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Control of Pyrotechnic Burn Rate

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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 esthetics 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 of the burn rate control factors act 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 flame temperature of a color star is too low, the result can be low light output because there are an insufficient number of electrons reaching excited states. However, conversely, when flame temperature is too high, the result can be bright but washed-out colors because the color producing molecules have thermally decomposed. 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 energy release, and thus to some extent the flame temperature of a star. More directly, burn rate determines the

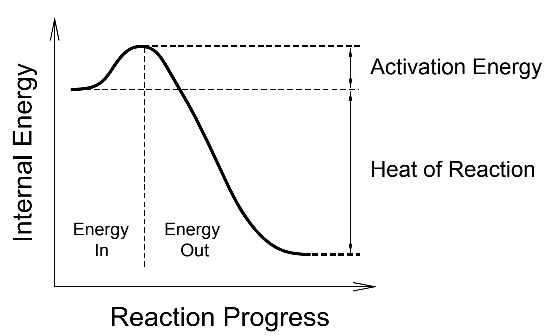

Figure 1. Changes in internal energy as a pyrotechnic composition ignites and burns.

rate of gas production from a propellant, and thus 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 article, 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 article, the minimum energy required for ignition is called the "activation energy" for the pyrotechnic composition, and is abbreviated as E_a. It is the requirement for the input of energy, to ignite a pyrotechnic material that 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.

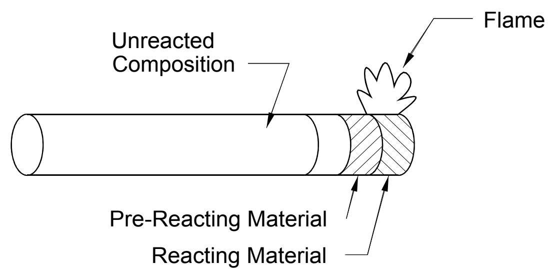

Figure 2. Burning "propagating" along a stick of pyrotechnic composition.

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 which 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, and which can be thought of as a series of thin disks of material. The end disk, designated as reacting material, has ignited as described above. 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 (i.e., it receives more energy than is required for its ignition), then it too will burn. If this process is repeated for each disk of composition, then the burning will propagate through the entire stick of pyrotechnic material.

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

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, i.e.,

(1) $$E_{fb} > E_a$$

The amount of energy fed back equals the heat of reaction times the fraction of energy fed back (F_{fb}), i.e.,

(2) $$E_{fb} = \Delta H_r \cdot F_{fb}$$

Thus the propagation inequality becomes,

(3) $$\Delta H_r \cdot F_{fb} > E_a$$

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 to the 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 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 radiation (infrared) is emitted from the flame (mostly from incandescent particles in the flame) and is absorbed by 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 rates or linear burn rates, with units of either the mass consumed per time (e.g., grams/second) or the distance the flame front progressed per time (e.g., cm/second). In this article, unless stated to the contrary, the term burn rate will mean linear burn rate.

Table 2. Decomposition Energies for a Few Common Pyrotechnic Oxidizers.

Oxidizer	Product	Decomposition Energy (cal/g)	Ref.
KNO_3	K_2O	–1500	4
Fe_3O_4	Fe	–1150	4
$Ba(NO_3)_2$	BaO	–400	4
$KClO_4$	KCl	9	4
$KClO_3$	KCl	87	8
	K_2O	410	8

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 article 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 article 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.

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 energies for a few common oxidizers are listed. (Note: A negative number indicates that an input of energy is necessary, while a positive number means that energy is produced during decomposition.)

Regarding heats 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 heats of reaction for some common fuels combining with oxygen.

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 carbon, 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

Table 3. Heats 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
PVC	—	4400	7
Dextrin	—	4200	9
S	SO_2	2200	9

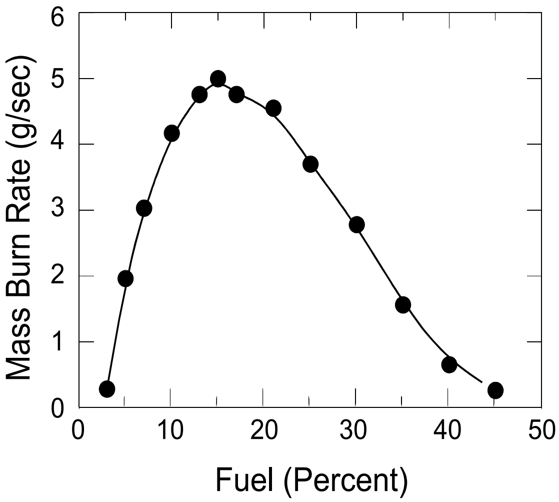

Figure 3. Burn rates for various mixtures of boron and barium chromate.

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 rates are 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 contributed to the production of thermal energy. The activation energy may change because of changes in the heat capacity of the composition and possibly changes in the ignition temperature. 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 rates derived from data reported for mixtures of boron and barium chromate,[10] presented in Figure 3. (Note, however, that this is a case where the maximum burn rate would seem to occur when there is a considerable excess of fuel.)

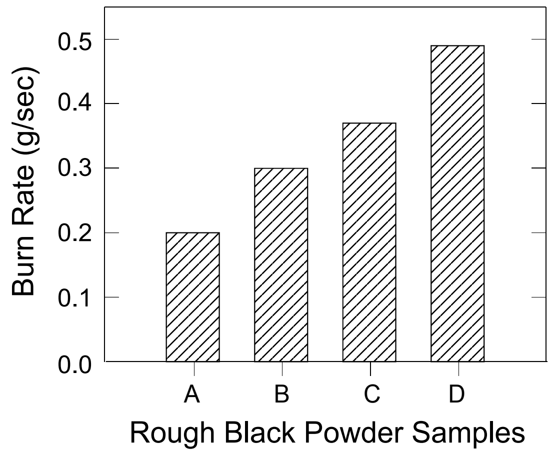

Figure 4. Mass burn rates of samples of rough Black Powder with varying degrees of mixing.

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. 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 rates. Each sample was a loose 1 gram pile of –100 mesh material, 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

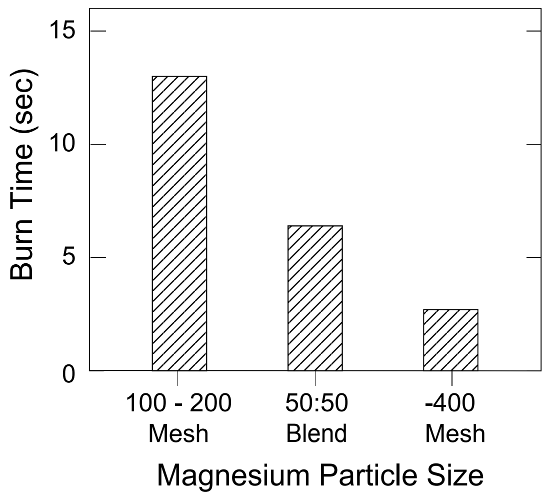

Figure 5. Burn times for flares made with varying magnesium particle size.

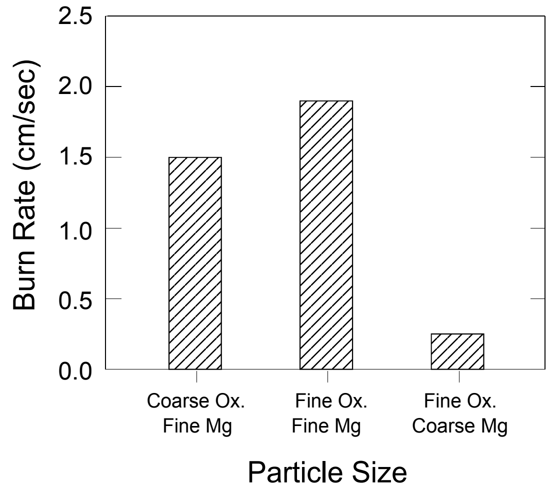

Figure 6. Burn rates for a red flare composition with varying fuel and oxidizer particle sizes.

milled for 8 hours; then dried and crushed to –100 mesh with a mortar and pestle. The average mass burn rates for three measurements of each sample of rough Black Powder are 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 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 increased heats of reaction for smaller particle sizes.

For a demonstration of the effect of magnesium particle size on the burn times of flares,[10] see Figure 5. (Note: The author did not specify the formulation for the flare composition.)

For most pyrotechnic compositions, it is the particle size of the fuel, with their typically high melting points, that 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. These are burn rates for a loose pyrotechnic composition with strontium nitrate (60%), magnesium (25%), and PVC (15%). 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 ranges for the strontium nitrate.)

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 others. Thin flakes also tend to have greater percentages of atoms on the surface. All else being equal, the order, from lowest to highest burn rate, are particles of the following shapes: spherical, spheroidal, granular and flake. As with particle size, it is 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, oxidiz-

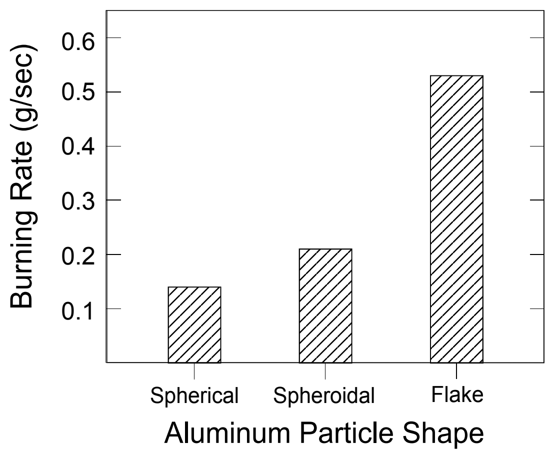

Figure 7. Mass burn rates for a composition using different fuel particle shapes.

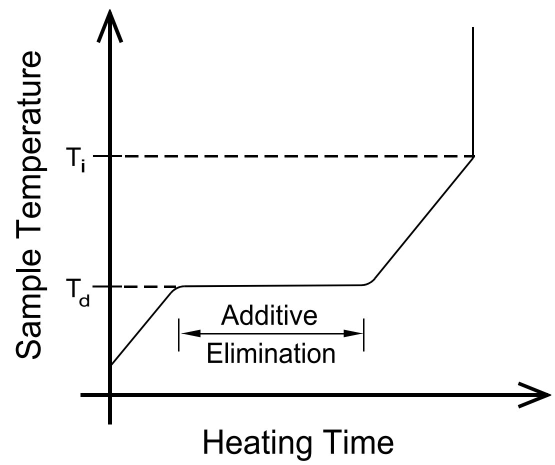

Figure 8. How an additive can act to raise the activation energy of a composition.

ers tend to melt or decompose at temperatures at or below the ignition temperature using different fuel particle shapes.

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 1 cm diameter paper tubes using a constant loading force. The burn times for 3.5 gram samples were measured using a stopwatch, and mass burn rates calculated. Average results from three measurements of each particle shape are presented in Figure 7.

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 which produce sparks; agents which 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 burn rates 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 270 ºC, which is its decomposition temperature (T_d). This is below the ignition temperature (T_i) of the composition, which is probably about 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 a period of time, when 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.)

A quantity of rough Black Powder was prepared by wet mixing, drying, and grinding to –100 mesh. A series of samples were made that

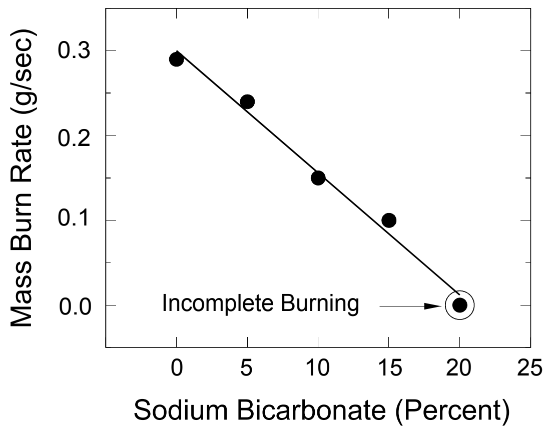

Figure 9. Mass burn rate for rough Black Powder with sodium bicarbonate added.

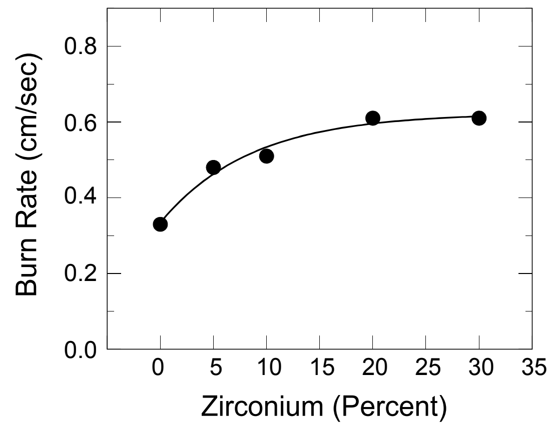

Figure 10. Burn rate for red tracer mix (R328) with zirconium added.

contained various amounts of sodium bicarbonate. The samples were burned by igniting loose 1 gram piles with a hot wire on the side about half way to the top. The times for complete burning were 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.

As an example of how an additive can act to lower the heat of reaction of a pyrotechnic composition, consider the addition of a 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 pound for pound basis, the composition produces less energy. In addition, as the composition burns, the carbonate will consume energy by decomposing, which reduces the heat of reaction still further.

While most additives to pyrotechnic compositions lower burn rate, it is sometimes possible to increase the burn rate of a pyrotechnic composition with an additive. 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 (R328), a significant increase in burn rate results,[10] 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).

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. 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

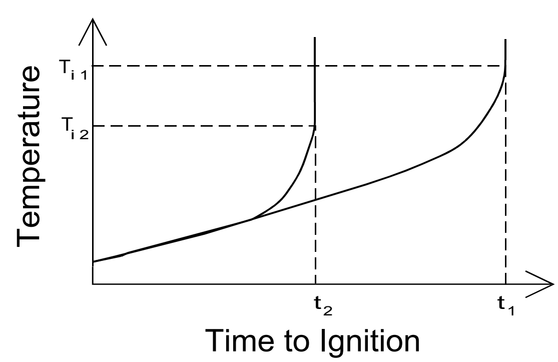

Figure 11. How a burn catalyst produces an increase in burn rate.

dioxide to potassium chlorate will lower its decomposition temperature by 70 to 100 ºC.[11] 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 any tiny sample 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).

A series of samples were made with potassium perchlorate plus potassium dichromate (70% total) and shellac (30%). The amount of potassium dichromate varied from 0 to 4%. Four gram samples of the mixtures were pressed into 1 cm diameter paper tubes, 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

Pyrotechnic burn rates increase 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.

As part of a study to determine the characteristics of visco fuse,[12] a measurement was made of the effect of temperature on its burn rate. In this study, groups of 10 pieces of 12.7 cm 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.

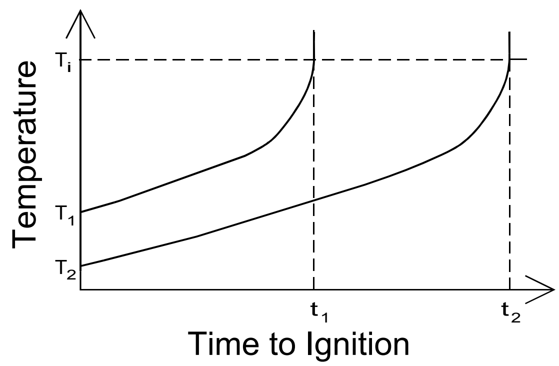

Figure 13. The effect of ambient temperature on burn rate.

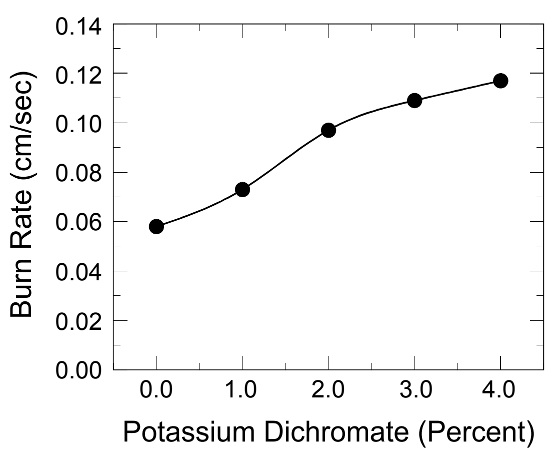

Figure 12. Burn rates of a pyrotechnic composition with varying amounts of potassium dichromate.

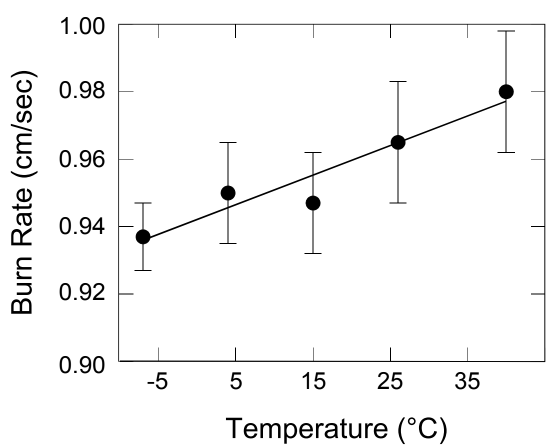

Figure 14. Burn rate of visco fuse as a function of ambient temperature.

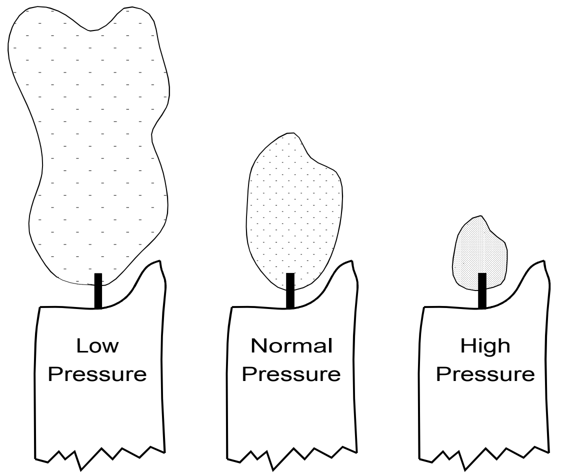

Figure 15. An illustration of the effect of local pressure on a candle flame.

(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 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]

The relationship between burn rate (R, in cm/sec.) and local pressure (P, in atmospheres) can be expressed mathematically as:

(4) $R = a \cdot P^b$

where a and b are constants depending on the pyrotechnic composition. Some values for a and b are given in Table 4.

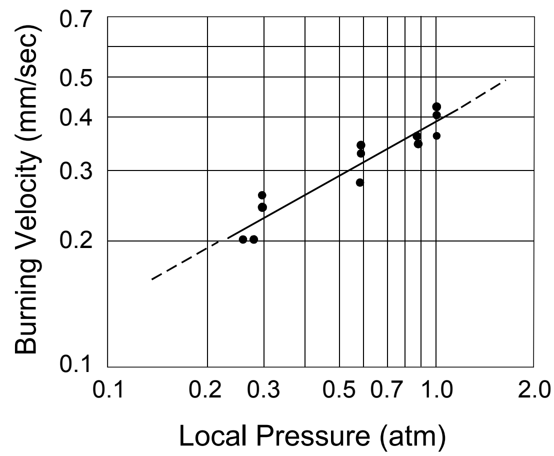

Figure 16. Burn rate of a smoke composition as a function of local pressure.

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 has 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, 0.32 cm 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 by high pressure to form a dense solid mass. The compacted material burned at a rate of about 1 cm/second; 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.

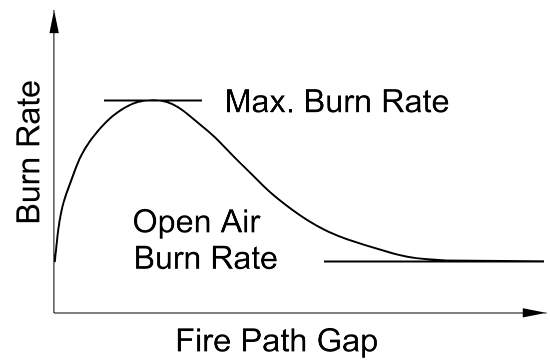

Figure 17. Quick match burn rate as a function of fire path gap.

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 an 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.

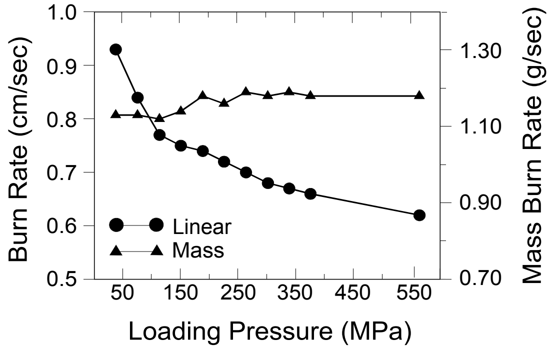

Figure 18. Linear and mass burn rate of Pyrodex® as a function of loading pressure.

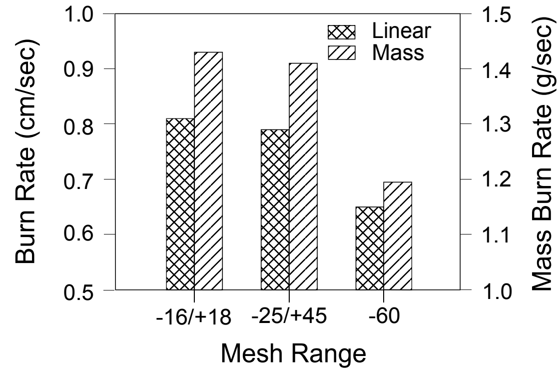

Figure 19. The effect of grain size on the linear and mass burn rate of Pyrodex®.

As an example, consider the effect of increasing loading pressure on the burn rate of granular Pyrodex® (HF-4) when pressed into 1.2 cm tubes.[13] (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 both the average linear and mass burn rate. Measurements were made using groups of three samples at each pressure. Note the significant decrease in linear burn rate. Note further the near constant mass burn rate; this is the result of the density of the pressed composition increasing as it is compacted more tightly by the increased loading pressure.

Presumably it is the collapse of the fire paths between the initial grains of powder that is responsible for the change in burn rate. Thus it may be interesting to consider the effect of using powder with different particle sizes. Figure 19 is a graph of the result of using three different granulations of Pyrodex® compacted into 1.2 cm tubes with a loading pressure of 225 MPa.[13] Note that only the –60 mesh material is significantly different. This might have been predicted, because this is the powder with the smallest and probably widest range of grain size. Accordingly, when compacted, this material should have the smallest and most frequently blocked fire paths.

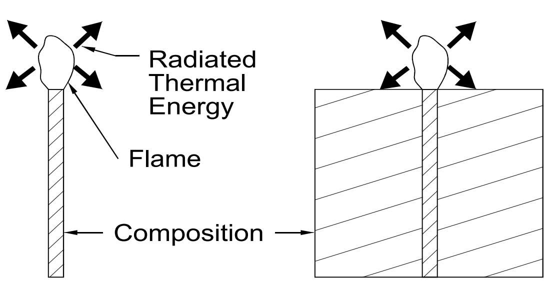

Figure 20. Radiant energy feedback for blocks of pyrotechnic composition.

Conversely to the above examples, 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 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 20. In the case shown on the left, 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 0.8 and 1.6 cm. Four trials of each, resulted in an average burn rate for the larger sample which was about 10% greater; a small but real difference.

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 purposes of this article, 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 crystal lattices. One crystal effect may result from the ability to store some of the energy from 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. Another possible crystal effect, which may be important in some transitions from burning to explosion, is the piezoelectric 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.[14]

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 wind speed. The speed at which a burning pyrotechnic moves through the air will affect the fraction of energy fed back. Consider the case illustrated in Figure 21; in the case of the moving

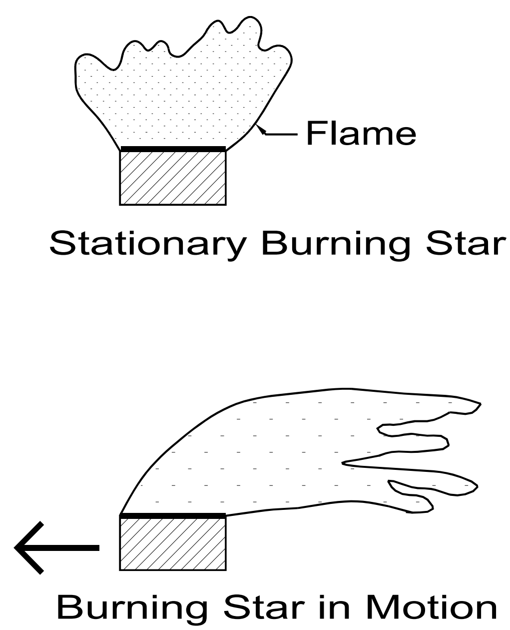

Figure 21. An illustration of the effect of air movement past a star.

star, the flame will be pushed away from the star by the air movement past it. That this occurs is confirmed by Figure 22, which is a photograph of a group of stars propelled through the air from an exploding shell. It is fairly clear that the stars (dark dots) have their flame envelopes (light areas) trailing behind them. The effect of this is to reduce the fraction of energy feedback, and thereby lower 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.

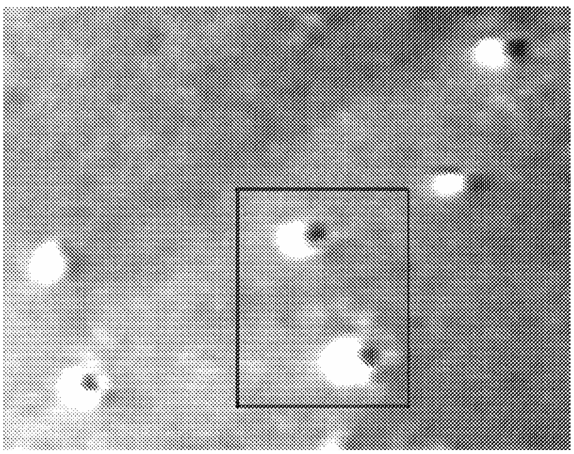

Figure 22. A photograph of high speed burning stars.

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References

1) K.L. and B.J. Kosanke, "The Chemistry of Fireworks (Parts 1–10)", Published Lecture Notes, PyroLabs, Inc., 1992.
2) K.L. and B.J. Kosanke, "Introduction to the Physics and Chemistry of Low Explosives (Parts 1–3)", *Pyrotechnics Guild International Bulletin*, Nos. 68, 69 and 70, 1990.
3) K.L. and B.J. Kosanke, "Parallel and Propagative Burning", *Pyrotechnics Guild International Bulletin*, No. 79, 1992.
4) A.A. Shidlovskiy, *Principles of Pyrotechnics*, Mashinostroyeniye Press, 1964.
5) J.H. McLain, *Pyrotechnics, From the Viewpoint of Solid State Chemistry*, Franklin Institute Press, 1980.
6) T. Shimizu, *Fireworks, From a Physical Standpoint, (Parts I–IV)*, Pyrotechnica Publications, 1981–1989 (English Translation).
7) J.A. Conkling, *Chemistry of Pyrotechnics*, Marcel Decker, 1985.
8) T. Shimizu, *Fireworks, The Art, Science and Technique*, Reprinted by Pyrotechnica Publications, 1988.
9) *Handbook of Chemistry and Physics*, 53rd ed., CRC Press (1972).
10) J.A. Domanico, *Pyrotechnic Design and Performance Factors*, Class materials from Manufacturing Safety and Technology, 1990.
11) H. Ellern, *Military and Civilian Pyrotechnics*, Chemical Publishing Co., 1968.
12) K.L. and B.J. Kosanke, "Burn Characteristics of "Visco" Fuse", *Pyrotechnics Guild International Bulletin*, No. 75, 1991.
13) B. Barrett, Hodgdon Powder Co., personal communication of unpublished data.
14) L.S. Oglesby, personal communication.