# By Tim Graham hat's the first thing that comes to mind whenyou think of the Fourth of July? If you're like most Americans, the answer is obvious...fireworks! The familiar sights and sounds of multiple-burst shells exploding in the night sky are forever joined with our country's celebration of its independence. Orange and yellow patterns that resemble flowers, green and red streamers, brilliant gold and white glimmers, a barrage of hissingand exploding reports and salutes...a fireworks display at an Independence Day celebration is as American as apple pie. But what might surprise most of us is that the history of fireworks had its beginnings long before Europeans ever set foot on this continent! Black powder The Chinese were probably the first to use "fireworks", as revealed in ancient writings dating as far back as 850 AD describing how to make black powder. It is not fully understood how Chinese alchemists came upon the first recipe for black powder-still a major component of almost all fireworks today. They were quick to discover that they could wrap the black powder in bamboo or paper tubes to make crude missiles and flares that could be used to frighten away potential invaders. By the 12th century, the Chinese had incorporated the use of fireworks into religious ceremonies and celebrations of all types. This, in effect, was the birth of what today is known as pyrotechnics, which means "the art and science of artificial fire". ChemMatters OCIOBER 1998 7

One of the earliest uses of fireworks in this country may have been in 1608, when Captain John Smith used "rockets" to frighten natives away from the Jamestown colony. The same soldiers who were responsible for firing cannons and rockets were often asked to fire off crude fireworks displays to celebrate victories. This soon led to the use of fireworks to celebrate many other occasions. By 1781, the use of fireworks had become an important part of our country's heritage in celebrating the Fourth of July.

### **Pyrotechnics**

The makeup of a standard pyrotechnical mixture or mortar is similar for all types of fireworks. The fireworks must contain an oxidizer (a chemical that supplies the oxygen for combustions) and a fuel (a reducing agent). Usually the solid oxidizer and fuel are physically mixed but do not chemically react until enough activation energy has been applied. The oxidizer is electron-deficient and finds the electrons it needs for more stability in the fuel. An oxidation—reduction or redox reaction occurs that results in very stable gaseous reaction products. Because these molecules



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are more stable than the reactants from which they were formed, there is an exothermic release of energy. Couple this with the fact that gases must occupy a much greater volume than the solid reactants and the result is explosive!

MAGNESIUM/ALUMINUM IRON/CHARCOAL

One of the most fascinating aspects of a fireworks display is the vivid colors that are produced against the black backdrop of the sky. The Italians were probably the first to experiment with color-emitting compounds in the early 1700s; but it wasn't until the mid-1800s that the use of these compounds was perfected. Although pyrotechnicians use a wide variety of special effects to keep our attention during a fireworks show, it is probably the vivid colors that attract the majority of spectators.

Visible light consists of electromagnetic radiation having wavelengths from 380 to 780 nanometers (nm). The colors of the visible spectrum are red, orange, yellow, green, blue, and violet, with the longer, low-energy wavelengths at the red end of the spectrum and the shorter, high-energy wavelengths at the violet end. If an object emits radiation across this entire spectrum, it will appear to

have a white color, but if the object only emits from a small portion of the spectrum, the light will appear as the color of that portion of the spectrum.

Most of us are

aware that objects emit light when they combust, but how they emit this light is a bit of a chemistry (and physics) lesson. Light is emitted by three basic processes: (1) incandescence, (2) atomic emissions, and (3) molecular emissions.

# CuCl<sub>y</sub> Ba Na Sr

Figure 1. Color by Incandescence

Some of the colors produced by fireworks are the

result of incandescent emission. Bright white

sparks are produced by igniting aluminum or

When powdered metals like aluminum and

magnesium are oxidized, they glow white hot

at temperatures approaching 3,000 °C. When

only reach about 1,500 °C, and the result is a

molecular emissions

as a shell bursts in the night sky are the

result of atomic and molecular emissions.

During atomic emissions, we can observe

light emitted by atoms of an element in the

The many brilliant colors that are seen

iron and charcoal particles combust, they

flash that appears gold (see Figure 1).

Atomic and

magnesium; the dimmer, golden light is

produced by iron or charcoal (carbon).

Figure 2. Color by Atomic and Molecular Emission

Other colors in fireworks are produced by atomic and molecular emissions. Sodium (Na) produces light in the yellow part of the spectrum, barlum (Ba) in the green, and strentium (Sr) in the red. Copper compounds containing chlorine (CuCl<sub>x</sub>) produce a blue color.

#### Incandescence

A light bulb is a perfect example of incandescence. When electrons flow through the tungsten filament in the bulb, there is a large amount of resistance to electron flow, the filament heats up, and it becomes "white hot". Because the energy is being emitted across the entire visible spectrum, it appears as white light. When materials are heated to high temperatures, they often emit light in this way. The white and gold colors of most fireworks explosions are the result of reacting metals in a high-temperature environment.

gaseous phase, and it is unique to that element. The high-temperature environment that is generated when a shell explodes causes electrons to jump to higher energy levels in atoms. When these "excited" electrons fall back to their normal energy positions, or ground state, they emit light of particular wavelengths.

Molecular emissions can produce similar effects but are a result of molecules instead of elements. Pyrotechnicians use many metal salts to achieve this wide range

of colors. Reds are produced by using strontium and lithium salts, greens by using barium salts, blues by copper-containing chloride salts, and yellow and orange light is produced by sodium salts. Because sodium is such a strong atomic emitter, even a slight sodium impurity can wash out any other color that might be produced in the flame. For this reason, the use of sodium salts in fireworks is carefully controlled (see Figure 2).

Pyrotechnicians use a considerable amount of art to perfect their fireworks design, but chemistry also plays a very important role in achieving the desired colors. Many of the metals that produce color cannot be packed directly into the fireworks and must be synthesized in the many chemical reactions that occur within the fireworks' flames. Such compounds as chlorinated rubber, polyvinyl chloride, perchlorate oxidizers, and chlorate oxidizers are packed into the shell to produce chlorine and oxygen atoms when these materials combust. In the hot flame, these energetic atoms react with the metal salts generating excited atoms that produce the vivid colors we have grown to expect from a fireworks display.

Blue is probably the most difficult color to achieve because the copper chloride salts that yield a blue color decompose quickly in the high-temperature flame. Purples (strontium and copper chloride salts reacting simultaneously) are also difficult to achieve. Pyrotechnicians must give special attention to the chemical mixture and particle size to achieve these much-desired colors.

## Designing fireworks

The visual effects that accompany a fireworks display are not only the result of good chemistry but also the result of good design. Although it may not often come to mind as we watch a beautiful fireworks display, the

Leader fuse Paper and paste casing Time-delay fuse Stars **Bursting** charge Time-delay fuse Stars Burstina charge Black powder lift charge Side fuse

Figure 3. Aerial Sheli Design Shell design controls the visual effect of fireworks. Common traits to all fireworks include the black powder propellant and side fuse used to launch the shell. Time-delay fuses are used to set off the bursting charges contained in several compartments after the shell is far above the ground. Stars are pellets of light-emitting compounds. Stars can be arranged randomly to produce irregular spiashes of color or symmetrically to produce regular patterns.

preparation of these shells is a timeconsuming process and a very dangerous one.

An aerial shell typically begins as a hard paper cylinder. The center of this cylinder is loaded with hundreds of little black balls called stars. These stars contain the light-emitting compounds. The stars are surrounded by the bursting charge-a powdered mixture containing an oxidizer and fuel. Often shells are designed with many separate compartments. These types of shells are known as multiple-burst shells. At the bottom of the shells is a compartment that contains the black powder propellant (see Figure 3).

Pyrotechnicians use a leader fuse to connect two other types of fuses that must be lit almost simultaneously to ensure the proper break or aerial explosion. The leader fuse lights a side fuse that ignites the lift charge in the lowest compartment of the shell. This propels the shell out of its mortar and high into the sky. At the same time, the first of a series of time-delay fuses has been lit, which subsequently will ignite the contents of the upper compartments to propel the stars out of the shell compartments.

The master pyrotechnician's ability to turn a seemingly inert package of material into a spectacular effect has, for centuries, delighted and fascinated people of all ages. It would seem that fireworks possess an almost magical quality. It has been said that, "One who has once smelled the smoke, is never again free!" The next time you view a fireworks show, think about whether you have become entranced by the magical effects of fireworks...and look around. You won't be alone!

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