

# The Chemistry of Pyrotechnics

## The Chemistry of Pyrotechnics

By Sparky

### Introduction

Pyrotechnics use a variety of chemistry concepts, which produce different effects of sound and color. Although fireworks are pyrotechnics, not all pyrotechnics are fireworks. Pyrotechnics include any effect that uses rapid oxidization to produce an effect of light or sound. This excludes almost all high explosives except for a very few used in pyrotechnics such as picric acid. Thermite reactions and decomposition of ammonium dichromate<sup>2</sup> are never used in commercial fireworks but they can be pyrotechnic displays. An important part of pyrotechnics to the amateur is synthesis of different chemicals to be used in certain reactions. Often chemicals cannot be acquired for reasonable prices, so the chemicals are manufactured at a home lab. There are a wide variety of chemistry principals that apply to pyrotechnics and making different chemicals for pyrotechnic use. These include the use of the periodic table and of course the elements, polyatomic ions and compounds, ionic, molecular compounds, hydrocarbons, synthetic substances, and sometimes balancing equations. They also include synthesis and decomposition reactions, double and single displacement reactions, controlling rates of reactions, endothermic and exothermic reactions, acids and bases, and element oxides. Of course combustion is a central part of pyrotechnics and is dealt with throughout the other topics instead of being given its own section.

### Technical Terms

There are many terms used by pyrotechnicians that are not in common use by the general public or words like 'whistle' that should be explained as they apply to pyrotechnics. Many pyrotechnic compositions used are given common names to which they are referred. The pyrotechnic jargon used in this report is explained here for the convenience of the reader.

Binders are used to hold the powder of a composition together in a lump. A common binder is dextrin, it is dissolved in water then mixed with the composition, then the composition is formed into stars. When the stars are dried they are held together by the binder.

Black powder is the most commonly used fast burning composition in pyrotechnics. It is also called gun powder but since it is rarely if ever used in modern guns it is usually referred to as black powder. It is a mixture of 75% potassium nitrate, 10% sulfur and 15% charcoal that has been specially treated to make it burn quickly. The product of simply mixing the ingredients is also used in pyrotechnics and is called green powder.

Compositions are a mixture of pyrotechnic chemicals that include at least one oxidizer and fuel. Different mixtures of chemical powders are used for different colors and effects.

Flame envelope is the visible part of the flame that is right next to the unreacted powder and still reacting enough to be separate from the surrounding atmosphere.

Flash powder is a composition that has a oxidizer mixed with a reactive metal that burns quickly and produces a flash of light. It is commonly used in small firecrackers and larger firecrackers called salutes. The most common flash powder mixture is 70% potassium perchlorate and 30% dark aluminum, by weight.

High explosives are explosives that detonate and in which the front of decomposition travels at a speed faster than sound. High explosives contain the oxygen and fuel in the same molecule. Primary high explosives are sensitive to shock, friction, flame or any combination of the three. A secondary high explosive requires a shock from a primary high explosive (a detonator cap) to explode. They are not commonly used in pyrotechnics but occasionally they are.

Lampblack is a form of carbon that is a very fine powder. It is essentially the soot from chimneys though of course it is manufactured not collected from chimneys!

Oxidizers in chemistry are the actual elements that have a negative charge and react with elements of a positive charge. In pyrotechnics oxidizers also include chemicals that yield oxygen when heated.

Precipitate method This is a method of treating gunpowder ingredients to make them burn faster. The potassium nitrate is dissolved in hot water, the charcoal and sulfur are added, and mixed well. Then the solution is poured into an amount of cold alcohol. The potassium nitrate is much less soluble in a mix of water and alcohol, and precipitates into small crystals around the fuels, making it burn much faster than simply mixing the ingredients.

Priming composition is a layer of composition that is put on a star if a star is difficult to light. The priming composition burns which in turn lights the main star.

Reducers are fuels that react with oxidizers.

Shells are containers of stars that are shot up into the air and then exploded, sending the stars burning and spreading out in the sky.

Stars are the most commonly used part of a pyrotechnic device. A star is a portion of composition that has been made into a solid chunk by a binder. Stars are made many different ways and with many different effects.

Strobe is an oscillatory burning effect. This effect consists of a smolder phase when the composition does not produce much visible light or gas then a more intense burn phase in which gas and heat is produced. Strobe compositions are used to make stars and rockets.

Whistle mix is a sensitive and fast burning composition that is pressed into tubes then ignited to produce a whistling sound. This mix is most commonly made of potassium benzoate and potassium perchlorate.

### **The Periodic Table and the Elements**

The actual periodic table itself has some usefulness in pyrotechnics. One of its uses is in finding stoichiometric mixtures for different reactions. The table is referred to for elemental weights to determine the different amounts of each chemical needed to make a reaction as efficient as possible. Most of the time however, efficiency of a reactions is not usually needed, since it does not necessarily mean the best effect.

Instances where it is used is in powders that are designed to burn as fast and cleanly as possible. Rockets are often designed to make the most efficient use of their fuel, and so should react all of the chemicals as fully as possible. Flash powder is meant to produce a report, and the report is louder the faster the flash burns. Therefore, the most common 70/30 flash mixture is very close to stoichiometric amounts. Whistle mix is also intended to burn as fast as possible, especially when used as a burst charge (used to explode a fireworks shell, lighting and sending the stars flying into a design). Without the periodic table as a reference, balancing, and predicting reactions for pyrotechnics would be much more difficult. Changing those reactions into the amounts needed in grams would also be difficult without the periodic table as a reference.

The most useful element in pyrotechnics that belongs in the alkali period is potassium. It is more common than lithium and does not produce a yellow flame like sodium. The strong sodium flame color easily washes out other and can contaminate other compositions to ruin them. The weak violet flame that potassium gives off is advantageous because it doesn't interfere with color production. It is rarely used by itself to produce purple, instead a mix of blue and red are used.

The most used metals in the alkali earth metals group are magnesium, strontium and barium. Magnesium is used in its metal form as a more reactive fuel than aluminum. It is used in flash powders and to make bright white lights. Magnesium reacts with water to produce magnesium oxide and hydrogen, so magnesium can be difficult to work with since all water must be avoided. Potassium dichromate added to water can discourage a reaction from happening between the water and the metal. Unfortunately potassium dichromate is carcinogenic, so many people choose not to work with it. Magnesium is also combined into an alloy with aluminum to form magnalium which is more reactive than aluminum yet does not have magnesium's troubles with water. Magnalium is finding a new advantage in recent days because it is now illegal in the U.S. to ship metal through US mail or couriers with a magnesium content of over 50%. Magnalium with a 49% magnesium content is expected to come into production soon. Strontium compounds are used to make red lights. Lithium is also used to make reds but it is typically more expensive and offers no advantages. Barium compounds are commonly used to make green lights. Soluble barium salts are poisonous but they are much less so than the old chemical used for green which was copper acetoarsenite, otherwise known as Paris Green. One way pyrotechnists try to counter the effect of barium poisoning is by eating magnesium sulphate. This forms insoluble barium sulphate if any barium compounds should react with the epsom salts in the stomach.

The most common transition metals used in pyrotechnics iron, copper and zinc. Sometimes titanium is used for sparks and priming compositions because of its large heat capacity. Zirconium is rarely used as a flash powder ingredient.

Iron is used as iron oxide for one of the favorite thermite reactions. Iron is also used in metal form to produce bright orange sparks, most notably in Clark's Giant Steel Fountain. Iron must be coated in a protective layer of something like linseed oil to prevent it from reacting with oxidizers and rusting. Finely divided iron is used with potassium permanganate as a slow fuse in some applications.

Copper is able to produce greens however it is not commonly used because barium compounds produce deeper greens. One copper compound that is used for green is copper acetoarsenite. This compound produces an excellent green however it is not

commonly used because of its high toxicity. Instead, copper compounds are used to produce blue. The copper ion itself produces a green, however copper(II) chloride produces blue when excited. Usually a copper compound such as copper oxide is used with a fuel, oxidizer and chlorine donor. When the oxidizer and fuel burn, the copper oxide decomposes giving off copper and contributing oxygen too. The chlorine donor such as polyvinyl chloride also decomposes giving free chlorine. Then the copper combines with chlorine in the flame envelope and produces copper(II) chloride while the composition is burning. Copper oxide is also sometimes used in a fast thermite reaction with aluminum.

Zinc is used in powdered metallic form to make zinc spreader stars and electric stars. Zinc produces a bluish or green color when burning. Zinc spreader stars break up into a number of smaller stars in the sky, producing a blue color. Electric stars are bright blue blue, with bluish zinc sparks coming off the main star, this gives an illusion of electricity. Zinc is also used in rockets with sulfur, which when burns forms zinc sulfide large amounts of heat.

Group 4 elements that are used in pyrotechnics are carbon, silicon, and lead. Bismuth, although of the group 5 elements is used interchangeably with lead.

Carbon is an extremely important fuel when it is in the form of charcoal and sometimes lampblack. It is used as the main fuel for black powder, to produce orange sparks and as a fuel in a number of other different compositions besides black powder, such as H3. While not very common, carbon electrodes are also used in the amateur production of perchlorates and chlorates. Graphite nozzles are sometimes used on rockets and fountains. Carbon is used in the form of carbonates combined with metals such as strontium to use as a coloring agent in different compositions.

Silicon metal is only used on occasion in priming compositions because of its large heat capacity and high burning temperature. Silicon dioxide is known as Cab-O-Sil or Aero-Sil and is used because it is free flowing and low density. It is added to powders to make them "fluffy" and easy to pour and handle.

Lead tetraoxide or bismuth trioxide are used in an effect called Dragons Eggs. The lead or bismuth oxides are mixed with magnalium, copper oxide, and nitrocellulose lacquer. Then the composition made into small granules. The mixture has an oscillatory burning effect that is much more vigorous than strobe mix. During the smolder phase the eggs remain silent, then when they reach the active phase they produce a sharp crack. Using large granules of the mixture is not effective because the egg will shatter itself and disperse the rest of it before it has a chance to react. Lead is more commonly used because it cheaper though bismuth is preferred because its reduced toxicity.

The only group three elements that is commonly used is aluminum, it is one of the most important fuels in pyrotechnics. Aluminum is manufactured in a very finely powdered to produce different products: atomized, flake and dark aluminums. The atomized aluminum are made by liquefying the aluminum then spraying the liquid into an atmosphere of inert gas. There are a variety of methods used to make the aluminum into very small particles during atomization, including ultrasonic speakers near the nozzle. Once the aluminum has cooled, cold air is slowly let into the container to minimize the aluminum oxide coating. Atomized aluminum is not used as much as the other two kinds because it does not have a shape that allows it to light easily. The other two manufacturing methods produce edges on the particles (instead of round particles) that

heat up quickly, making the powder more reactive. Flake aluminum is similar to aluminum foil cut up very small. A sheet of aluminum is pounded very thin then cut up into small pieces. This kind of aluminum powder is used for sparks in stars and fountains, some rocket fuels and some slow flash powders, as well as other non pyrotechnic uses such as paint pigment and radiator sealant. The fourth and most reactive type of aluminum is dark aluminum. Called "Indian blackhead" or "dark German aluminum", this kind of aluminum powder is the most reactive. So reactive in fact that some suppliers will not sell over two pounds of it per year to a customer without seeing a high explosives license! This kind of aluminum is manufactured similarly to flake aluminum but it is pounded thinner, and it is covered by paper during the pounding process, to keep an oxide layer from forming. Then the aluminum is cut and ground until it is very fine. Then the powder is heated under an inert atmosphere to get rid of the paper. This leaves a fine dark carbon layer on the aluminum, which gives it its name. The carbon layer prevents an oxide layer from forming, making this aluminum very reactive. The particles are only a few microns big. This type of aluminum is typically used in flash powder, which is used for salutes and burst charges. The maximum amount of flash allowed in firecrackers is 50 milligrams.

There is a fourth method of academic interest that involves a vacuum and vaporizing aluminum to condense it onto the container wall. This method is used by NASA to produce sub-micron (around 4000 mesh) particles for their rockets. The smaller particles result in significant fuel savings by making the reaction more efficient. This type of aluminum is not available for consumer retail and is too expensive for pyrotechnic use.

Group 5 elements used today are nitrogen, antimony, phosphorus and sometimes bismuth as less toxic substitute to lead. Arsenic used to be used in a compound with copper to produce green, but that has been phased out in favor of less toxic barium salts. Arsenic is still used, but not commonly, as realgar, in smoke compositions and some firecrackers, but is too toxic for common use.

Nitrogen is used in the form of nitrates, which are very common in pyrotechnics. Potassium nitrate is the most common, used in black powder. Barium nitrate, and strontium nitrate are also used as oxidizers and double as color producers.

Antimony is used in the form of antimony trisulfide. This was originally used in "bengal fire" to produce a bright light with a blue tinge to it. This was the beginnings of color production in pyrotechnics. It is still used today for sparks and as a fuel to produce a bright light.

Phosphorus is not used for a wide variety of things but it forms a very sensitive and powerful explosive mix when mixed with chlorates. The strike plate of a matchbox is made of powdered glass and red phosphorous. When a safety match is lit, the chlorates (potassium or sodium chlorate) in match heads come into contact with the phosphorous on the strike plate. Friction from the ground glass produces enough heat to react the chlorate and phosphorous, which in turn produces enough heat to light the rest of the match head. This works in combination with the red phosphorous being converted to white phosphorous from the heat and the white phosphorous burning. Matches used to contain white phosphorous but it was connected to a terrible bone disease known as "phossy jaw" and was put out of use. The chlorate and red phosphorous mix is called "Armstrong's mix" but it is far too sensitive to be used in any real quantity in most pyrotechnics. This mix is so powerful and the fact that it contains chlorates (which can

act as a high explosive) that it is one of the few explosives to border the line between the high and low explosives. It is the composition used in toy cap guns to produce the bang sound. White phosphorous is still used in tracer bullets by burning in the air as it travels.

Bismuth is used in dragons eggs instead of lead, as mentioned earlier.

Group six elements that are commonly used are of course oxygen, as well as sulfur.

Oxygen is used mostly in the form of different polyatomic molecules that release their oxygen at high enough temperatures. Examples of the most common are nitrate and perchlorate. Chlorate is also used but is not preferred because of its incompatibility with sulfur and acids that make it very sensitive to decomposition. Carbonates, and oxides are used to a lesser degree in high temperature reactions.

fulminating powdered, gunpowder, chlorates incompatibilities. Oxygen from the air is also used in pyrotechnic compositions by burning sparks. Compositions also use some atmospheric oxygen. Oxygen is the most important element in pyrotechnics as an oxidizer.

Sulfur is used in pyrotechnics as an oxidizer, but mostly as a fuel. It is used in zinc sulfur rockets as an oxidizer. It is used in black powder as a fuel as well as in matches, fulminating powder, and many other compositions. Sulfur has a very low ignition point and a certain form of it (flowers of sulfur) is acidic. These are some of the reasons that it makes chlorate mixtures very sensitive and dangerous. In fulminating powder it is combined with potassium carbonate and heated to form potassium polysulfides. These polysulfides are very good reducing agents and are combined with potassium nitrate to form fulminating powder which burns much more quickly than black powder.

Halogens have some use in pyrotechnics. The only one that is used in any specific amount is chlorine. It is used to enhance colors of different compositions and is a necessity to produce some colors. Compounds such as polyvinyl chloride (PVC), Parlon, and a number of other chlorine donors are used. They decompose in the heat of the reaction and give free chlorine gas that combines with metals in the flame envelope to enhance color.

### **Ionic Compounds**

Ionic compounds are used much more than molecular compounds. There are a number of different compounds used, most of them are oxidizers or coloring agents, a few are fuels. There are quite a few oxidizers that are made up of barium, strontium, calcium, potassium, sodium, lithium, and sometimes copper or ammonium for the cation. The anions for oxidizers commonly are chlorate, perchlorate, nitrate, and sometimes oxide. The anions for color producers are commonly also nitrates and oxide as well as carbonate, chloride, and oxalate. Fuel anions can be salicylates, and benzoates used in whistle compositions. Some ionic compounds such as sodium silicate are used for their resistance to flame to protect paper casings and it is as glue.

### **Molecular Compounds**

Molecular compounds are used mostly for fuels and binders or solvents. Fuels used in pyrotechnics are red gum and sugar (dextrose, sucrose and even sorbitol). Sugars are used mostly in rocket fuels and one favorite mixture is a sugar with potassium nitrate.

This mixture is often melted to form an intimate mixture, then poured into tubes to make rocket engines. Red gum is used as a fuel and sometimes a binder because it is soluble in alcohols and other non polar solvents. Stearin –  $C_{21}H_{42}O_4$ , is used as a fuel sometimes and is used to protect metal fuels such as iron from oxidization. Solvents such as acetone, alcohol and methyl ethyl ketone (MEK) are used to dissolve binders. Dextrin is a water soluble binder that is made by pyrolyzing a starch such as corn or potato starch.

#### Polyatomic ions and compounds

Mentioned earlier in the ionic compounds section, the most common polyatomic ions are oxidizers such as chlorate, perchlorate, and nitrate. Ammonium is the only common cation used in pyrotechnics. One polyatomic anion that is not used as an oxidizer is dichromate. There are quite a few polyatomic ions so only the most common are mentioned. These ions form polyatomic compounds with many positive ions, most commonly potassium, and sodium.

Chlorates ( $ClO_3^-$ ) are notoriously sensitive and dangerous because of this. The most common chlorate is potassium chlorate because it does not interfere with color production, it is not hygroscopic and it is not very toxic or expensive. When mixed with sulfur or salts of sulfur such as antimony trisulfide they make a dangerous mixture that is avoided. Chlorate mixes are also made more sensitive by acidic conditions, and strong acid can cause them to spontaneously combust. One way of lighting a thermite mix is to prepare chlorate and sucrose composition then drip concentrated sulfuric acid on it to act as a delay then the acid will light the mix. Because of this incompatibility with sulfur, contact with mixtures containing sulfur must be kept separate from chlorates. This includes black powder, which can be very inconvenient. A few years ago a high school teacher from Lackawanna New York lost part of his hand while mixing potassium chlorate, sugar and sulfur for a smoke mix to test the fume hood system in the laboratory for leaks. Chlorates give off all of their oxygen atoms at a low temperature. While not applying to pyrotechnics, chlorates such as sodium chlorate can form a high explosive called a cheddite. When sodium chlorate is mixed with vaseline it can be detonated though it has a very low velocity of detonation. Ammonium salts must be avoided when using chlorates because ammonium chlorate might form which is a sensitive explosive. The actual explosion is not a danger because it forms in such small amounts, but it can lead to spontaneous combustion.

Perchlorates ( $ClO_4^-$ ) are similar to chlorates but they are more expensive and more stable. The most commonly used is again the potassium salt. Perchlorates give off their oxygen at higher temperatures and also give off more of it. Perchlorates are still sensitized by sulfur and acids but there are acceptable mixtures containing unacidic sulfur. Both chlorates and perchlorates give off chlorine during decomposition, so they can perform double duty as a chlorine donor. Neither chlorates or perchlorates are very water soluble.

Nitrates ( $NO_3^-$ ) are much less vigorous oxidizer. They give off only one of their oxygen and at higher temperatures than the other oxidizers. When thermally decomposed, nitrates form metal oxides, nitrites and of course give oxygen gas. The further down the group the metal is, the more difficult it is to decompose the nitrate. For example sodium nitrate is less stable than potassium nitrate. Sodium nitrate decomposes at  $380^{\circ}C$  and potassium nitrate at  $400^{\circ}C$ . Nitrates are much more water soluble than chlorates or

perchlorates. Potassium nitrate is the most commonly used nitrate. It is used in black powder which is used in rockets and mortars to fire fireworks shells. Variations on black powder are used very widely for different stars effect. The solubility of nitrates is put to use in the precipitate method of black powder. Nitrates are more stable than the other oxidizers but they also have an incompatibility. Ammonium salts such as ammonium perchlorate must be avoided when nitrates are concerned. Nitrate salts and ammonium salts may perform a double decomposition reaction to form ammonium nitrate which is hygroscopic and will make a composition difficult or impossible to ignite.

Ammonium ( $\text{NH}_4^+$ ) As mentioned previously, ammonium has a few incompatibilities. Despite this it is still used in the form of ammonium perchlorate. Ammonium perchlorate is used in rocket fuels such as the ones used in the space shuttle because it decomposes to entirely gaseous products. This leaves nothing to clog up nozzles and enables it to use all of its mass to propel the rocket. Ammonium perchlorate is also used in blue stars with copper salts. It is used because it decomposes to hydrochloric acid gas which is an excellent chlorine source. It also has almost no flame color to wash out the delicate blue of copper(II) chloride. Ammonium nitrate is sometimes used with energetic fuels such as magnesium for rockets, but it is not common because ammonium nitrate is hygroscopic.

Dichromates ( $\text{Cr}_2\text{O}_7^{2-}$ ) are used rarely because of their carcinogenicity and toxicity. Their most common use is as potassium dichromate in solution with water to prevent the evolution of hydrogen when the water is used in a composition with magnesium. The water is used in the composition to dissolve the binder which is usually dextrin. Their other common use is in catalysts. One pyrotechnics display that is a favorite in the lab is thermal decomposition of ammonium dichromate. Once started the reaction produces chromium oxide, nitrogen and water. The chromium oxide is not very dense and it forms a cone around the reacting ammonium dichromate to make it look like a volcano.

### **Hydrocarbons**

Hexamine is sometimes used as a fuel in different pyrotechnic mixtures, though it is not very common. More commonly used hydrocarbons are not used in compositions. They are used as solvents to dissolve binders. Acetone, for example is used to dissolve nitrocellulose. Methyl ethyl ketone is used as a solvent for Parlon. Naphthalene (used in mothballs) is used to make fireballs in the air. The naphthalene is dispersed in the air and then ignited to make fireballs like those used in movies. Gasoline and methyl alcohol are also used in a similar manner. Gasoline (or any other very flammable liquid) is used for a simple fireball. Methyl alcohol is used in a device called a flame projector. The methanol is mixed with different metal salts to produce different colors of fireballs or columns of fire. A typical way to disperse and light these fuels is to put the fuel in mortar tube with a charge of black powder on the bottom. The liquids are kept in plastic bags. Lastly, many amateur pyrotechnicians enjoy filling balloons with propane or acetylene and lighting them from a distance.

### **Synthetic Substances**

Plastics are used in shells sometimes as a replacement for paper casing. Often

these shell casings are biodegradable. Synthetic HDPE mortar tubes are becoming more popular because they last longer than paper tubes and stretch instead of breaking into shrapnel if an explosion were to occur in the tube. An emerging practice that many traditional pyrotechnicians do not support is the use of synthetic fiber tape for spiking shells. Spiking shells is the process of reinforcing a shell wall with fiber tape or twine. This makes the case stronger and results in a more even brake.

### **Balancing Equations**

Pyrotechnicians rarely need to balance equations because there are formula databases that they can refer to. However, some formulas follow simple balanced equations. For example, potassium nitrate and magnesium flash powder is sometimes used for a bright flash. It follows the reaction  $\text{KNO}_3 + \text{Mg} = \text{MgO} + \text{KNO}_2$ . This reaction ends up using 50% potassium nitrate and 50% magnesium by moles because magnesium can only react with one oxygen from the potassium nitrate.

### **Synthesis and Decomposition Reactions in Pyrotechnics**

There are few simple decompositions or synthesis reactions in pyrotechnics, and many of them have to do with making chemicals for pyrotechnic use. Many amateurs cannot buy from pyrotechnics suppliers, often because they live too far away for shipping to be feasible. To get certain chemicals, the amateur has to make them. Dextrin is one of the easiest chemicals to make, it used as a water soluble binder and is very useful. To make it from home materials amateurs often pyrolyze a starch such as corn starch by heating it. Another kind of decomposition reaction commonly used in pyrotechnics is burning nitrocellulose. Nitrocellulose is used as a binder and used to waterproof fuses. Decomposition is of course essential to pyrotechnics as the oxidizers must decompose to give oxygen.

Simple synthesis reactions in pyrotechnics are also few, but a good example of one is zinc and sulfur rockets. Fine zinc powder and fine sulfur are mixed in a ration of 66 percent zinc to 33 percent sulfur, by mass. This is a common rocket composition though it in fact is not very efficient because of the high weight of zinc and the low specific impulse of the propellant. When the composition burns, of course zinc sulfide is synthesized. Another example of synthesis is making chlorides in the flame envelope of a colored composition. Copper and chlorine are used to combine in to form copper chloride which gives off a blue light when excited. Magnesium is rarely burned in air during a pyrotechnic display, but on occasion this would be an example of a synthesis reaction. A synthesis reaction does occur in effect when fuels are burned with an elemental fuel since oxygen is released then reacted with the fuel. However, the total reaction is more complex than reacting two elements.

### **Double Displacements**

Double displacement reactions are not used in pyrotechnic reactions themselves, but they are used extensively in making useful pyrotechnic chemical by the amateur. For example, sodium nitrate is often easier to obtain than potassium nitrate. Potassium chloride is available as a salt substitute. A simple double decomposition reaction results in potassium nitrate which is much more suitable to pyrotechnics use because it is not hygroscopic like sodium nitrate, nor does it produce a strong yellow flame. Sodium

chlorate is sold as weed killer in many garden stores. It is however not suitable for fireworks because it is hygroscopic and a sodium salt. It converted to potassium chlorate with potassium chloride. For green colors this salt can be converted to barium chlorate or strontium salts. In this manner, with a few basic chemicals many different metal salts for different uses can be made.

Some double displacement reactions must be avoided because they can be dangerous by spontaneously igniting a mixture or simply ruin the effect. Ammonium salts and chlorates are to be avoided because of the formation of ammonium chlorate which can lead to spontaneous combustion. Nitrates and ammonium salts should be avoided because they can form ammonium nitrate which will absorb moisture and make a composition difficult or impossible to ignite.

### **Single Displacements**

Single displacement reactions are more common in pyrotechnic reactions. For example the popular thermite reaction with a metal oxide and more reactive reducer metal. The most common is iron oxide and aluminum. Different mixtures such as copper oxide and aluminum can produce different results, the copper oxide mixture burns much faster than the iron oxide mix though it lets out less total energy. Thermite reactions are not used in commercial fireworks but they are popular with amateurs.

A more complex reaction is burning magnesium in the presence of water. If a pile of magnesium shavings is lit on dry ground, it will burn with an intense white light. If a similar pile of magnesium is lit on damp ground it will burn with a flash and a small explosion. The high temperature of magnesium allows it to use the water as an oxidizer, forming magnesium oxide and hydrogen gas which burns in the air to make the explosion. This is one of the reason that magnesium fires are so dangerous and cannot be put out with water.

Ammonium nitrate and copper metal or compounds should be avoided because of the formation of Tetramminecopper (II) nitrate, which is a “brissant and sensitive compound”<sup>1</sup> though it is hygroscopic, so the danger is not necessarily great.

Zinc powder can be made for pyrotechnic use with hydrochloric acid and zinc metal. Zinc chloride is formed and hydrogen gas is released, then the zinc chloride is reacted with aluminum to form zinc metal precipitate and aluminum chloride. The zinc metal is filtered and dried for use.

### **Controlling Rates of Reactions**

Usually slowing chemical reaction speeds is done by adding an excess of oxidizer or fuel, or even a chemical such as a carbonate that will take energy from the reaction and slow it. Similar to the effect when sodium chloride is used in explosives to cool the explosive and make it less vigorous.

One way to change the speed of a reaction is to use different oxidizers or to treat the mixture in a special way. Nitrates are the least vigorous oxidizers, then perchlorates and finally chlorates make things burn the fastest. Sometimes catalysts are used, especially in rocket fuels or salutes that require a sharp report. Catalysts for chlorates and perchlorates include manganese dioxide, red iron oxide, and potassium dichromate for strobe rockets. Treating the mixture in a special way could be something like making gunpowder (the previously described precipitate method or the other methods). It could

be something like melting the chemicals together or dissolving the chemicals then letting the solvent evaporate to achieve a good mixture.

The most common way of increasing reaction rate is by surface area and by making sure the reactants are well mixed. In pyrotechnics the size of particles are usually graded by mesh or micron. The mesh system is based on how many holes are in a square inch, thus the higher the mesh the smaller the particle. There are extensive systems for grinding and mixing chemicals. Ball mills are in essence a jar with lead balls in it, the jar turns and the balls tumble over themselves in the jar. Powder is put into the jar with the balls and the jar is turned to grind the chemical(s) up very fine and mix them well. There are many variations used for grinding metals and to make use of materials available to the builder of the mill. There are other, more exotic examples of mills such as vibrating mills where a number of balls are put on a platform with the powder and the platform is vibrated. These systems are hardly ever used because they are usually expensive. Black powder is often mixed and milled in a ball mill though in commercial production companies often use a flour mill configuration.

### **Exothermic and Endothermic Reactions**

There are no endothermic reactions that actually become cold in pyrotechnics, so the total output of reactions is exothermic. However, as they run their course, reactions do require heat to decompose chemicals and liberate oxygen. Reactions also need heat to produce an effect such as vaporizing a dye (in many smoke compositions) or decomposing compounds to produce elements so that they can be excited and give off light. Once started of course compositions can give themselves the heat needed by burning the fuel. Complex fuels may decompose before they react with the oxidizer element.

Exothermic reactions are of course much more common, as they occur every time anything is oxidized. Listing and describing even the most common endothermic reactions in pyrotechnics would take far too much time and space. Possibly the most endothermic reaction commonly used is the thermite reaction with stoichiometric amounts of aluminum powder and iron oxide.

### **Acids and Bases**

Acids are used sometimes to synthesize useful pyrotechnic chemicals such as zinc powder, or copper chloride. This is only done if these chemicals are bought for some reason. The reactants are almost always more expensive than if the end product was bought from a pyrotechnic supplier, since the chemicals are cheaper when produced in bulk. A more common use of acids is when aluminum and nitrates are mixed. Alkaline conditions can lead to spontaneous combustion in these mixtures. To prevent this boric acid is added. Another incident where acids play a role is in the different forms of sulfur. Sublimed sulfur, or flowers of sulfur is slightly acidic because of its partial oxidation. This can cause concerns by sensitizing mixtures, especially those containing chlorates. Either a carbonate salt is added to the sulfur or flour of sulfur is used instead. Chlorates are sensitive to acids and a composition containing chlorates can spontaneously combust when exposed to strong acid.

### **Elements and Oxides**

Metal oxides form even when metal fuels are not burned. When nitrates and other oxidizers decompose one of the products is a metal oxide. Metals are commonly used, however as a fuel. Metal fuels are commonly aluminum, magnesium, magnesium and zinc. When these fuels are used in compositions they of course almost always end up as metal oxides. Some exotic fuels people have used even include uranium! Some metal oxides can be dangerous. When potassium permanganate is mixed with organics, problems may occur. Manganese septaoxide can be formed which is a strong oxidizer and also acidic. This can lead to spontaneous combustion and is one of the reasons that permanganates are not commonly used. Metal oxides are used as oxidizers in thermite reactions and as a color producer in the case of copper oxide.

Non- metal oxides are the products of burned compounds. Typically they are sulfur dioxide, carbon dioxide, and water. Gases such as sulfur dioxide are to be avoided because they react with the water in lungs to produce sulphuric acid when breathed in.

### **Conclusion**

Pyrotechnics use almost all of the principals taught in the chemistry unit. There are a large variety of reactions and chemicals used in pyrotechnics, some of which can be very dangerous. Not only are there many chemicals used in pyrotechnics, but there are even more used in the synthesis of pyrotechnic chemicals. Perhaps this proves the statement by 'Fulmen' that "half the fun is making the chemicals".

## **Bibliography**

1. Hans Josef Wagemueller, Rec.pyrotechnics FAQ,  
**<http://www.faqs.org/faqs/pyrotechnics-faq/>**

This file contains all kinds of information about pyrotechnics. It has common chemicals and uses. It also contains information about incompatibilities between chemicals.

2. Chemlab, The Periodic Table, Demonstration 6.

This demonstration is that of ammonium dichromate decomposing. This is an example of a simple decomposition reaction in a pyrotechnic display.

### Rec.pyrotechnics

I have been following this newsgroup for a number of months, reading different information about pyrotechnics. It contains all different kinds of information. Among some of the more respected posters, there are professional pyrotechnicians who make fireworks and publish newsletters and run subscription websites by themselves, officers of the Pyrotechnics Guild International, and people who work in the industry making fireworks.

- Skylighter, Inc., Pyrotechnic Fireworks and Chemicals,  
**<http://www.skylighter.com/mall/chemicals.asp>**

This site contains information about different pyrotechnic chemicals. Skylighter is a retailer of pyrotechnic chemicals and supplies. They sell a wide variety of chemicals, some that are very obscure.

Administrator: NBK2000, The Explosives and Weapons Forum, [www.roguesci.org](http://www.roguesci.org)

This forum is where I learned about manganese septaoxide formation from potassium permanganate and organics. They have a section on low explosives that deals with pyrotechnics.

John Donner, A Professionals Guide to Pyrotechnics, **Chapter 3: Chemicals**

I used this chapter to find different formulas, origins and spellings of chemicals. There is also some information about incompatibilities and uses of the different chemicals.

Wouter Visser – Practical Pyrotechnics, A Collection of Pyrotechnic Compositions,  
**<http://huizen.dds.nl/~wvisser/compoDB.html>**

This is a compilation of different compositions for stars, rockets, sparklers and many other types of composition. It was used for the ingredients to dragons eggs. It was also used to confirm the spelling of certain chemical.