

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 be-

cause 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 article.

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

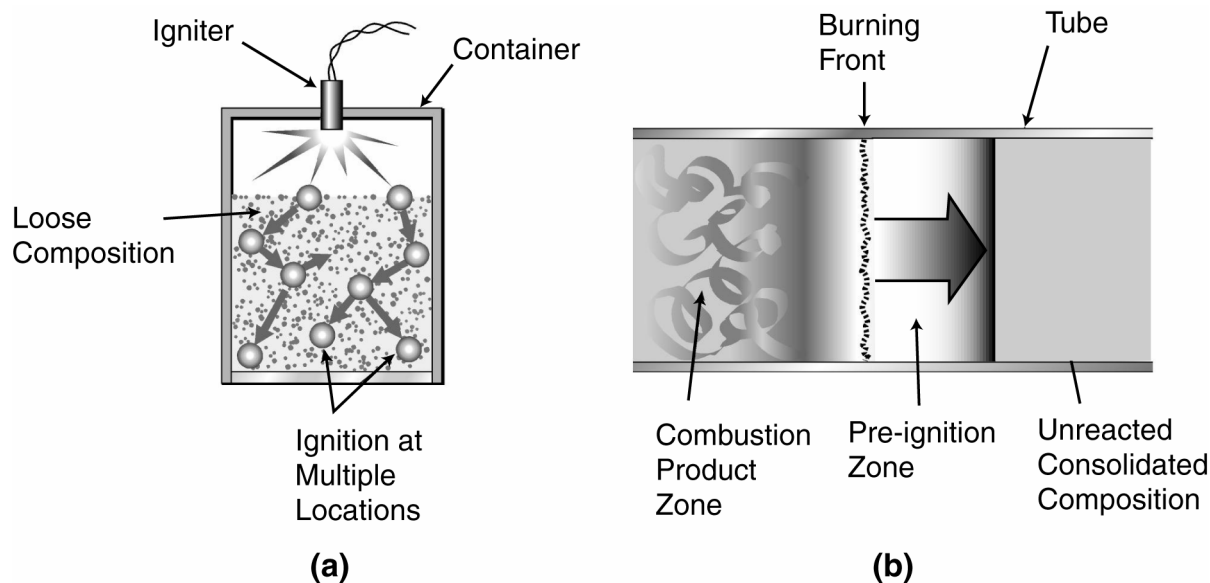


Figure 1. Combustion in the loose and consolidated states.

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.

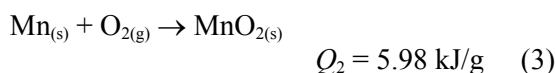
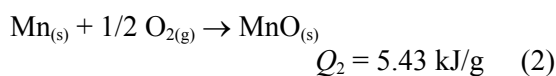
Thermochemistry and Stoichiometry

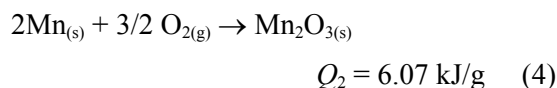
The intrinsic burning rate of a delay composition is mainly determined by the chemical ingredients, their proportions in the composition, and also their thermochemical properties. For example, an oxidiser that decomposes exothermically (such as potassium perchlorate, $\Delta H_r^\circ = -3.7$ kJ/mol 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 $\text{Ba}(\text{NO}_3)_2$). 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:

$$Q_1 = \frac{\Delta H_f^\circ}{mA} \quad (1)$$

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:





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

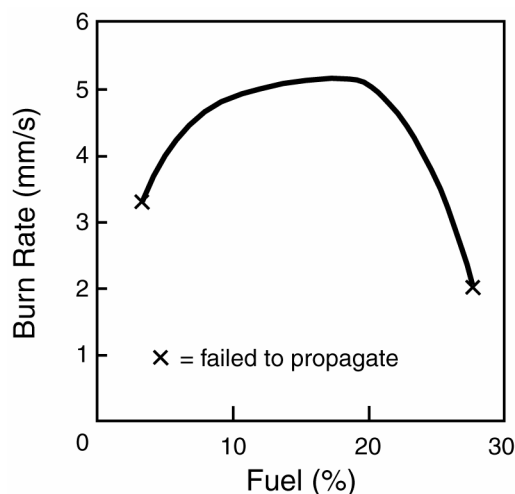


Figure 2. Burning rate vs. fuel content for a binary delay system.

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.

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. This diagram shows the relative percentages of the oxidisers plotted against the per-

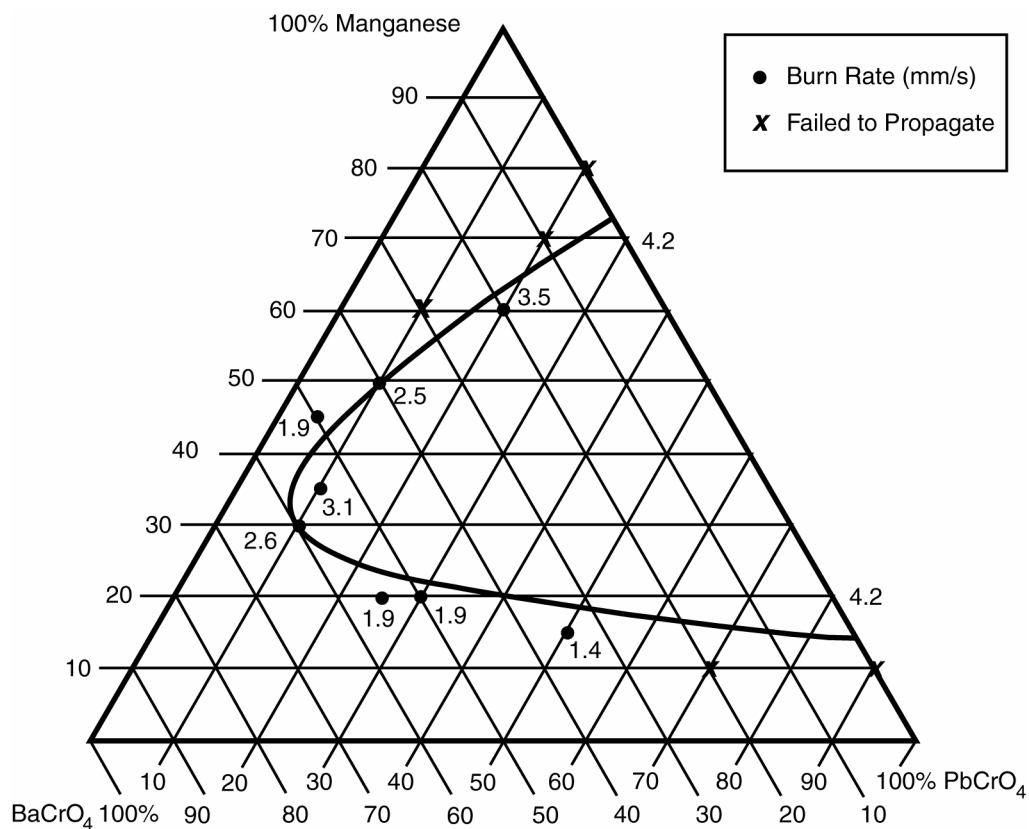


Figure 3. Burning rate vs. ingredients content for a ternary system.

centage 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

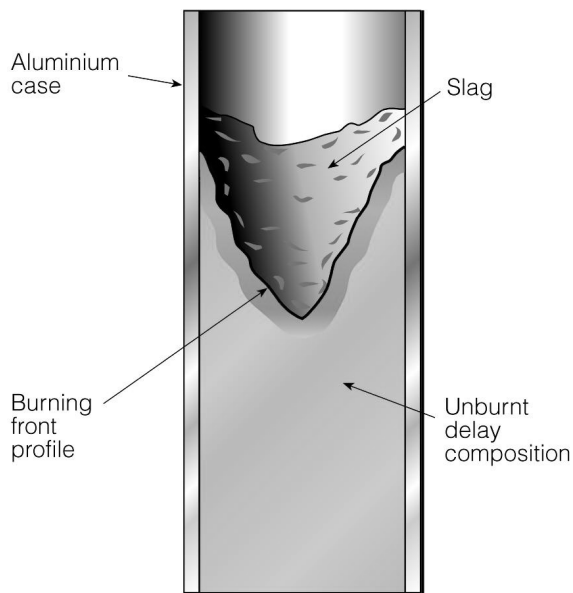


Figure 4. A delay column that has failed due to heat losses.

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.

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.

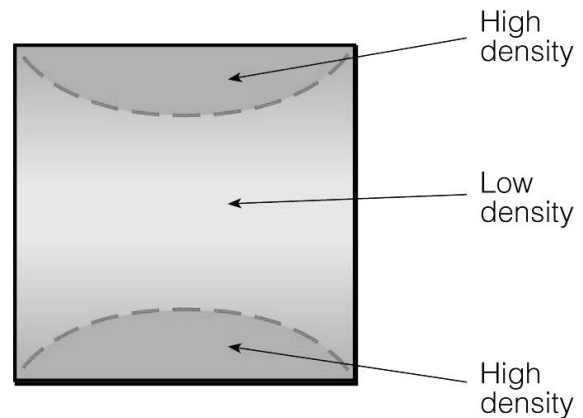


Figure 5. Density variations in a pressed column.

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.

(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), tetranitroxanilide (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),

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

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.

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.

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 com-

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

pounds 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 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:

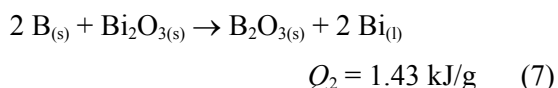
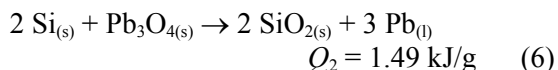


where metal M_1 is oxidised to M_1O by a metal oxide, M_2O , which is, in turn, reduced to its metallic form M_2 . Over the years, many delay compositions have been developed for particu-

Table 4. Burning Rates of a Tungsten Fueled Delay Composition System.

Ingredient	Percentage in Composition					
	27	33	49	63	80	58
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

lar applications and some likely chemical reactions of the simpler systems are:



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, B₂O₃. 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 en-

vironment), 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]

$$R = R_o P^n \quad (8)$$

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 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.

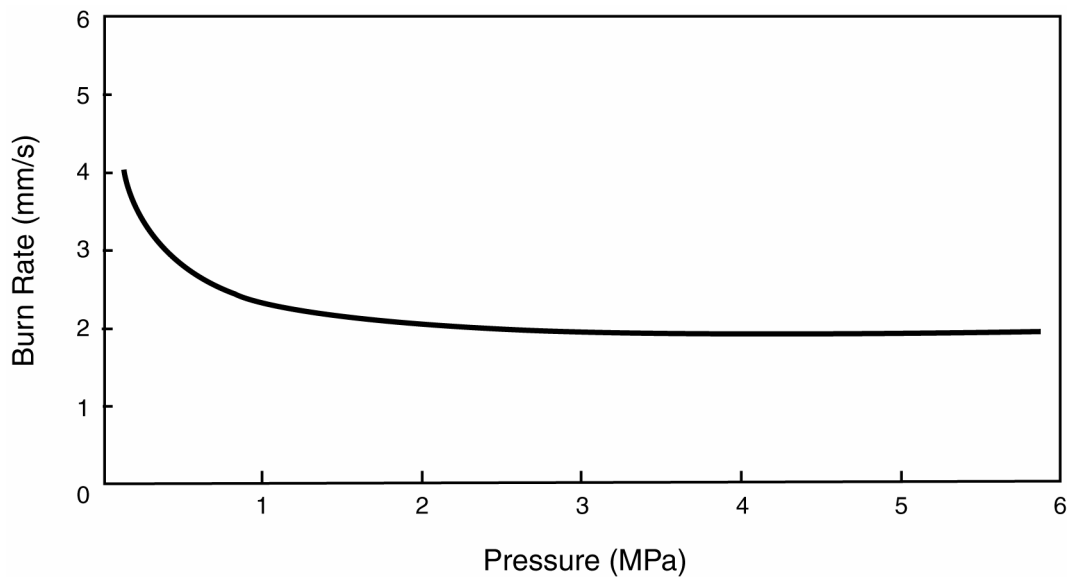


Figure 6. Burning rate vs pressure curve for B/BaCrO₄.

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 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

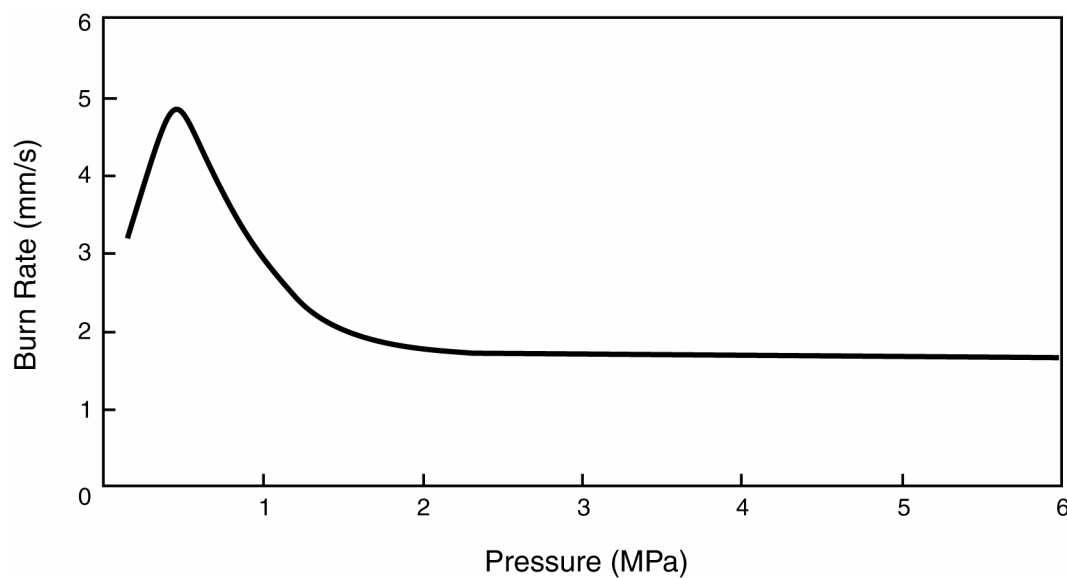


Figure 7. Burning rate vs pressure curve for B/Si/K₂Cr₂O₇.

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.

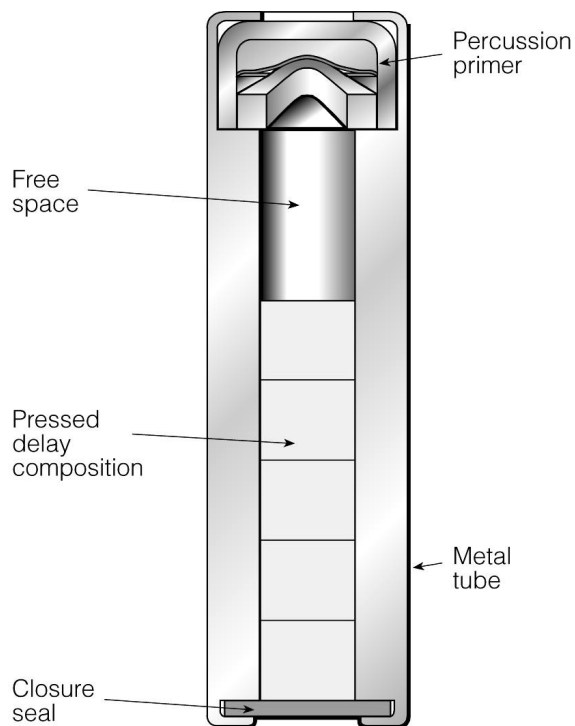


Figure 8. A typical pyrotechnic delay element.

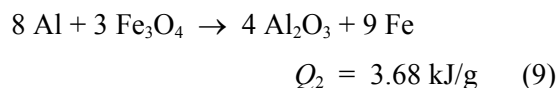
A simple gasless delay element consists of a metal tube into which the delay composition is directly pressed at high compaction pressure to form a column. The tube is fitted at the ignition end with an ignition source (a percussion primer in the illustrated case in Figure 8). Beneath this is the free 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.

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:



The characteristics that distinguish a thermite reaction from other pyrotechnic reactions are:

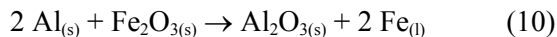
- an almost complete absence of gaseous reaction products after combustion
- a high reaction temperature (typically 2000–3000 °C)
- the formation of a molten slag that can be used to burn, cut or weld

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



Heat of Reaction, ΔH°

$$= \Delta H^\circ (\text{Products}) - \Delta H^\circ (\text{Reactants})$$

$$= (-1675.7) - (-824.2)$$

$$= -851.5 \text{ kJ/mol}$$

It is possible to estimate the maximum theoretical combustion temperature of a thermite reaction using the equation:

$$Q = m S (T_o - T) \quad (11)$$

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

$$298 - T_{max} = -851.5 \times 1000 / (27.2 \times 7)$$

$$\text{therefore } T_{max} = 4770 \text{ K.}$$

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:

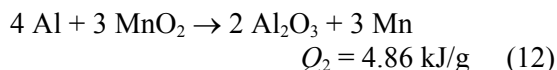
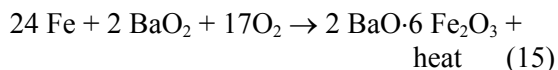
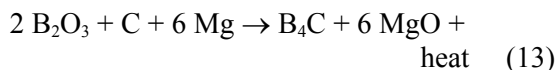


Table 6. Key Characteristics of Some Thermite Fuels.^[16]

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 (%)		Thermal Output (kJ/g)
						Fuel	Oxidiser (Fe ₂ O ₃)	
Al	2054	3000	2.7	Al ₂ O 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 ₂ O ₃	1273.5	12	88	2.48

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:



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 usu-

ally 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 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 syn-

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 ₂ O 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 ₂ O 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 ₂ O ₃	824.2	30	5.1	1538	2861	25	75	3.98
Fe ₃ O 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 ₃ O ₄	718.4	9	9.1	327	1749	10	90	2.00

thetic 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 Fe₃O₄ are easier to ignite than those containing Fe₂O₃. The reason is thought to be related to the crystal structure of the oxide, Fe₃O₄ having an inverse spinel structure of the general classification AB₂O₄.^[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 (MnO₂) in the crystal lattice as a ferritic structure. For example, the ferrite, CuFe₂O₄, can be prepared by heating a mixture of CuSO₄·5H₂O and FeSO₄·7H₂O in the appropriate ratios.^[18] McLain^[19] reports the calorimetrically measured heat of reaction for a 50:50 mix of CuFe₂O₄ and Ti as 5.7 kJ/g, whereas for Fe₂O₃ 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 (MoO₃), tungsten oxide (WO₃) and

lead oxide (Pb₃O₄) 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/MoO₃, Zr/WO₃ and Si/PbO₂.

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 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

Table 8. Explosive Sensitiveness Data for Typical Thermite Compositions.

Type of Thermite Composition (%)	Hazards Assessment Data			
	F of I ^a	T of I (°C)	Friction ^b	Ignition by electric spark
Mg/Fe ₂ O 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-Al/Ba(NO ₃) ₂ (40/60)	50	> 400	100-100-50	Nil at 4.5 J
Si/PbO/Bi ₂ O 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]

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/Bi₂O₃ 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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