CHAPTER 7

High Energy Materials in Pyrotechnics

7.1 Introduction

Common man understands rather simplistically that "pyrotechnics" means fireworks. It is generally known that the first people to develop fireworks were the Chinese more than 1000 years ago. The Chinese were experts in the field of pyrotechnics, and as early as the tenth century they had developed rockets. As mentioned in Chapter 1, the English scientist Roger Bacon made a quantitative study of gunpowder during the thirteenth century, and the use of gunpowder as a propellant for cannons was prevalent in Europe in the fourteenth century. When the application of pyrotechnics (meaning the art of making and using fireworks) underwent a transition from civilian use to military use, enormous efforts to search for suitable chemicals and innovation in formulation and processing led to significant progress in the field of pyrotechnics.

7.2 Applications

Let us consider the following scenario. A multistage rocket takes off either for a military or for a space mission. First-stage propulsion is only possible if the propellant is suitably ignited by an igniter, which is basically a pyrotechnic composition. In the case of one-stage, small-size rockets, it may be a cartridge containing gunpowder of certain charge weight and granular size. The higher version of the propulsion may engage an igniter containing a pyrotechnic mixture of magnesium, potassium nitrate (KNO_3), and a binder.

The very success of the mission depends on the correct formulation, charge weight, and granular size of the igniter. Examples include the following:

1. An igniter composition for a double-base rocket propellant is mainly based on gunpowder. The design of the igniter (quantity, particle size, shape of the container containing the igniter) depends on the propellant characteristics, and many trials need to be conducted to ensure the propellant-igniter matching. The gunpowder is housed in a cambric cloth bag and placed in the port (annular) area of the propellant grain.
2. A common igniter composition for a composite rocket propellant consists of an oxidizer, a metallic fuel, and a binder (e.g., boron/KNO_3/binder). The igniter composition is housed in a metallic tube, which easily ruptures on initiation of the igniter, spreading the flame throughout the port area of the propellant. There often

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arises a need to introduce a delay of a certain fixed period (varying from milliseconds to seconds) to actuate a device, which may be a detonator or a propulsive system. A delay cartridge containing certain pyrotechnic composition helps to achieve this. The formulation of the composition must be extremely precise and calls for thorough knowledge and experimental trials involving various pyrotechnic ingredients. A typical delay composition follows is barium chromate ($BaCrO_4$)/antimony trisulfide/potassium perchlorate.

In certain war scenarios, it becomes necessary to destroy the enemy targets by sheer heat rather than explosion. Incendiary ammunitions used for this purpose are basically pyrotechnic compositions and use pyrophoric (ignites when comes into contact with air) ingredients such as zirconium. A typical incendiary composition based on zirconium is zirconium/crepe rubber.

During night warfare, it often becomes necessary to illuminate the enemy territory using illuminating pyrotechnic compositions with a specified illuminating time and intensity to the tune of several thousands or millions of candelas. A typical illuminating composition is magnesium/sodium nitrate ($NaNO_3$)/resin (binder).

Signaling plays a crucial role in any warfare and during emergencies in peace time. (Signaling pyro compositions were launched in large numbers when the *Titanic* was sinking during night more than a century ago.) Pyrotechnic compositions with varying signaling implications were developed a long time ago and are still in use. Typical signaling compositions include

- Magnesium/strontium nitrate (Sr(NO3)2)/resin
- Magnesium/$NaNO_3$/resin

Pyrotechnic compositions are also used to track a target in air. They are also known as "tracer compositions." A typical tracer composition is magnesium/$Sr(NO_3)_2$/$NaNO_3$/resin.

In tactical warfare, decoy flares are still being used to decoy the heat-seeking enemy missiles and protect the aircraft from which flares are launched to divert the missiles. The pyrotechnic composition of the flares fakes the signals (mainly infrared (IR)-based signals) of the aircraft. A typical decoy composition is magnesium/Teflon/Viton.

Several pyrotechnic compositions produce smoke for visual obscuration (some special compositions also produce smoke that is impervious to IR radiation) or signaling (using smokes of specific colors). An example is red phosphorous/KNO_3/resin.

It is interesting to note that certain pyrotechnic compositions have been developed either for signaling or distraction purposes. For example, a certain composition may create the sound of an aircraft to confuse the enemy.

7.3 Basic Principles of Pyrotechnics

7.3.1 The Chemical Components of Pyrotechnics

The basic chemical ingredients of pyrotechnics are an oxidizer, a fuel, a binder (in most of the cases), and often a chemical or mixture of chemicals added to give various effects as seen in Section 7.2. At times, the term "pyrotechnics" is loosely used even in the case in which there is no burning involved. For instance, a smoke composition to produce smoke may involve a compound such as titanium tetrachloride, which on hydrolysis gives intense smoke, and such a composition is also categorized under pyrotechnics.

7.3.1.1 Oxidizers

Pyrotechnic reactions are mostly solid–solid reactions. All oxidizers used are solid ones in the form of fine powder, and the particle size of the oxidizers to be used should strictly fall within a specified range. Most of the oxidizers are salts of metals such as chlorates (e.g., potassium chlorate), chromates (e.g., $BaCrO_4$), dichromates (e.g., potassium dichromate), nitrates (e.g., KNO_3), and oxides (e.g., barium peroxide). All of these salts evolve oxygen during decomposition, which is used to oxidize the fuels. Halogens are known to be good oxidizing agents; therefore, compounds such as Teflon (C_2F_4 polymer) are used effectively in certain pyrotechnic compositions as oxidizers. While choosing an oxidizer for certain pyrotechnic compositions, the following factors should be carefully considered:

1. Energetically, the oxidizer must have an acceptable heat of decomposition. If the value is too high, then the high exothermicity may result in the explosion of the pyrotechnic composition. If it is too low, then the low heat output may not even ignite the pyrotechnic composition or the rate of burning may be quite low.
2. Most of the oxidizer salts used contain alkali metals (e.g., KNO_3) or alkaline earth metals (e.g., $Sr(NO_3)_2$) as cations because these metals are poor electron acceptors (rather excellent electron donors); hence, they will not react with metallic fuels such as magnesium or aluminum. For example, we can never expect a reaction such as

$$2Na^+ + Mg \rightarrow 2Na + Mg^{2+}.$$

3. Because ingress of even a very small amount of moisture content plays havoc with the performance of pyrotechnic compositions (leading in extreme cases to fire or explosion), the oxidizer must have very low hygroscopicity. The strict adherence to humidity control during the processing of pyrotechnic compositions is due to the same reason.
4. The chosen oxidizers should be low in toxicity and should not be too sensitive to friction and impact to ensure safety of personnel during processing, transport, and storage.

7.3.1.2 Fuels

The fuels used in pyrotechnics are powdered elements (either metals or nonmetals) that provide sufficient energy on oxidation. While choosing a fuel–oxidizer combination, one should carefully assess the quantum of heat output (that determines the flame temperature) and the nature of the products. Metallic fuels are used where there is a need for high heat output and hence high flame temperature. For example, in illuminating compositions, a high flame temperature is a must to ensure intense light emission. Magnesium is one of the favorite candidates in many illuminating compositions because the heat of oxidation of magnesium is very high, resulting in the formation of incandescent magnesium oxide (MgO) particles that help in the highly intense light output. Conversely, metals such as magnesium cannot be used in compositions in which heat output has to be low, as in colored smoke compositions using organic dyes. High heat output will decompose the dyes, defeating the very purpose of the colored smoke production. In such a composition, low-calorie fuels such as sugars can be used.

7.3.1.3 Binders

We have seen [refer 6.7.1.3] that binders play dual role in processing composite rocket propellants. They not only give structural integrity to the finished propellant but also act as a source of organic fuel during propellant burning. Binders used in pyrotechnic compositions (both natural binders such as shellac, beeswax, and artificial ones such as polyvinylchloride and epoxy resins) play the following roles:

1. consolidate the composition by increasing the cohesive forces between all of the particles.
2. Binders coat and protect reactive ingredients such as metal powders, which otherwise may easily be oxidized by atmospheric oxygen.
3. Binders reduce the sensitivity of the composition to impact and other sources of stimuli.
4. In some cases, binders modify the burning rate of the final composition.

The binder chosen must be neutral (neither acidic nor basic) and nonhygroscopic to prevent any problems during the production of the pyrotechnic composition or storage. For example, a water-based binder is bound to create problems where magnesium is used because the latter is very reactive with water. Also, the binder should result in the proper consolidation/structural integrity of the final product.

7.3.1.4 Other Ingredients

Retardants are chemicals that are added to certain pyrotechnic compositions to reduce the burning rate below a desired level. These retardants are basically chemicals that absorb heat (endothermic) for their decomposition, such as carbonates, bicarbonates, and oxalates of alkali and alkaline earth metals.

For instance, calcium oxalate (monohydrate) added to the composition endothermically decomposes as follows:

$$Ca(C_2O_4) \cdot H_2O \xrightarrow{\text{Heat}} CaO + CO + CO_2 + H_2O$$

Because the oxalate absorbs heat during this decomposition, it produces the cooling effect and thereby decreases the flame temperature and hence the burning rate of the pyrotechnic composition.

7.3.2 Factors Affecting the Performance of Pyrotechnics

Pyrotechnic reactions are basically solid–solid reactions, and the performance of a pyrotechnic composition largely depends on certain parameters concerning those solids (powders), whether they are oxidizers, fuels, inert fillers, etc. Some of these parameters are presented in the following subsections.

7.3.2.1 Stoichiometry

The reactants involved in a pyrotechnic reaction should be taken in the stoichiometric ratio to achieve a balanced reaction. This will ensure the maximum output of heat and the highest rate of burning. On the other hand, if excess of either fuel or oxidizer is taken, then the net heat output per gram of the composition will be lower than what is required.

7.3.2.2 Particle Size

The importance of the particle size of ingredients in determining the rate of burning of a high-energy material composition has been already dealt with in earlier chapters when we discussed linear and mass burning rates. In the case of pyrotechnic performance, which is a solid–solid reaction, this factor becomes extremely important. The average particle size of a compound (roughly assuming a spherical nature of each particle) determines the specific surface area (expressed as m^2/kg or cm^2/g). It is the specific surface area and the thoroughness of mixing the ingredients that will determine how "intimate" the contact between an oxidizer and a fuel (or any other ingredients) is in a pyrotechnic composition. Therefore, this calls for a serious quality-control check at the time of ingredient preparation with respect to the adherence to particle size limits as specified for a given pyrotechnic composition.

7.3.2.3 Avoiding Material Degradation during Storage

Almost all of the pyrotechnic compositions involve an intimate mixture of finely divided metals, fine powders of oxidizers, and other ingredients. Because of the high specific surface area involved, these compositions are highly vulnerable to degradation during storage. For example, finely divided magnesium powder is quite susceptible to oxidation by atmospheric oxygen, and the formation of any MgO coating will hamper the performance of the composition. To obviate such a problem, magnesium powder is coated with inert materials, such as lacquers and varnishes, before it is incorporated in the composition. Some of the oxidizers such as $NaNO_3$ are known for their hygroscopicity and, on storage, the ingress of moisture and the subsequent moistening or even the dissolution of the oxidizer component in the composition will severely hamper the satisfactory performance of the pyrotechnic composition. Therefore, it is imperative that the finished product should be hermetically sealed to prevent any ingress of moisture.

7.3.3 Safety Aspects Involving Pyrotechnics

Following strict safety precautions becomes mandatory at every stage when it concerns pyrotechnics, including at the design/formulation of composition, the preparation of ingredients, the processing of the final composition, packing, transport, and storage. The high level of hazard connected with pyrotechnic compositions is due to two factors: (1) the ingredients are very sensitive either individually (e.g., pyrophoric Zr) or in combination (e.g., thermite composition such as $Al + Fe_2O_3$) and (2) the exposed surface area of ingredients is very high because of the low particle size, at times going down even to the submicron level in certain compositions. In some cases, the hazard is enhanced because of the gritty or sharp-edged nature of some crystalline powders, in which case due care must be taken during processing.

Before embarking on any new composition, a thorough literature survey and analysis of the Material Safety Data Sheet should be performed to evaluate the hazards (fire, explosion, and toxicity hazards) of the proposed ingredients. Even more important is the careful study of the compatibility of the ingredients proposed to be incorporated in the composition. Many ingredients, although harmless individually, may result in disasters when mixed with others without taking adequate precautions. Some examples are as follows:

1. Chlorates are highly incompatible with sulfur and phosphorous (the slow formation of the acids of sulfur and phosphorus on storage in the presence of moisture and their subsequent reaction with chlorates result in highly unstable and explosive chloric acid) as well as with carbonaceous and ammonium compounds.
2. Very fine ammonium perchlorate or ammonium nitrate can be dangerously sensitive to impact in the presence of carbonaceous impurities.
3. Even traces of water can be very dangerous when it comes into contact with mixtures containing finely divided zirconium, titanium, magnesium, zinc, or aluminum.

By and large, most of the pyrotechnic compositions are sensitive to friction, impact, flame, and static discharge. When preparing large quantities, operations such as mixing are done under remote control. Although hand-mixing is done for smaller quantities, it is mandatory to use safety equipment/infrastructure such as conductive mats, conductive gloves, etc., that are all connected to a properly working static discharge system. This will ensure that no static charge is allowed to remain in the vicinity of the composition being mixed. We must remember that certain compositions can be ignited with a static discharge of a potential as low as a few millivolts. Because the development of static charge is closely related to the humidity level in the processing room (lower humidity favoring it), humidifiers should be in operation during processing to maintain the specified range of relative humidity.

Many accidents have been reported during the waste disposal of pyrotechnic stores. Proper standard operating procedures should be formulated and strictly followed for each type of pyrotechnic composition when it comes to its disposal.

7.4 Conclusion

Pyrotechnics have come a long way over centuries, from gunpowder to sophisticated pyrodevices used in various applications for defense as well as space missions. The very success of such missions heavily depends on the reliable and satisfactory performance of the pyrotechnic component in the explosive train involved. Although it may be commonly said that "pyrotechnics making is an art," the fact is that this field is a multidisciplinary one involving solid state chemistry and engineering. Despite their usefulness, it should be remembered that pyrotechnics are very sensitive to mechanical impacts, heat/fire, and static discharge and can result in disasters if the safety rules are not respected.

Suggested Reading

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Questions

1. Which is the oldest pyrotechnic composition known to man?
2. What factors of gunpowder are important when it is to be used as an igniter for a rocket propellant?

3. A typical igniter composition used in a composite rocket propellant is given as boron/KNO_3/plasticized ethyl cellulose. What is the role of each of these ingredients?
4. What is meant by the term "pyrophoric"? Give an example of a pyrophoric substance.
5. Teflon is a well-known polymer and does not contain oxygen in its molecule. How then is it used as an oxidizer?
6. Most of the oxidizer salts used in pyrotechnic compositions contain either alkali or alkaline earth metals. Why?
7. Why can we not use a high caloric value composition for producing color smokes?
8. What is specific surface area and what are its units? Why is this parameter very critical when formulating pyrotechnic compositions?
9. Why do we prefer to coat magnesium powder with lacquers or varnishes before we use it in pyrotechnic compositions?
10. Why are lower humidity levels dangerous when processing pyrotechnic compositions?