

Pyrotechnic Primes and Priming

K. L. and B. J. Kosanke

PyroLabs, Inc., 1775 Blair Road, Whitewater, CO 81527, USA

ABSTRACT

If a pyrotechnic item fails to ignite when intended, it is a failure. It makes no difference that had it ignited; it would have produced a spectacular display or a life-saving distress signal. Primes and priming techniques are important in producing high quality pyrotechnic effects, because it is through their use that reliable ignition can be achieved.

In this review article, after presenting some basic information, propagation energy diagrams are explained and used to discuss the role and manner of functioning of pyrotechnic primes. In the course of the discussion, a number of ignition and propagation problems will be investigated and solutions demonstrated. The article concludes with a discussion of some basic prime formulations and methods for their application.

Introduction

A pyrotechnic prime is a composition applied to the igniting surface of the main pyrotechnic composition, to enhance the probability of successful ignition. Figure 1 illustrates the basic manner of use of a prime layer to aid in the ignition of an aerial signal flare and a fireworks gerb. In the simplest terms, the characteristics of a good prime are that:

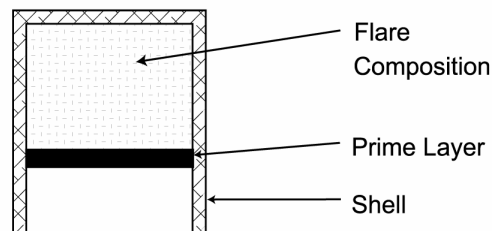
- It is easily ignited (but not so much so that accidental ignition is likely).
- It generates abundant thermal energy upon burning.
- It has an efficient mechanism for energy feedback to unignited composition.

Before the discussion of primes and priming techniques, a review of pyrotechnic ignition and propagation is appropriate (for a more complete discussion, see reference 1). Following this is a discussion of propagation energy diagrams of the type introduced by Shimizu.^[2]

Pyrotechnic Ignition and Propagation

Pyrotechnic materials are said to exist in a “meta-stable” state. That is to say, under normal circumstances they are stable (they do not spon-

Primed Aerial Flare



Primed Gerb

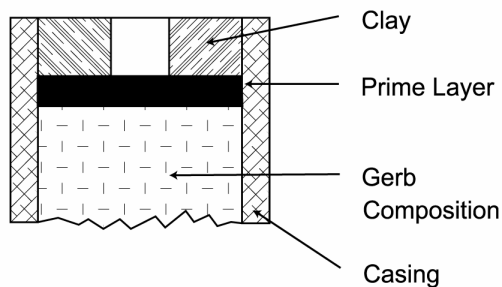


Figure 1. Illustration of a prime layer on an aerial signal flare and a fireworks gerb.

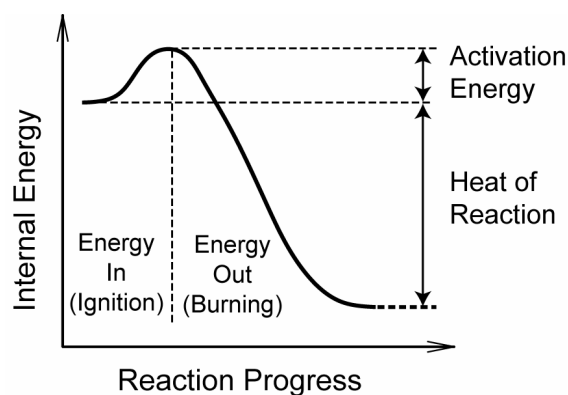


Figure 2. Changes in internal energy as a pyrotechnic composition ignites and burns.

taneously ignite). However, once ignited, the combustion reaction is self-sustaining, producing an excess of thermal energy. Pyrotechnic materials do not spontaneously ignite under normal conditions because the ignition process first requires the input of energy into the composition to raise its local temperature. Once ignited, pyrotechnic combustion reactions can be self sustaining, because there is a net production of energy as the composition burns. This two step energy relationship is illustrated in Figure 2, which tracks the internal energy of a tiny portion of pyrotechnic composition during its ignition and burning. The first step, when energy is added to the composition, is seen as an increase in the internal energy of the material. Within the formalism adopted for this article, the minimum energy required for ignition is called the “activation energy” for the pyrotechnic composition and is abbreviated as E_a . The requirement of an input of energy to cause the ignition of a pyrotechnic material, allows pyrotechnic compositions to be safely made and stored prior to use. If it were not for this activation energy barrier, fuels and oxidizers would ignite on contact. In the simplest of terms, it is possible to think of activation energy as the energy needed to raise a tiny portion of the material to its ignition temperature. The second step in Figure 2, when the burning composition produces energy, is seen as a decrease in internal energy. The net amount of energy produced during burning is the “heat of reaction” for the composition, abbreviated as ΔH_r (In modern parlance, heat of reaction is more properly termed enthalpy of reaction).

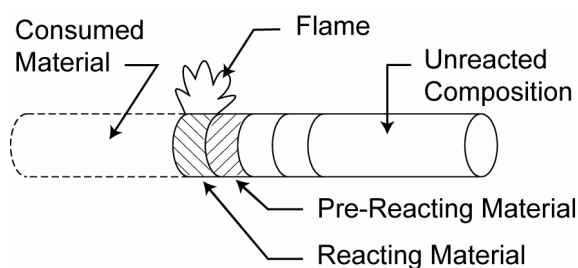


Figure 3. Burning “propagating” along a stick of pyrotechnic composition.

In terms of chemistry, the process of ignition and burning can also be considered as two steps. The first step can be thought of as when chemical bonds are being broken between individual atoms in the tiny particles of fuel and oxidizer. This requires the input of energy (the activation energy). In the second step, new chemical bonds are formed between individual fuel and oxidizer atoms forming the products of the reaction. This bond forming produces energy which flows from the chemical system (the heat of reaction). If the new chemical bonds (fuel to oxidizer) are stronger than the original bonds, more energy is produced than is consumed, and there will be a net production of energy. Note that for pyrotechnic materials, the bonds within fuel and oxidizer particles tend to be weaker than the new bonds formed during burning, and this is the reason these materials produce energy upon burning.

In the simplest of terms, pyrotechnic propagation can be thought of as continuing self-ignition. To illustrate this, consider Figure 3, which is a sketch of a stick of burning pyrotechnic composition, and which can be thought of as a series of thin disks of material. The composition to the far left in Figure 3 has already been consumed by burning. The disk, designated as “reacting” layer, has ignited as a result of having received its needed activation energy. As this layer of material burns it produces energy, most of which is lost to the surroundings. However, some of the thermal energy produced is transferred to the next thin disk, designated as “pre-reacting” material. If the amount of energy delivered to the pre-reacting layer exceeds its activation energy requirement (i.e., it receives more energy than is required for its ignition) then it too will burn. If

this process is repeated for each successive disk of composition, the burning will propagate through the entire stick of pyrotechnic material.

It is possible to quantify the requirement for propagation in what might be called the “propagation inequality”. Propagation within a pyrotechnic composition will continue only so long as the amount of energy fed back to the next layer (E_f) exceeds its activation energy requirement

$$E_f > E_a \quad (1)$$

The amount of energy fed back equals the heat produced (heat of reaction) times the fraction of that energy being fed back (F_{fb})

$$E_f = \Delta H_r \times F_{fb} \quad (2)$$

Thus the propagation inequality becomes

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

So long as the inequality is met, a pyrotechnic composition will propagate. However, if any-time during its burning, the inequality fails to be met, burning will cease at that point.

There are three mechanisms by which energy can be transferred from reacting to pre-reacting layers: conduction, convection and radiation. In conduction, thermal energy, as atomic and molecular vibrations, is passed along from hotter to cooler regions. The factors maximizing conductive heat transfer are those things that increase thermal conductivity, for example having compacted composition, the use of metallic fuels, and the presence of metal casings or core wires around or within the composition. In convection, hot gases penetrate the composition along the spaces between grains (generally called “fire paths”). The factors maximizing convective heat transfer are those things that allow for gas penetration, for example having uncompacted composition and granulated or cracked masses of composition. In radiation, thermal energy is passed from hotter to cooler regions as long wavelength light (infrared). The factors maximizing radiative heat transfer are those things that facilitate the emission and absorption of thermal energy, for example having abundant incandescent particles (solid and liquid) in the flame and using a dark colored or black pyrotechnic composition.

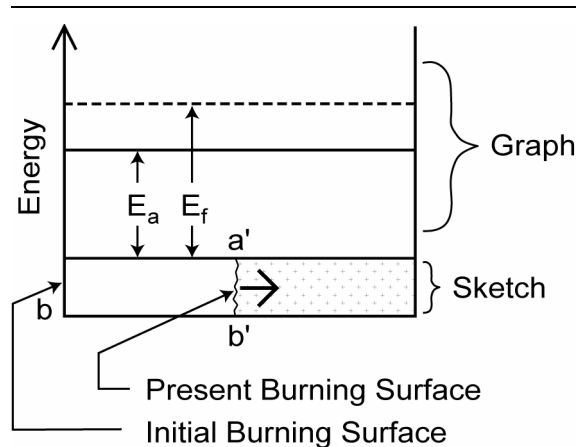


Figure 4. Illustration of Shimizu's Ignition and Propagation Energy Diagram.

Given the relationship in equation 3, it is clear that the factors favoring propagation are: high heat of reaction (much thermal energy produced), a relatively large fraction of energy fed back (efficient energy feedback), and low activation energy (low ignition temperature and low specific heat of the composition). When the propagation inequality is just barely met, burning proceeds feebly and is easy to extinguish. When the inequality is abundantly met, the burning proceeds fiercely and is difficult to extinguish.

Propagation Energy (Shimizu) Diagrams

The nature of ignition and propagation problems and how priming can overcome these problems can be difficult to comprehend. However, a qualitative understanding can be facilitated through the use of propagation energy diagrams, such as used by Shimizu.^[2] These diagrams are a clever combination of a sketch and a graph. See Figure 4. The lower portion of the diagram is simply a sketch of a stick of pyrotechnic composition as in Figure 3. The composition is shown as initially having a burning surface $a-b$, which has burned to the current burning surface $a'-b'$. Above the sketch is a graph of energy as a function of distance along the composition. Here the two terms from the propagation inequality, equation 1, are charted. The energy being fed back, E_f , is shown as a

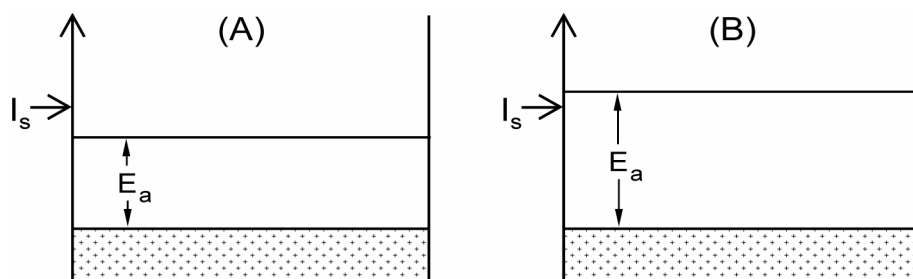


Figure 5. Illustration of varying activation energy requirement for ignition.

dashed line. Activation energy, E_a , is shown as a solid line.

When the process of ignition is discussed, the amount of energy (ignition stimulus) being delivered to the exposed surface of the composition is shown as an arrow from the side, labeled I_s in Figure 5. The source of the ignition stimulus can take any of several forms. It could be direct thermal energy, such as provided by a burning fuse. However, it could also be mechanical energy such as from impact or friction, or electrical energy such as from an electrostatic discharge.

Consider the two cases illustrated in Figure 5. In case **A**, the activation energy required for ignition is relatively low, well below the amount of energy being supplied by the ignition stimulus. In this case, ignition of the composition is assured. (For simplicity, the amount of energy fed back during burning has not been shown.) However, in this case, since the activation energy requirement is quite low, it is possible that accidental ignition could result from unintentionally supplying sufficient energy during the preparation or loading of this composition. In case **B**, the activation energy require-

ment is quite high and exceeds the level of the ignition stimulus. In this case, the pyrotechnic composition will not be ignited by this level of stimulus.

In Figure 6, propagation is considered for three compositions with varying activation energy needs. In each case, it is assumed the ignition stimulus exceeds the activation energy requirement and has not been shown. In case **C**, the activation energy needed is greater than the amount of energy being fed back (solid line is higher than dashed line). Accordingly, even though the ignition stimulus is sufficient to cause ignition of a small portion of the composition, it will fail to propagate once the stimulus ends. As soon as the input of ignition energy has ended, burning must cease.

In case **D**, the activation energy requirement is less than in case **C**. Now, slightly more energy is fed back to pre-reacting layers than is needed to cause their ignition. Accordingly, there will be propagation of burning throughout the length of composition. However, because there is only a slight excess of thermal energy being fed back, the burning will be feeble and the flame will be relatively easy to extinguish.

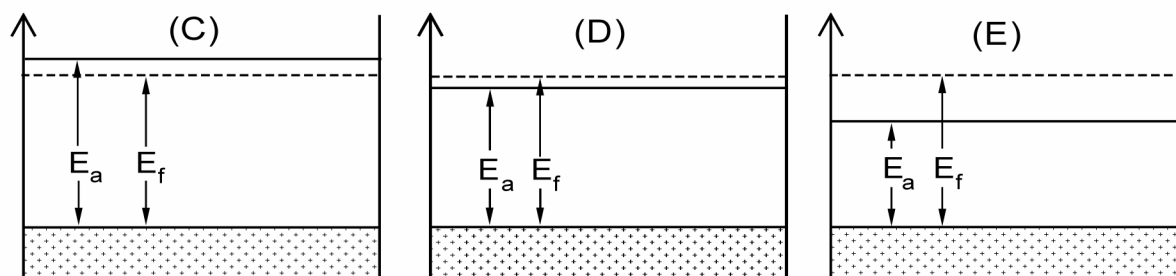


Figure 6. Illustration of the effect of varying activation energy on propagation.

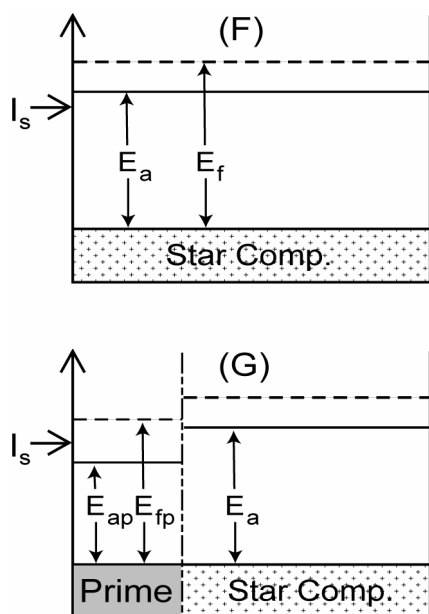


Figure 7. Illustration of how priming aids ignition.

In case E, there has been a further reduction of the needed activation energy, with a relative abundance of energy being fed back to pre-reacting layers. As a result, propagation is assured and burning will proceed vigorously.

Basic Priming Situations

The role of a pyrotechnic prime is to help assure the ignition of the main pyrotechnic composition. Consider the situation illustrated in case F of Figure 7. For the purpose of this example, the pyrotechnic composition might be

for a signal flare or a fireworks star. Based on what was discussed above, if this composition were successfully ignited, it would propagate successfully and burning would be fairly vigorous. (Ample energy would be fed back, E_f , compared with that needed for propagation, E_a .) However, the level of ignition stimulus, I_s , is not sufficient to accomplish ignition, it is less than E_a . In this case it is irrelevant how well the item was capable of functioning had it ignited, since it does not ignite.

Now consider case G, this has the same main composition and ignition stimulus as in case F. However, a prime layer has been included (thickness exaggerated). Note that the activation energy requirement for the prime is less than that of the main composition. Accordingly, the ignition stimulus is now sufficient to achieve ignition. Further, the prime will successfully burn to the interface with the main composition, E_{fp} is greater than E_{ap} (the subscript "p" denotes the prime composition). At the interface between the compositions, burning continues because the energy supplied by the prime, E_{fp} , also exceeds that needed for ignition of the star composition, E_a . In this case, the use of a layer of prime was successful in causing the ignition of the main (star) composition.

There are many times when different pyrotechnic compositions are in contact and when successful performance depends on the burning of one composition to successfully ignite the next. One example would be in a thermite grenade, where the delay column must eventually ignite the thermite composition. Another example would be in a color changing fireworks star,

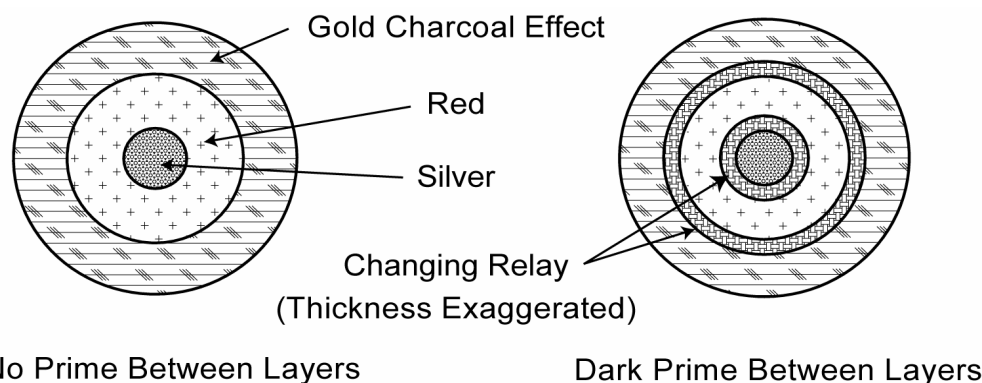


Figure 8. Illustration of the cross section of color changing fireworks stars.

where a burning outer layer of composition must ignite the inner star composition. (See Figure 8.) In fireworks there can also be aesthetic reasons for using a special prime between compositions of color change stars. These special prime compositions are ones that burn with the emission of very little visible light and may be called “dark prime” or “color change relay”. The first aesthetic problem is that when the star burns through the interface, for a brief time, both compositions will be burning. At best this will produce an output that is some mixture of the two intended effects, which may not appear as a crisp and clean change. Further, sometimes neither effect will be successfully produced by the mixed burning compositions.

A second aesthetic reason is that as a practical matter, it is not possible to make color change stars so perfectly and ignite them so consistently that all stars burn through the color change at the very same instant. Human perception is such that a momentary random dimming of a collection of burning stars as they are changing color is less noticeable than having a mixture of stars burning to produce two different colors at the same time. As a result, the effect of using a dark prime layer, even when there is no need in terms of successful propagation, is to create the illusion of a perfectly synchronized and precise color change. Figure 9 is an example of a competition grade aerial shell burst, in which the stars used a layer of dark prime. In this time exposure photograph, note the brief periods of no light emission between the production of the color and comet spark effect.

Some propagation scenarios are illustrated in the diagrams in Figure 10. In case **H**, burning will successfully pass the interface between the two compositions because E_{f1} is greater than E_{a2} . (The subscripts 1 and 2 denote compositions type 1 and 2.) If the order of the two compositions is reversed, which would be the case for a color change from something like willow to silver flitter, a situation like the diagram shown as case **I** results. This time the burning will not pass through the interface between the compositions because E_{f2} does not exceed E_{a1} . The solution to this problem can be to include a prime layer between the two star compositions,

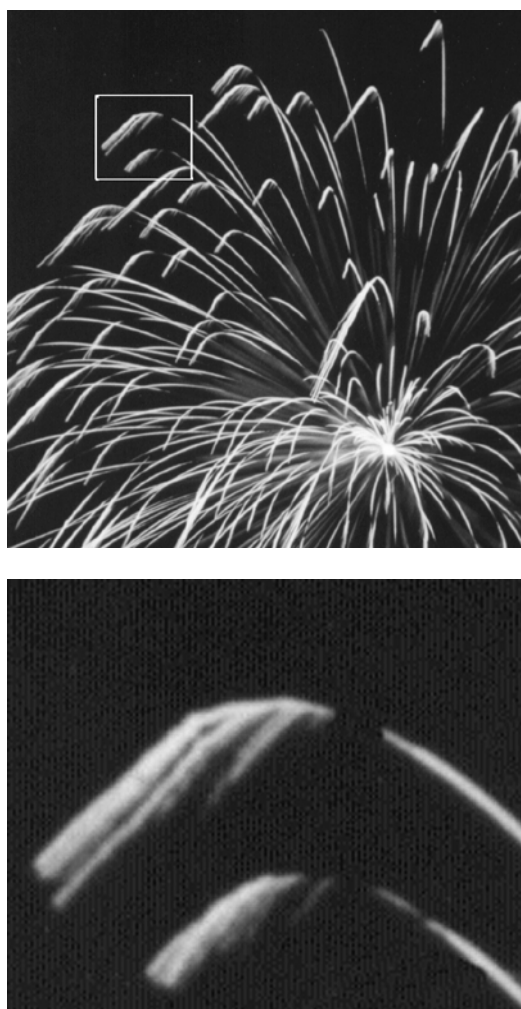


Figure 9. Demonstration of the use of a “dark prime” in a color changing fireworks star.

as illustrated in case **J**. This time the burning composition 2 will ignite the prime layer, $E_{f2} > E_{ap}$, and the burning prime will ignite composition 1, $E_{fp} > E_{a1}$.

Typically for military applications a prime will be specially formulated for each use. However, in some fireworks applications, it is common to create the prime by simply mixing compositions 1 and 2 in roughly equal proportions. When the two compositions are chemically compatible, the resulting mixtures tend to have an activation energy requirement and energy feedback that is approximately midway between the two. (See reference 3 for some information regarding pyrotechnic chemical compatibility.)

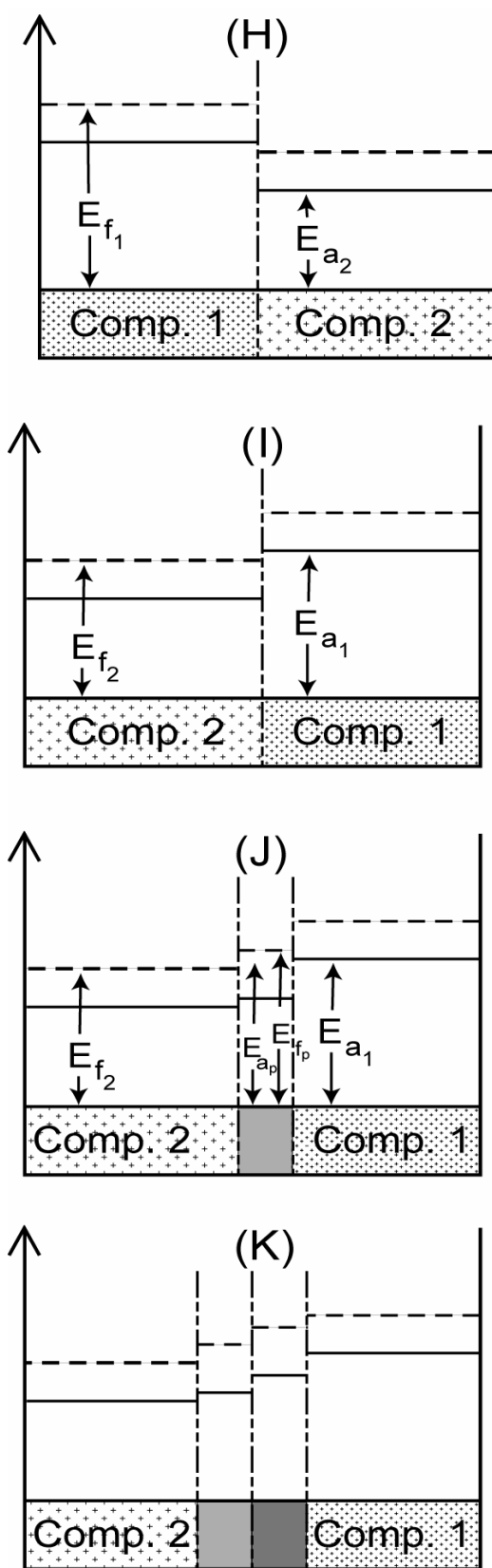


Figure 10. Potential successful and unsuccessful burning of pairs of pyrotechnic compositions.

Probably the most common use of such “composition mixture” primes is in the rolling of color changing stars. However, in some instances the gap between the energy feedback by the first composition and the needed activation energy of a second composition is too large to be reliably spanned through the use of a single intervening prime layer. Such a difficulty can be overcome simply by using more than one prime layer, each formulated to bridge part of the gap. In fireworks this can be accomplished by varying the ratio of the two compositions in the mixture. For example, instead of using about 50% of each composition, one could first use a mixture of 67% of the first composition and 33% of the second. This could be followed by a mixture of 33% of the first composition and 67% of the second composition; such a 2-layer prime is illustrated as case **K** in Figure 10. In principle, the use of successive layers of variously formulated primes can be used to successfully span any gap between E_f and E_a .

Other Propagation Problems

There are a series of other propagation problems that can be visualized through the use of propagation energy diagrams. Although not all of these are problems to be solved through the use of primes, for completeness, they are nonetheless included in this article.

Many pyrotechnic devices are made using solvents added to the pyrotechnic composition. This may be done to activate a binder, to temporarily suppress sensitivity to accidental ignition, to minimize dust production while loading, or to facilitate compaction of the composition to greater density. If use of the pyrotechnic device is attempted while it still contains a significant amount of this solvent, there can be a failure of the item. The basic reason for this is shown in Figure 11, which illustrates the process of raising such a composition to its ignition temperature (T_i). As thermal energy is added, at first its temperature rises with a slope dependent on the rate energy is supplied and the heat capacity of the composition. However, when the boiling point of the solvent is reached, for a period of time the temperature remains nearly constant because the added thermal energy is being consumed in the process of evaporating

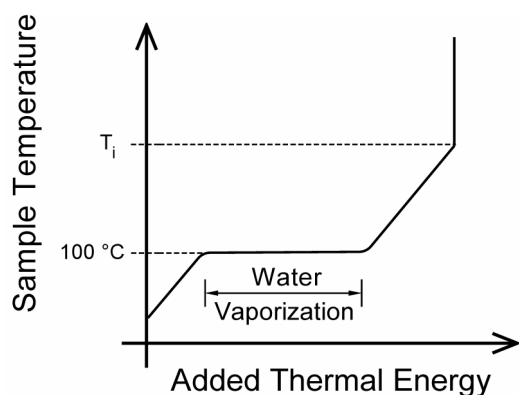


Figure 11. Illustration of the energy consumed by vaporizing water from a moist composition.

the solvent. Once the solvent has been eliminated, the temperature of the composition again rises toward the ignition temperature. Obviously, in this case considerably more thermal energy was required to reach the ignition temperature. In effect, such a solvent containing composition has a significantly higher activation energy requirement, which is dependent on the amount of solvent it contains.

When a pyrotechnic item still containing some residual solvent is used, it can fail to burn completely. This can be illustrated using Figure 12, which is a simplified propagation en-

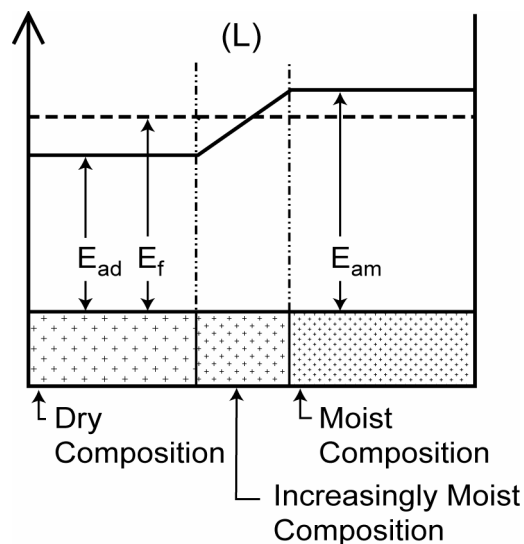


Figure 12. Propagation energy diagram for a progressively moist composition.

ergy diagram for a pyrotechnic device still containing some residual water from the time of its fabrication. The outside of the item (toward the left), where it is exposed to the air, is shown as having dried completely. The inside of the item (toward the right) is shown as being moist as a result of the water added when it was made. In between is a band of composition shown as having increasing moisture content. When this item is ignited, at first, where the composition is dry, it will burn successfully because the energy being fed back exceeds its activation energy requirement. Burning will continue into the zone of increasing moisture content, even though the burning becomes more feeble as the activation energy requirement increases. However, when the point is reached where E_a has risen to equal E_f , burning must cease. Here, the obvious solution is to use no more solvent than necessary and to allow sufficient time for its substantially complete evaporation before its use.

The feedback mechanism for some pyrotechnic compositions is primarily thermal conduction. These tend to be compositions that produce essentially no gaseous combustion products, most notably delay compositions used in military devices such as hand grenades. For such items, a crack through or separation of the delay column can result in a failure to propagate past that point. Figure 13 is a propagation energy diagram illustrating the cause of such a failure. When the delay column is initiated, it

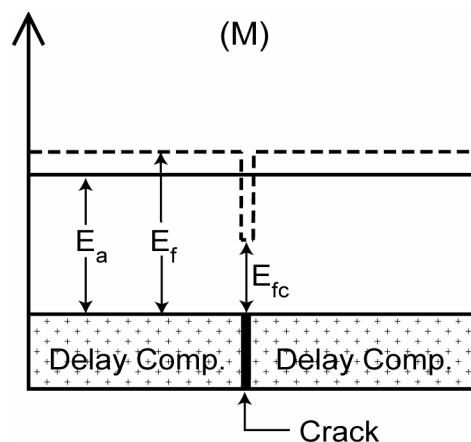


Figure 13. Propagation energy diagram for a delay column with a crack in the composition.

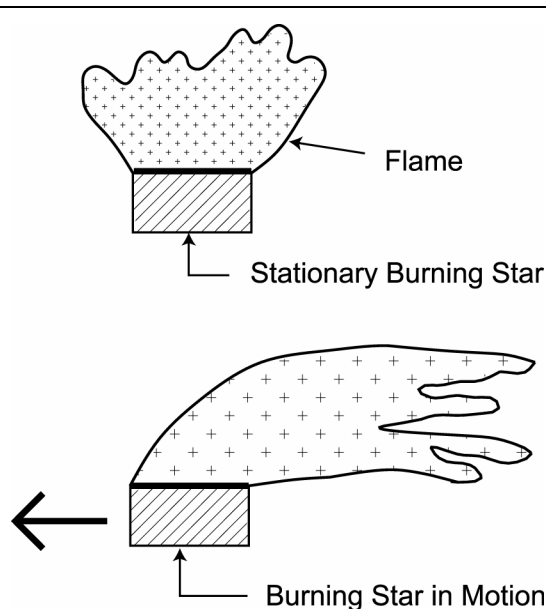


Figure 14. Illustration of a burning fireworks star, when stationary and when moving through the air.

propagates successfully because E_f exceeds E_a . However, at the point of the crack or separation, there will be a substantial decrease in the amount of thermal energy being feedback. This is because the air gap, even if quite narrow, has

significantly reduced thermal conductivity. At this point, when E_{fc} falls below E_a , propagation must cease.

In fireworks, a somewhat similar propagation failure can occur as stars are expelled from a Roman candle or hard bursting aerial shell. In these cases, propagation can sometimes fail because E_f momentarily drops below E_a . Figure 14 is an illustration of two burning stars. In the case where the star is stationary, the flame hovers relatively close above the burning surface of the star. This allows ample opportunity for thermal energy to be feedback from the flame to the burning surface via radiation. However, in the case where the star is moving rapidly through the air, the flame will be cooled because of greater mixing with air and will be deflected away from the burning surface. In effect, the amount of thermal energy being feedback to the burning surface will be reduced. Figure 15 is a photograph taken while measuring the explosive force of a bursting fireworks aerial shell. However, it also documents the way the flame trails behind moving stars.

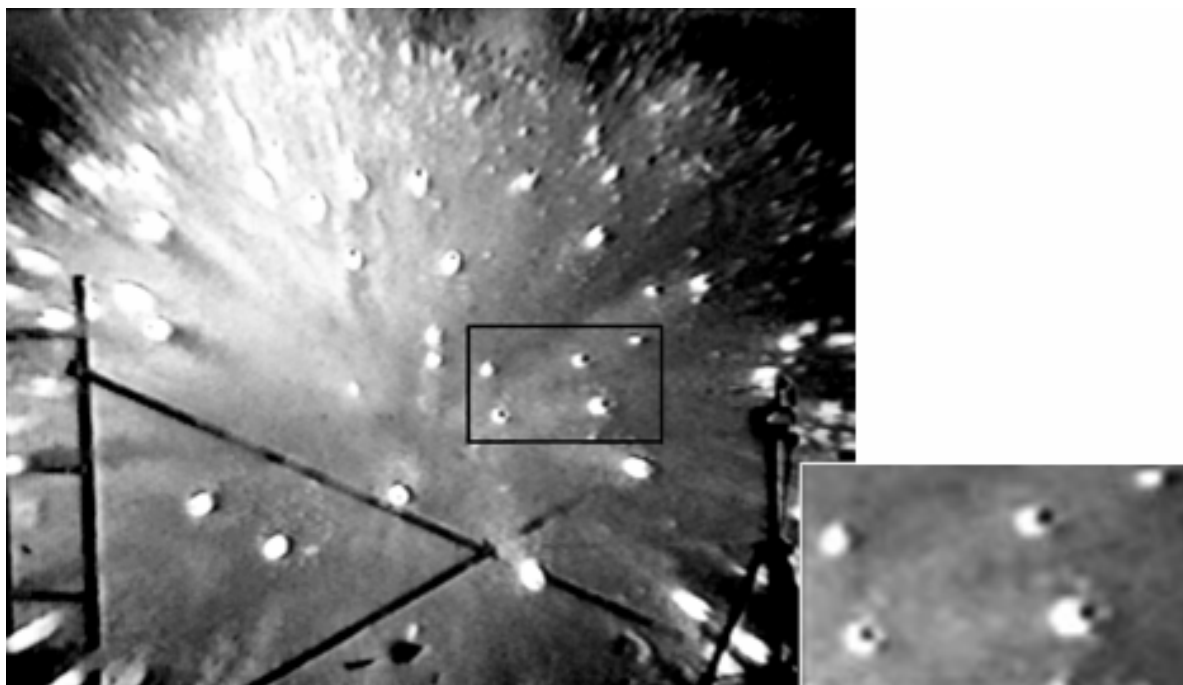


Figure 15. Photo and enlargement taken of a bursting fireworks aerial shell demonstrating the way the flame trails behind the moving star.

Case N in Figure 16 is a propagation energy diagram for an unprimed fireworks star as it is expelled from an exploding aerial shell. (Note that the amount of star burning before the shell burst has been exaggerated.) Initially the star ignites and burns because E_f exceeds E_a . However, as the aerial shell bursts, and the star is expelled at high velocity, E_f drops because the flame now trails significantly behind the star. In this case, because E_f falls below E_a , the star is extinguished. (This effect is sometimes referred to as a star being “blown blind”.) Note that if the star had somehow managed to stay lit, as aerodynamic drag acts to quickly reduce the speed of the star, and as a result the flame moves back closer to its surface, E_f would increase, soon exceeding E_a and approaching its initial value that is to say, the stars would stay lit.

Unlike the previous two examples of propagation failure, this is a case where priming can help. In case O of Figure 16, a layer of prime (thickness exaggerated) has been applied to the star’s surface. In this example, when the aerial shell bursts, again there is a drop in the energy fed back (E_{fp}). However, because it is a characteristic of the prime that there is a larger differential between E_{fp} and E_{ap} , this time E_{fp} does not fall below the activation energy requirement of the prime, and the prime layer continues to burn. If the prime layer is thick enough such that the star slows sufficiently by the time the prime layer is depleted, E_{fp} will have risen sufficiently that burning will continue and the star will be consumed in its intended display.

Prime Formulations

The most widely used pyrotechnic primes are based on Black Powder. Some typical applications are in helping assure the ignition of signal flares, fireworks stars and fountains, special effect gerbs, and fusing systems. When cost is not a major consideration, the Black Powder would be commercially manufactured. Where the prime is to be pressed into place, any of the granulated powders in the range of 20 to 60 mesh may be used. Where a slurry is to be prepared, a fine grained powder such as meal D or fine meal will be combined with a suitable binder before use. In fireworks, typically a less

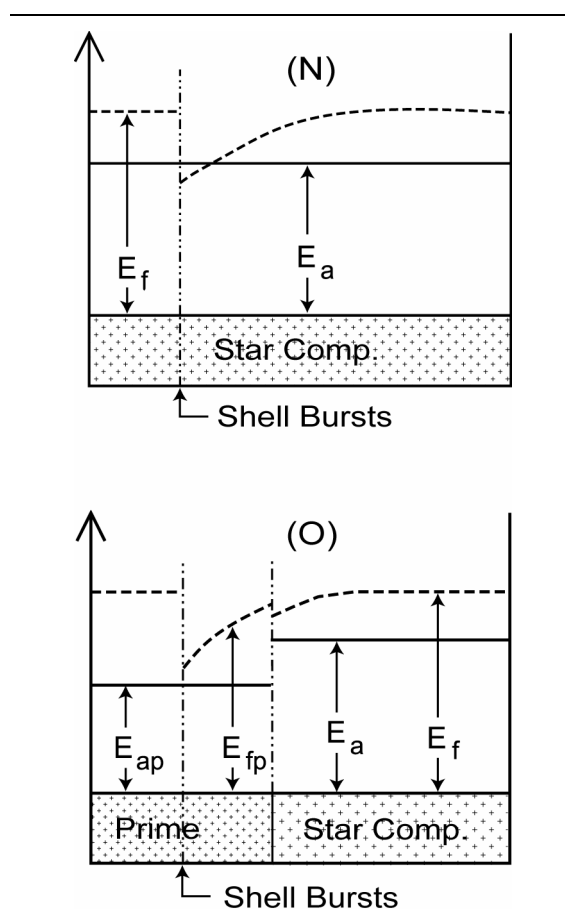


Figure 16. Ignition and propagation energy diagram of unprimed and primed stars as they are expelled from a bursting fireworks aerial shell.

expensive “rough powder” will be used. Rough powder is a handmade powder with the same basic formulation as Black Powder (see Table 1) but without the extensive mechanical processing of Black Powder. As a consequence, rough powder has burning characteristics, some of which are inferior to Black Powder, but fully adequate its for use as a fireworks prime.

There are occasions when the thermal output of Black Powder or rough powder may not be adequate to reliably ignite the main pyrotechnic composition. One such example from fireworks is in the priming of some strobe star compositions. A common method for increasing thermal output is the addition of a high energy fuel, such as fine mesh aluminum, to the basic rough powder prime. The choice of aluminum will be effective in increasing the heat of reaction of

Table 1. Prime Formulations (without listing the binder used).

Ingredient	Rough Powder	Enhanced Rough Powder	Potassium Perchlorate Based	Enhanced Perchlorate Based	Dark Prime	Alternate Dark Prime
Potassium nitrate	75	75	—	—	75	78
Potassium perchlorate	—	—	70	70	7	—
Potassium dichromate	—	—	—	+5 ^(c)	—	—
Charcoal (very fine)	15	15	10	10	8	12
Sulfur	10	10	—	—	—	—
Antimony sulfide	—	—	—	—	3	—
Red gum (accroides)	—	—	20	20	2	—
Shellac	—	—	—	—	—	10
Silicon (–200 mesh)	—	+5 ^(b)	—	—	—	—
Reference	Common	Kosanke ^(a)	Kosanke ^(a)	Kosanke ^(a)	Shimizu ^[4]	Jennings-White ^[5]

- (a) These particular formulations were developed in about 1980; however, it is not intended to imply that similar or identical formulations had not been previously developed and used by others.
- (b) The amount of silicon powder used can be varied according to the need. Typically 3 to 10% was found to be effective.
- (c) Smaller amounts of potassium dichromate (as little as 1 or 2%) are effective in improving the vigor of the propagation of this prime. Because of the various serious health hazards associated with potassium dichromate,^[6] it is advisable to use no more of this chemical than is necessary to accomplish the need.

the prime, and there are instances where this is sufficient. (The use of fine aluminum also tends to increase the light produced, which can be aesthetically undesirable.) Fine mesh silicon is another fuel that can provide the same increase in thermal output and also improve the efficiency of energy feedback. Upon burning silicon forms molten silicon dioxide (glass). This combustion slag can aid in the conduction of thermal energy to the yet unignited composition. One place where such a high temperature slag is particularly effective is where the prime is employed to cause the ignition of material that is not in direct contact with the prime. An example is the prime applied to a Bickford type fuse on the inside of a pyrotechnic device, in which a spray of combustion products from the end of the fuse is intended to provide the ignition stimulus for the device. When silicon is used as an additive in the prime, not only will additional energy be produced, but also molten droplets of glass will be included in the combustion products. The “enhanced” rough powder formulation in Table 1 is an example of such a prime. Note that the amount of silicon used in the prime formulation can be adjusted

to meet the need. Note further that the silicon powder has been added to rough powder without reformulating the prime for the maximum production of energy. At the time this formulation was used, this was mostly done for convenience, as a supply of rough powder was already available for other applications, and various amounts of silicon powder could be added to fit the particular need at the moment. The lack of necessity to reformulate the prime tends to demonstrate the efficacy of the prime. However, to some extent, this thermally enhanced prime relies on atmospheric oxygen for complete combustion.

There are times when a nitrate-based prime such as Black Powder is inappropriate; for example when priming a composition including ammonium perchlorate. In this case, when either composition is moistened with water (or more slowly by withdrawing moisture from the air) a double decomposition (metathesis) reaction can occur to form the hygroscopic oxidizer, ammonium nitrate. When this occurs, the application of the prime may prevent the ignition of the device. There are also times when the pres-

Table 2. Prime Formulations.

Ingredient	Starter Mixture ^(a)	Thermite Igniter ^(b)	First Fire ^(c)	Tracer Igniter ^(d)	Magnalium Thermite ^(e)	Hot Perchlorate Prime ^(f)
Potassium nitrate	70	—	—	—	—	—
Potassium perchlorate	—	—	—	—	—	60
Barium peroxide	—	31	—	78	—	—
Iron(II-III) oxide (black)	—	29	—	—	—	—
Iron(III) oxide (red)	—	—	25	—	75	—
Red lead oxide	—	—	25	—	—	—
Charcoal (very fine)	30	—	—	—	—	15
Calcium resinate	—	—	—	2	—	—
Red gum (accroides)	—	—	—	—	—	5
Aluminum (fine)	—	40	—	—	—	—
Magnesium (fine)	—	—	—	20	—	—
Magnalium 80:20 (200 mesh)	—	—	—	—	25	—
Silicon (fine)	—	—	25	—	—	10
Titanium	—	—	25	—	—	—
Zirconium (60–200 mesh)	—	—	—	—	—	10
Reference	Ellern ^[7]	Ellern ^[7]	Ellern ^[7]	Ellern ^[7]	Jennings-White ^[5]	Jennings-White ^[5]

- (a) “Sulfurless Black Powder” is typically bound using nitrocellulose lacquer.
- (b) A high thermal output, relatively easily igniting, modified thermite used as an ignition mixture for normal thermite.
- (c) An easily igniting, high thermal output prime based on Goldschmidt (thermite) reactions.
- (d) Good resistance to high speeds through the air, used to prime tracers.
- (e) The use of 80:20 magnalium overcomes much of the ignition difficulties of normal thermite, allowing its use as a prime.
- (f) Essentially a modification of the potassium perchlorate prime from Table 1 that produces significantly greater thermal output.

ence of sulfur in a prime can be problematic; for example when priming a composition containing a chlorate. In this case, the chlorate and sulfur combination gives rise to concern regarding the sensitivity to accidental ignition. A prime formulation avoiding the use of both a nitrate and sulfur is the potassium perchlorate-based prime in Table 1. This prime is useful in many applications, but it does not offer the same level of burning persistence as Black Powder primes. This can result in problems maintaining the burning of items moving rapidly through the air. When necessary to overcome this problem, a fiercer burning prime will result when a small amount of the burn catalyst potassium dichromate is added to the composi-

tion. However, because of the health risks associated with potassium dichromate,^[6] appropriate precautions must be employed, and no greater concentration of potassium dichromate than necessary should be used.

Finally in Table 1 are two dark prime (color change relay) formulations. The first formulation is fairly traditional. Whereas the second is simpler and avoids the use of antimony sulfide, which may produce sensitiveness problems when priming compositions containing a chlorate. Another group of prime formulations is presented in Table 2 without comment except for the table notes.

Prime Binding

In most instances, it is necessary to attach the prime composition to something, such as a pyrotechnic device or a fuse. To hold the mass of prime together and in place on the item, some form of binding system must be used. Probably the most common method, especially for fireworks, is to add a small amount (typically about 5%) of an aqueous binder to the prime composition. The binder is activated with the addition of water; the prime is applied to the component being primed and allowed to dry. Dextrin (made from corn or potatoes) is the most common aqueous binder used in Western countries, and soluble glutenous rice starch is the most common in the Orient. In the past, gum Arabic was also commonly used, especially in the manufacture of black match and for priming fuses. Recently, several new families of aqueous binders with variable thixotropic properties are being employed, including polyvinyl alcohol, sodium carboxymethylcellulose, and hydroxyethylcellulose. For these binders, the length of the polymer chain (whether manmade or natural) is selected to control their viscosity and thus their thixotropic properties. Such binders can be useful when it is desired to hold the components of a prime in suspension in a slurry and retard their settling out during use.

Water activated primes require fairly long periods to dry, typically several hours and potentially even days. The drying period must be especially long in some applications, such as when there is a chance that water has migrated from the prime into the powder core of a fuse. To some extent drying time can be reduced when a water plus alcohol mixture (typically 50:50) is employed. Another advantage of a water / alcohol mixture is that surface tension is reduced, making it somewhat easier to mix the solvent into the binder and to coat surfaces with the prime. However, it is thought that the use of alcohol may inhibit the effectiveness of some aqueous binders.

With the wider range of chemicals in use today, and especially with metal fuels, there may be concern about the water reactivity of pyrotechnic compositions. (For more information on potentially hazardous chemical combinations, see reference 3.) One effective solution to this

problem is simply to avoid the use of aqueous binding systems. When prime formulations already contain red gum or shellac, typically as fuels, they can also be employed as the binders for these primes when they are activated with a suitable solvent, most commonly an inexpensive alcohol. Both methanol (wood alcohol) and isopropanol (rubbing alcohol) are frequently used. However, methanol vapors are hazardous to breathe, potentially producing optic nerve damage,^[8] and isopropanol typically contains up to approximately 30% water. Thus the best choice for an alcohol is denatured ethanol (grain alcohol). When compositions do not already contain an alcohol activated binder, a small amount of such binder can be added to the formulation. Probably the most commonly employed nonaqueous binding system is nitrocellulose lacquer, usually 5 to 10% nitrocellulose in an acetone solution. Typically, the drying time for nonaqueous binding is shorter than for water activated binding systems, and the nitrocellulose lacquer system is especially fast drying. However, some systems, such as red gum activated with alcohol, form a gummy mass and can be especially slow to dry.

All materials, even crystals, are capable of plastic flow under the influence of a sufficiently high pressure. This plastic flow of material can be effective to bind a prime together and to other materials. When a pyrotechnic formulation contains relatively soft materials like shellac, red gum, asphaltum, or sulfur, the pressures required for plastic flow binding are sufficiently low as to be readily accomplished by pressing, even into paper casings. Obviously, because no solvent is involved, no drying time is required for plastic flow binding.

Prime Application Techniques

Often, especially in fireworks, the main pyrotechnic composition is prepared wet, using a solvent to activate its binder. If the same solvent will dissolve the binder in the prime composition, the simplest method of application is to apply loose dry prime composition to the exposed surfaces of the main composition. In so doing, some of the solvent will migrate from the main composition into the prime composition thus activating the binder in the prime

composition. Accordingly, when the item dries, some of the prime will then be bound to the surface of the main composition. This “dusting” process can be more thoroughly described using the example of “cut stars” in fireworks. Cut stars are prepared by first forming amply moistened star composition into a “loaf”, which is a solid block of hand-compacted composition. This loaf is then cut using the equivalent of a dull knife, first into slices, and then each slice is diced into cubes. To apply the prime to such stars, first the work surface is dusted with a thin layer of prime composition. When a slice of the star composition is cut from the loaf, it is allowed to fall onto the loose prime composition, some of which will stick to its moist surface. Then additional prime composition is dusted onto the top surface of the slice, to which some will adhere. After dicing the slice of star composition into cubes, to the extent practical, prime composition is dusted onto the freshly exposed surfaces of the cubes. Using dusting to prime pyrotechnic compositions is fairly simple and, providing an excess amount of prime has been used, has the advantage of producing a prime surface which tends to readily take fire. This is because the outer most surface of prime is relatively loose, rough-textured and free from any significant buildup of binder (discussed further below). However, dusting suffers from the disadvantage that generally only a small amount of prime can be made to stick to the surfaces; for most items, this is probably only a few percent by weight.

Some pyrotechnic items, such as color changing fireworks stars, as illustrated in Figure 8, are made as a series of layers, like the structure of an onion. In western countries, the layering process is commonly produced by alternating the application of a spray of water (or other solvent) and dry pyrotechnic composition. The spray of water causes the surface of the item to become sticky, providing a ready surface for the dry composition to adhere. For such items, probably the most effective method of applying the final prime coating is simply to conclude the cumulative layering process with some number of layers of prime. (Similarly, the dark prime between the color compositions can be applied in layers.) The use of a layering process has the advantage of allowing any

number of layers of prime to be applied (i.e., any amount of prime to be applied). This can be quite important in some situations; for example, when difficult to ignite and easily extinguished fireworks stars are propelled from hard breaking aerial shells. To maintain their burning, there must be sufficient prime to continue burning until the stars have slowed sufficiently for the star composition itself to be able to remain ignited (as depicted in Figure 16). In these cases, often the outer prime layer may be 10 to 20% by weight of the star. For easy ignition of prime composition applied by layering, it is important that the very last application of dry composition be in excess to what would normally adhere to the surface. This will help produce an outer surface that is rough and mostly free of solvated binder, similar to that described above for prime applied by dusting.

For small completed items and especially fuses, “slurry” priming is often used. In this case, sufficient binder solvent is added to the prime composition to make a thick but flowing slurry. The viscosity of the slurry is controlled by the amount of solvent and the choice of binder (and possibly flow control additives). Viscosity is adjusted to meet the needs of the particular application method, which tends to fall into three categories. In many cases the prime slurry is simply applied by painting using a small brush. Another common method (to apply a more viscous prime slurry) is from a container under pressure, for example using a squeeze bottle such as used for food products like mustard or catsup. This has the advantage of generally allowing the application of a thicker coating of prime than is practical by painting with a brush. The third slurry application method is sometimes used to completely coat the surface of the item or device to be primed. In this case, the item is briefly submerged in the prime slurry, either individually using a forceps (tweezers) to hold the item, or in batches using a coarse screened basket containing the items. Following the dipping process it is common to dust a layer of dry prime onto the exposed surfaces of the items.

Many pyrotechnic devices have the main pyrotechnic composition compacted using a press. Examples of such items are signal flares, tracers, whistles, fountains, drivers, etc. For

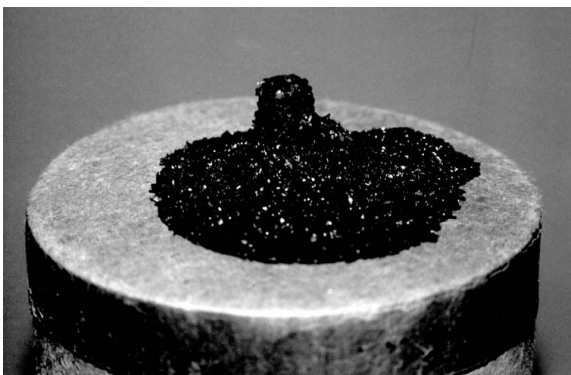


Figure 17. Examples of fuse priming methods with greatly differing probabilities for successful ignition.

these items, it is often convenient to apply the prime layer using compaction (plastic flow binding). In these cases, one or more increments of prime composition are used in the pressing of the item, such as illustrated in Figure 1 for an aerial flare or gerb. For devices made using compaction, this is probably the most common prime application method.

Regarding prime application methods, there are a few additional subjects that should be considered that can greatly affect ignitability. Figure 17 has photographs of two fireworks aerial shells with their Bickford-style timing fuses primed. The shell in the top photo has had a layer of prime painted over the end of the fuse. The shell in the bottom photo has had larger amount of prime applied using a squeeze bottle, then the prime was pressed lightly into a bed of loose granular Black Powder, some of which then adhered to the prime surface.

All else being equal, the larger the primed surface area, the greater the probability it will successfully be ignited by any given ignition stimulus. The reason is simply one of probability. If all locations on the primed surface have

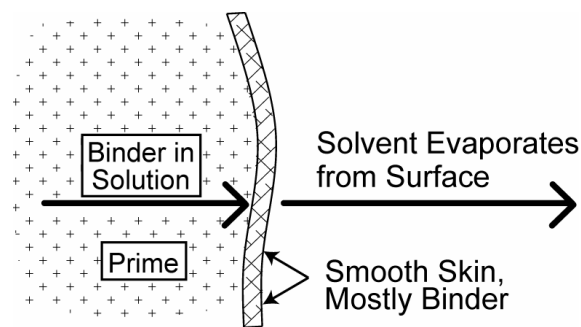


Figure 18. Illustration of the formation of a "skin" of mostly binder on the surface of prime.

an equal chance of being ignited, the probability of ignition increases as the number of locations (surface area) increases. In the upper photo in Figure 17, the total prime surface area is approximately $\frac{1}{4}$ square inch (1.5 cm^2), while that in the bottom photo has approximately 8 times more primed surface.

The surface texture of the prime coating is also important. Generally, if the surface is smooth and hard, such as pictured for the prime layer in the upper photo of Figure 17, ignition will be more difficult than if the surface is rough, such as for the prime layer in the lower photo. With a rough surface, the tiny exposed points will raise more quickly and to higher temperatures than the bulk of the prime coating. Accordingly, these points are more likely to take fire and cause the rest of the prime to ignite, even when the amount of energy supplied would not otherwise have been sufficient.

Another potential surface problem for prime compositions applied wet with solvents, is that during the drying process a thin layer of binder can form on the surface. As illustrated in Figure 18, this can occur because, as the solvent migrates to the surface, it carries dissolved binder with it. Then as the solvent evaporates, the binder (and other soluble components) are left behind on the surface. This collection of binder can produce a surface that is quite resistant to ignition, both because of its chemical composition and because it can be quite smooth. The likelihood of experiencing this problem can be reduced if a minimum amount of solvent is used, and if the surface is dusted with dry prime composition or granular Black Powder.

Alternatives to Priming

One alternative method applies to Bickford style fuse. It is more common to “cross match” such fuse as shown in Figure 19, than it is to apply a coat of prime composition. In this case a hole has been punched through the fuse, intersecting the powder core of the fuse. Inserted into the hole is a thin piece of black match (cotton strings impregnated and coated with Black Powder). In this case, if any point on the surface of the black match is ignited, quickly the entire black match is consumed and the powder core of the time fuse is ignited.

In some cases, the main pyrotechnic composition of an item itself has ignition and burning properties that are similar to prime compositions. If that is the case, there is no need for the application of a prime to its surface to help insure ignition. Examples of some pyrotechnic compositions that will likely have properties that are sufficiently prime-like are: rough powder-based spark-producing compositions, most fireworks glitter compositions, and chlorate-based colored flame compositions. However, as with prime compositions, consideration must be given to the physical condition of its surface. To achieve successful ignition, rough textured surfaces are preferred to those that are hard and smooth.

Conclusion

Many failures of pyrotechnic items and devices are the result of the inability to cause their ignition at the time of their intended use. Properly formulated and applied pyrotechnic prime compositions when present on the ignition surface can significantly improve the probability of successful ignition. Prime compositions are those that: are easily ignited (have a low activation energy requirement), but not so easily ignited that accidental ignitions are likely; upon burning, produce abundant thermal energy (have high heats of reaction); and have efficient means of feeding thermal energy to the main pyrotechnic composition.



Figure 19. Example of a fireworks aerial shell with a “cross matched” time fuse.

References

- 1) K. L. and B. J. Kosanke, “Ignition and Propagation”, *Journal of Pyrotechnics*, No. 6 (1997) pp 17–29. Also in *Selected Pyrotechnic Publications of K. L. and B. J. Kosanke, Part 4 (1995 through 1997)*, Journal of Pyrotechnics, 1999.
- 2) T. Shimizu, *Fireworks from a Physical Standpoint*, Pyrotechnica Publications, 1981, pp 16–21.
- 3) C. Jennings-White and K. L. Kosanke, “Hazardous Chemical Combinations”, *Journal of Pyrotechnics*, No. 2 (1995) pp 22–35. Also in *Selected Pyrotechnic Publications of K. L. and B. J. Kosanke, Part 4 (1995 through 1997)*, Journal of Pyrotechnics, 1999.
- 4) D. Bleser, *Round Stars and Shells*, American Fireworks News, 1998, p 48.
- 5) Private communication c.a. 1990. Also in K. L. and B. J. Kosanke and C. Jennings-White, *Lecture Notes for Pyrotechnic Chemistry*, Journal of Pyrotechnics, 1997.
- 6) M. Rossol, “A Brief Survey of Chromium Toxicity”, No. 13, *Journal of Pyrotechnics* (2001) pp 61–62.
- 7) H. Ellern, *Military and Civilian Pyrotechnics*, Chemical Publishers, 1968, pp 378–381.
- 8) Merck Index, 11th ed., Merck and Co., 1989, p 939.