infrequently Happens	
○ 4 - Multiple Minor Injuries	○ 3 - Rare	
○ 3 - Single Minor Injuries	● 2 - Very Rare	
○ 2 - Multiple Trivial Injuries	○ 1 - Extremely Rare	
○ 1 - Single Trivial injuries	○ 0 - Never	
○ 0 - No hazard		

Minimise Risk By: Exposed quanity to be kept to a minimum. Approved packaging and methods

○ 10 - Multiple Fatalities	○ 10 - Will Happen	MR_Risk
○ 8 - Single Fatality	○ 8 - Frequently Happens	6
● 6 - Multiple Major Injuries	○ 6 - Happens	
○ 5 - Single Major Injuries	○ 4 - Infrequently Happens	
○ 4 - Multiple Minor Injuries	○ 3 - Rare	
○ 3 - Single Minor Injuries	○ 2 - Very Rare	
○ 2 - Multiple Trivial Injuries	● 1 - Extremely Rare	
○ 1 - Single Trivial injuries	○ 0 - Never	
○ 0 - No hazard		

Comments:

Figure 5. Data entry screen.

hardly better than merely photocopying old risk assessment forms. Instead it encourages the user to re-examine old entries on the database pertinent to the tasks being examined, and to enter and quantify newly identified hazards, particularly site-specific hazards for pyrotechnic and firework displays. It does, however, provide examples on which to base the current risk assessment and outputs data in a concise manner.

Conclusions

The process of assessing the risks from any operation, facility or event is a complex process, but one that ultimately not only helps quantify the risks involved but highlights, sometimes surprisingly, the highest risk operations.

Good analysis of risk also leads to identification of control measures, and thus the basis of operating procedures. However, the risk reductions achieved on paper only are meaningful if these operating procedures are adopted and monitored.

This paper presents a semi-quantified risk assessment protocol based on biased 0–10 scales for both hazard and frequency that we hope will find widespread use within the vast variety of operations throughout the pyrotechnic industry.

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