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***Fireworks** have marked celebrations for centuries.*
Behind the flashes and bangs lies the science of pyrotechnics.

Pyrotechnics

The secrets behind dazzling fireworks displays are yielding to scientific snooping. Similar principles are at work in devices ranging from the space shuttle to safety matches

by John A. Conkling

A distant, muffled "whoomp" resounds, and a trail of yellow-orange sparks tumbles into the night sky, culminating in a circular burst of brilliant blue and green streaks. Another explosion shoots out a ragged arc of red streamers, followed by a shower of white and gold sparks. A third firework produces a staccato barrage of bright flashes of white light and thunderous noise.

These effects have been a familiar part of major celebrations for centuries. For most of that time, the design and composition of fireworks was a craft, not a science. Only in recent decades have researchers begun to unravel the physical processes that underlie the production of dramatic colors and special effects. As a result of these investigations, a true discipline of pyrotechnics—the "science of fire"—has emerged. Pyrotechnics embraces not only fireworks but a whole range of devices that use similar materials, including hazard flares, safety matches and even the solid-fuel rocket boosters of the space shuttle.

One of the oldest pyrotechnic compositions, black powder, serves as both the propellant and explosive charge in modern firework shells. The Chinese developed black powder (the original gunpowder) more than 1,000 years ago for use in crude missiles and firecrackers. Awareness of black powder traveled west during the Middle Ages. The English monk Roger Bacon disclosed a formula for the explosive mixture in 1242 as part of his defense against accusations of witchcraft. He considered it such a dangerous material that he wrote about it in code. As the formula became more widely known, black powder revolutionized quarrying and construction. Weapons such as muskets and cannons, developed during the 14th century, exploited black powder as a propellant.

The basic formula for black powder has persisted essentially unchanged throughout the centuries: an intimate blend of potassium nitrate (commonly known as saltpeter), charcoal and sulfur in a 75:15:10 ratio by weight. It may in fact be the only chemical product that is produced today using the same ingredients, the same proportions and the same manufacturing process as were used in the time of Columbus. This constancy reflects the fact that black powder is a nearly ideal pyrotechnic substance. It consists of abundant, inexpensive chemicals that are relatively nontoxic and environmentally safe. The mixture is so stable that it can be stored for decades without deteriorating, if kept dry. Black powder is easily ignited by means of a moderate jolt of energy, such as a spark or a small burning fuse.

Historically, only a handful of families have dominated the fireworks industry in the West. Details such as chemical recipes and mixing procedures were cloaked in secrecy and passed down from one generation to the next. Families remain an important force in the industry. In the U.S., for instance, there are the Gruccis of Bellport, N.Y., the Zambellis of New Castle, Pa., the Rozzis of Loveland, Ohio, and the Souzas of Rialto, Calif. One effect of familial secretiveness is that, until recent decades, basic pyrotechnic research was rarely performed, and even when it was, the results were not generally reported in scientific journals.

In principle, the pyrotechnic process is not unlike normal combustion. A pyrotechnic composition contains an oxygen source (oxidizer) and a reducing agent (fuel). They are usually separate, solid chemicals that must be physically mixed together. When heat is applied, an electron-transfer, or oxidation-reduction (redox), reaction takes place.

Atoms in the fuel lose electrons to atoms in the oxidizer. In the process

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the fuel atoms bond to the oxygen atoms that are liberated from the oxidizer and form stable reaction products. The new chemical bonds are more stable, and so energy is released in the form of heat; the same process occurs in combustion. In combustion, however, the oxygen comes from the air. In a pyrotechnic mixture the oxygen is self-contained, and the heat is much more closely confined.

As long as a pyrotechnic mixture remains cool and dry, it is generally quite stable. A solid mixture experiences only a very slow surface reaction controlled by diffusion. When the composition is ignited, it begins to liquefy and vaporize in the resulting pyrotechnic flame, and the fuel and oxidizer closely intermingle. This proximity leads to faster chemical reactions and, in turn, still more rapid energy release.

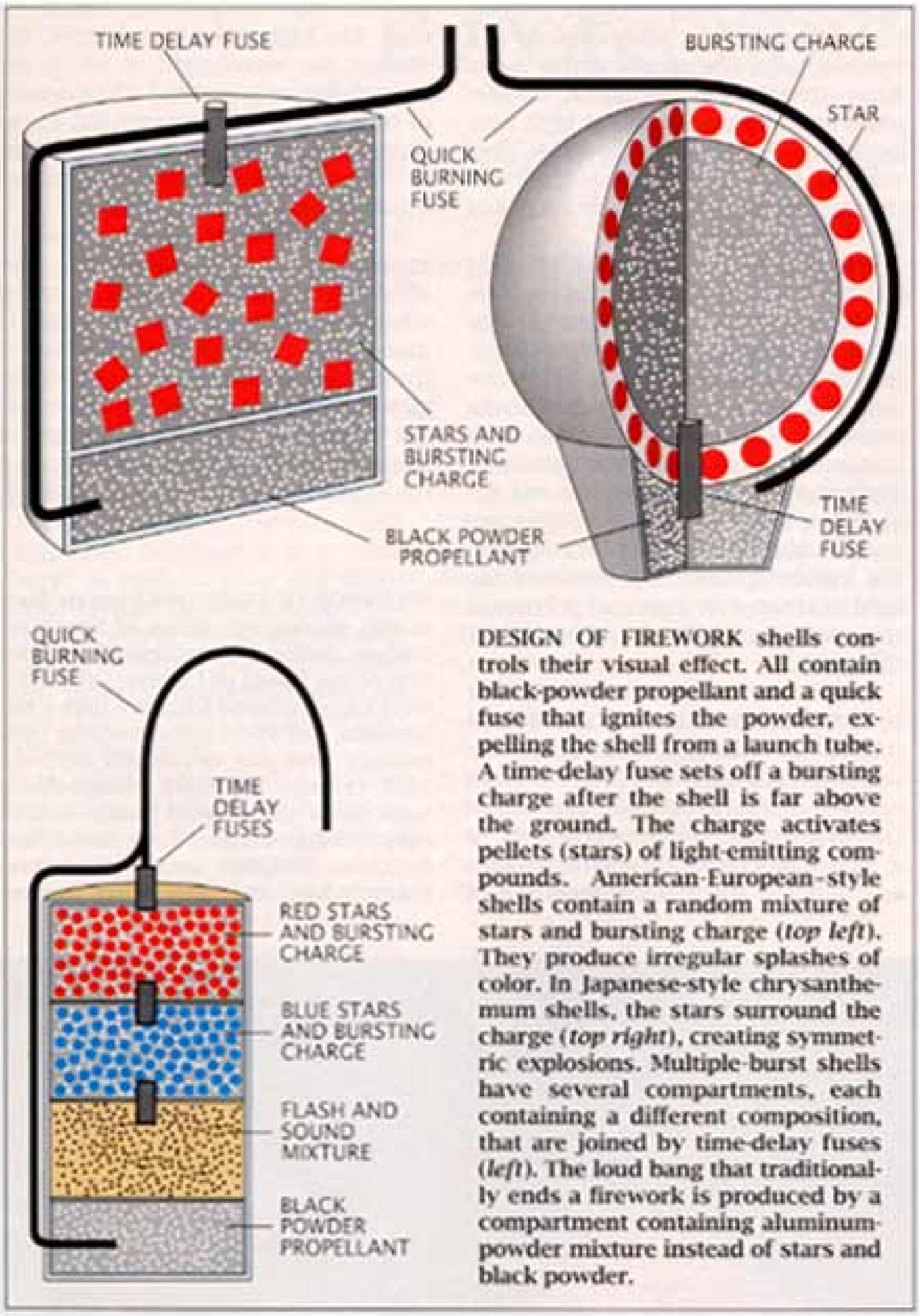
Pyrotechnics makes use of a variety of fuels. Many mixtures incorporate organic (carbon-containing) materials, such as charcoal (used in fireworks and gunpowder) or sugar (in smoke grenades). Other common fuels include nonmetallic elements, such as sulfur, silicon and boron. Silicon and boron release a large amount of energy when oxidized, and they do not produce gas in the process. They are used in delay fuses to ignite other compositions at a desired time. Chemically active metal fuels—most often aluminum, magnesium and titanium—burn at high temperatures and emit bright light. They came into use in the 19th century and dramatically improved the brilliance of pyrotechnic explosions.

The spectacular splashes of light produced by fireworks are the most famous pyrotechnic phenomenon. The color of the light depends on its wavelength. Visible light consists of electromagnetic radiation having wavelengths between 380 and 780 nanometers (a nanometer is one billionth of a meter). The longest visible rays appear red, the shortest, violet. A glowing object appears white if it radiates throughout the visible spectrum. If most of the light is emitted in a narrow portion of the spectrum, it takes on the color of that portion.

Pyrotechnic compositions emit light by three basic processes: incandescence (blackbody radiation), atomic emission and molecular emission. Incandescence occurs when solid or liquid particles in the pyrotechnic flame are heated to a high temperature. The hot particles emit a broad spectrum of radiation as they attempt to shed their excess energy. The higher the temperature, the shorter the wavelength at which the most radiation is emitted. The intensity of the emission is proportional to the fourth power of the flame temperature, so a moderate increase in temperature drastically brightens the flame.

White-light flares contain a reactive metal, such as magnesium, as a fuel. Solid metal oxide particles, created when the fuel is oxidized, are heated to more than 3,000 degrees Celsius; at these temperatures, their incandescent glow is white-hot. A mixture of potassium perchlorate and fine aluminum or magnesium powder produces a powerful explosion along with a burst of

SPLENDOR OF FIREWORKS bursts forth in this photograph taken of New York Harbor during the centennial celebration of the Statue of Liberty. Crude fireworks have existed for more than a millennium, but vivid color-emitting compounds were not developed until the 19th century. Firework compositions were often closely held family secrets; only in recent decades have researchers begun to decipher the chemical processes behind the flashes and booms.



DESIGN OF FIREWORK shells controls their visual effect. All contain black-powder propellant and a quick fuse that ignites the powder, expelling the shell from a launch tube. A time-delay fuse sets off a bursting charge after the shell is far above the ground. The charge activates pellets (stars) of light-emitting compounds. American-European-style shells contain a random mixture of stars and bursting charge (*top left*). They produce irregular splashes of color. In Japanese-style chrysanthemum shells, the stars surround the charge (*top right*), creating symmetric explosions. Multiple-burst shells have several compartments, each containing a different composition, that are joined by time-delay fuses (*left*). The loud bang that traditionally ends a firework is produced by a compartment containing aluminum-powder mixture instead of stars and black powder.

white light. Such "photoflash" or "flash and sound" compositions have a wide range of uses, from firecrackers to special effects for rock concerts to bursts of light for nighttime photography. These compositions produce the bright flash that traditionally terminates a firework explosion.

Larger metal particles retain their heat longer than powders and can continue to burn by drawing on the oxygen in the air. They create white sparks rather than an instantaneous flash. The bigger the particles, the longer the sparks last. Charcoal and iron particles do not become as hot as active metal particles—only about 1,500 degrees C—and so they produce dimmer, gold-colored sparks.

The brilliant colors seen in modern fireworks displays are generated either by atoms or by molecules present in a vapor form in the pyrotechnic flame. In the former case, the heat of the flame excites an electron in an atom and bumps it from its normal, ground-state orbital to a higher-energy one. The electron rapidly returns to its ground state and emits the excess energy as a photon (a single particle, or unit, of radiation) of a specific wavelength.

Sodium is one of the most potent atomic light emitters. Sodium atoms heated above 1,800 degrees C give off yellow-orange light having a wavelength of 589 nanometers. The process is so efficient that it tends to overwhelm any other atomic or molecular light sources in a pyrotechnic flame. Even small amounts of sodium-containing impurities can ruin efforts to produce a flame of any other color.

In other applications, sodium's prodigious light emission can be helpful. Sodium nitrate oxidizer combined with magnesium metal fuel is the principal composition used by the U.S. military to illuminate nighttime operations. The magnesium is oxidized by the sodium nitrate when the mixture is ignited; the resulting hot magnesium oxide particles shine with a white incandescent glow. High temperatures (3,600 degrees C) in the magnesium flame also broaden the range of wavelengths emitted by the sodium atoms. The result is an intense white light.

As with atomic emission, molecular emission involves a transition from a ground state to an excited one. The molecule must be in gaseous form in the pyrotechnic flame, and it must be heated to a temperature high enough to reach the excited state that causes it to radiate. If the flame is too hot, however, the molecule disintegrates into its constituent atoms and no light is emitted. Moreover, the molecules must be sufficiently concentrated in the flame to generate intensely colored light, but the production of solid or liquid particles must be kept to a minimum because they give off incandescent radiation that washes out the color.

In the absence of theoretical understanding, colors were generated in fireworks by a trial-and-error process. Over the past several decades Bernard E. Douda and Henry A. Webster III of the Naval Weapons Support Center in Crane, Ind., and David R. Dillehay of the Longhorn Division of the Thiokol Corporation in Marshall, Tex., have conducted research that has helped identify the principal colored emitters in pyrotechnics. Takeo Shimizu of the Koa Fireworks Company in Japan also has contributed to this area.

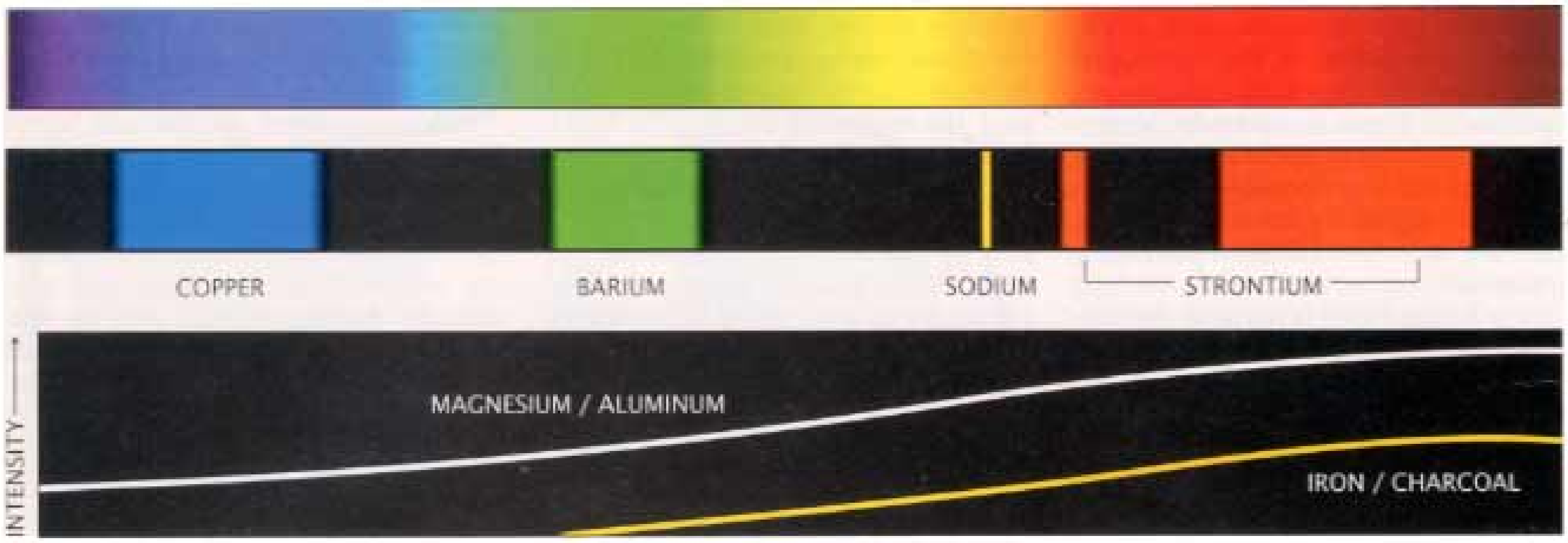
A few groups of molecules are responsible for nearly all the colors in fireworks. Compounds of the element strontium produce the reds: stronti-um hydroxide ($SrOH$) and strontium chloride ($SrCl$) emit red light at wavelengths between 605 and 682 nanometers. Molecules containing barium create the greens. Barium chloride ($BaCl$), for instance, emits green light at wavelengths between 507 and 532 nanometers.

These molecules are so fragile that they are unstable at room temperature; consequently, they cannot be packed directly into a firework. Instead they are synthesized in rapid reactions in the flame. Manufacturers add such compounds as chlorinated rubber, polyvinyl chloride (a chlorine-containing plastic) or perchlorate or chlorate oxidizers (containing a chlorine atom and four or three atoms of oxygen, respectively). These compounds decompose at high temperatures and release free chlorine. The chlorine atoms combine with barium or strontium, briefly creating the desired light-producing molecules.

A rich blue flame is perhaps the ultimate challenge to the pyrotechnician. The best blue emitter yet identified—copper chloride (CuCl)—is unstable at the elevated temperatures needed to produce intense light in fireworks. If the flame temperature exceeds that necessary for optimal molecular emission, the molecules disintegrate rapidly. Distinctly blue fireworks therefore demand especially precise control over the relative proportions and particle size of the necessary chemicals. The same holds true for purple or violet colors, which are created by combined emission from strontium chloride and copper chloride formed in the flame. I pay close attention to flame colors when I view a fireworks display; if a decent blue color appears, I am always impressed and curious to know what chemical mixture was used.

Color-generating compounds combined with the appropriate fuels and oxidizers can produce special effects. Red sparklers derive their color from the combination of strontium carbonate (which emits red light) and aluminum granules (which provide the sparks). These ingredients are mixed with fuels, binders and an oxidizer to create a thick slurry; wires are dipped into the slurry and allowed to harden

SHAPES AND COLORS of firework bursts reflect the type of shell and the composition of the stars. A ragged spray of light is the signature of an American-European shell (*top left*). Round, flower-shaped explosions result from the aptly named chrysanthemum shell (*top right*). Multiple-burst shells or volleys of single-burst shells can produce dramatic effects by incorporating a variety of pyrotechnic compositions that emit different colors and sounds when ignited (*bottom*).



FIREWORKS GLOW by incandescent, atomic, and molecular emission. The color depends on where the emission falls on the visible spectrum (*top*). Atoms and molecules become excited at the high temperatures in a pyrotechnic flame and release their excess energy as light. Atomic sodium is an intense yellow-orange emitter. Fragile compounds containing copper, barium and strontium produce blue, green and red colors, respectively (*middle*). These unstable molecules are created only briefly in the hot flame. Aluminum or magnesium particles appear as white-hot incandescent sparks when ignited; iron or charcoal particles do not become so hot and therefore radiate dimmer, gold-tinged light (*bottom*).

to create sparklers. Another strontium compound, strontium nitrate, is blended with potassium perchlorate (an oxidizer and chlorine source) and various fuels to create the distinctive red glow of roadside hazard flares.

The structure of a firework is also an intricate brew of craft and engineering. There are two kinds of firework "shells." Cylindrical American-European-style shells, typically seven to 30 centimeters in diameter, are launched from metal, cardboard or plastic mortar tubes. A portion of black powder in the bottom of the shell is ignited, which propels the tube a few hundred meters into the air. A time-delay fuse begins burning when the shell is set off; some seconds later, when the shell is far above the ground, a bursting charge of black powder breaks the shell open and ignites pellets of color composition (called stars), which are irregularly packed into the shell. The stars are expelled in a random pattern of light and color. This type of firework may also contain several ounces of flash-and-sound powder rather than stars and a bursting charge. Such a shell, called a salute, produces a flash of light and a loud boom instead of a burst of colors.

Round Japanese-style chrysanthemum shells are similar in diameter to American-European shells, and they, too, are launched from mortar tubes. In chrysanthemum shells the stars are arranged in a sphere about a central black-powder bursting charge. When the charge explodes, it ignites the numerous stars and distributes them in a round, symmetric pattern. Depending on the size and chemical composition of the stars, the result can vary from a quick flash to an extended trail. The trail may even change color if the stars contain more than one layer of color-producing composition.

Some American-European shells contain several compartments, each with its own bursting charge and stars (or flash-and-sound powder). When one compartment explodes, it ignites a time-delay fuse that leads to the next compartment. In this way, a single shell can produce multiple bursts. Incredibly, the protective barriers that separate the explosive compartments are fabricated from nothing more exotic than cardboard.

In addition to light, pyrotechnics is often exploited for its production of heat. The best-known heat-generating pyrotechnic—the safety match—contains an energetic blend of potassium chlorate oxidizer and sulfur, along with a gluelike fuel and binder.

Calcium silicide fuel mixed with iron oxide generates a moderate amount of heat but no gas. During World War II small pyrotechnic devices containing this composition and a fuse were built into cans of rations so that they could be warmed in the absence of a stove. Time-delay mixtures, usually pressed columns containing boron, tungsten or silicon fuel, produce a controlled dose of heat for a specific length of time that can then set off a larger reaction. Such mixtures are used to control the timing sequence in various aerospace devices, including the exploding bolts that rapidly jettison emergency-exit hatches and spent rocket stages; similar time delays prevent hand grenades from exploding as soon as the pin is pulled and the lever released. Decoy compositions have been developed to protect aircraft from enemy heat-seeking missiles. These compositions emit infrared radiation that emulates the thermal signature of a jet engine.

Heat production is often associated with the emission of smoke and gas. Colored smoke grenades, used for signaling and for daytime displays, contain a mixture of potassium chlorate oxidizer and sugar fuel that, when activated, vaporizes organic dyes to create a richly hued smoke cloud. Sugar is used because it burns at a low temperature; a hotter flame would disintegrate the dyes.

Solid-fuel rockets are in essence giant pyrotechnic devices designed to optimize gas production. Each space-shuttle booster rocket contains half a million kilograms of a propellant consisting of energetic pulverized aluminum fuel and ammonium perchlorate oxidizer; the mixture also includes a special fuel and binder called polybutadiene–acrylic acid–acrylonitrile terpolymer (PBAN). When oxidized, PBAN releases copious quantities of carbon monoxide and carbon dioxide gas and steam that help loft the shuttle into space. Ammonium perchlorate is well suited for this application because its decomposition products are all gases, and so it enhances the rockets' thrust.

Gas generation on a smaller scale creates the whistle effect heard in some fireworks. Compositions containing potassium perchlorate oxidizer and an organic acid salt (such as sodium salicylate—a chemical cousin of aspirin) burn one layer at a time and emit gas in spurts. When such compositions are pressed into narrow tubes, the rapid pulses of escaping gas create a whistling sound.

The most appropriate application for a particular pyrotechnic mixture is largely determined by the reactivity of its oxidizer and its fuel. The reactivity of the fuel is closely related to the amount of energy (heat of combustion) liberated when it combines with oxygen. Metals release large amounts of energy when oxidized; sugar releases relatively little. Charcoal and natural materials such as red gum—a tree secretion—produce the moderate heat needed to activate the color-producing compounds in a firework.

The reactivity of an oxidizer depends on two main factors: decomposition temperature and heat of decomposition. At decomposition temperature, the oxidizer begins to release oxygen at a significant rate. Heat of decomposition, as the term implies, is the amount of heat required to decompose the oxidizer in order to release the oxygen. This amount can be positive (endothermic), in which case decomposition absorbs heat, or negative (exothermic), in which case it generates heat.

Potassium chlorate decomposes at a low 360 degrees C and is exothermic; it is used in smoke grenades and household matches because it is energetic and easily activated. At the other extreme, iron oxide decomposes at nearly 1,500 degrees C and is strongly endothermic. It can be activated only by an energetic metallic fuel such as aluminum.

Packaging and the homogeneity of a pyrotechnic mixture also affect its reaction rate. As every maker of a pipe bomb knows, confinement significantly speeds up the pyrotechnic process by concentrating heat and hot gas near the reaction site. A mixture that burns at a controlled rate in the open can explode violently if confined. In general, the greater the homogeneity of the fuel and oxidizer, the faster the burning rate.

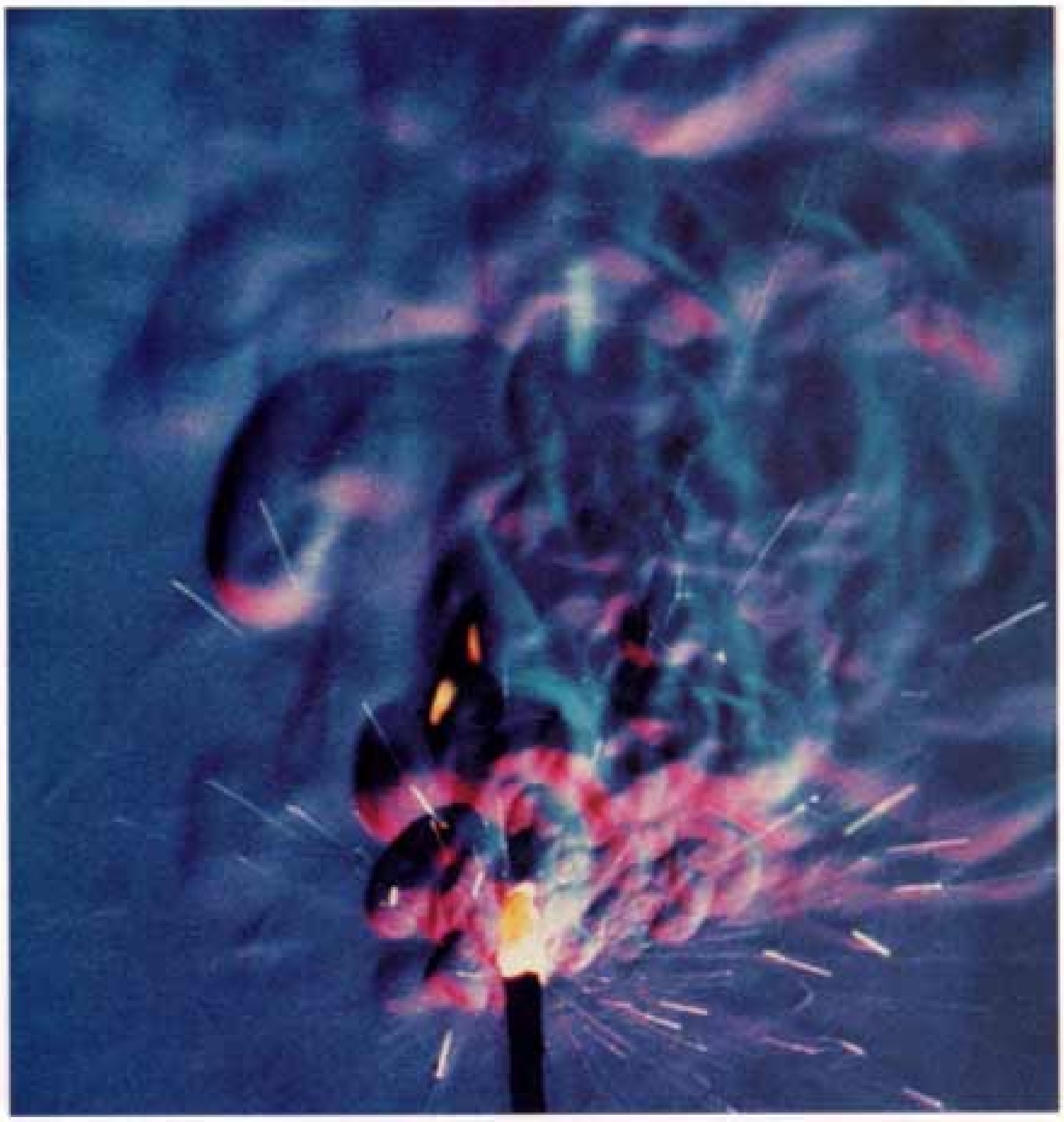
Once, while conducting a seminar, I was asked why liquids are not widely used as pyrotechnics, since they should mix more thoroughly and so produce more reactive compositions than solids. The answer, I realized, is that liquids intermingle too well. Liquid compositions would be extremely homogeneous and therefore highly reactive and sensitive to ignition. Liquids also could settle out during storage, thereby upsetting the chemical balance. Early versions of dynamite, which consisted of porous materials (such as sawdust) soaked in liquid nitroglycerin, were extremely unstable precisely for this reason.

Reactivity is greatest when the oxidizer and fuel are blended at the atomic level and the electron-accepting oxidizer is located immediately adjacent to the atom or ion of fuel that donates the electrons when the pyrotechnic reaction is initiated. Such energetic atomic mixtures are, strictly speaking, explosives not pyrotechnics, but the principles underlying their behavior are similar. Nitroglycerin, for instance, has the molecular formula $C_3N_3H_5O_9$. A small disturbance (heat or impact, for instance) causes it to decompose into carbon dioxide (CO_2), water (H_2O), nitrogen (N_2) and a little excess oxygen (O_2). In the process, nitrogen-oxygen atomic bonds are replaced by far more stable carbon-oxygen, hydrogen-oxygen and nitrogen-nitrogen bonds; the result is a violent release of energy.

A less familiar, but increasingly important, material of this kind is sodium azide, the active component in automotive airbags. This compound consists of interpenetrating lattices of ions of sodium and azide (a group of three chemically bound nitrogen atoms). An energetic impact disrupts the lattice structure. The sodium combines with oxygen while the nitrogen atoms regroup into pairs to form a large quantity of nitrogen gas.

The history of the pyrotechnics industry, both in the U.S. and abroad, has been filled with tragic accidents that have occurred during the manufacturing process, such as the devastating explosion that destroyed the Grucci plant in Long Island, N.Y., in 1983. Improving safety demands a detailed understanding of the phenomenon of ignition.

Ignition begins when energy from

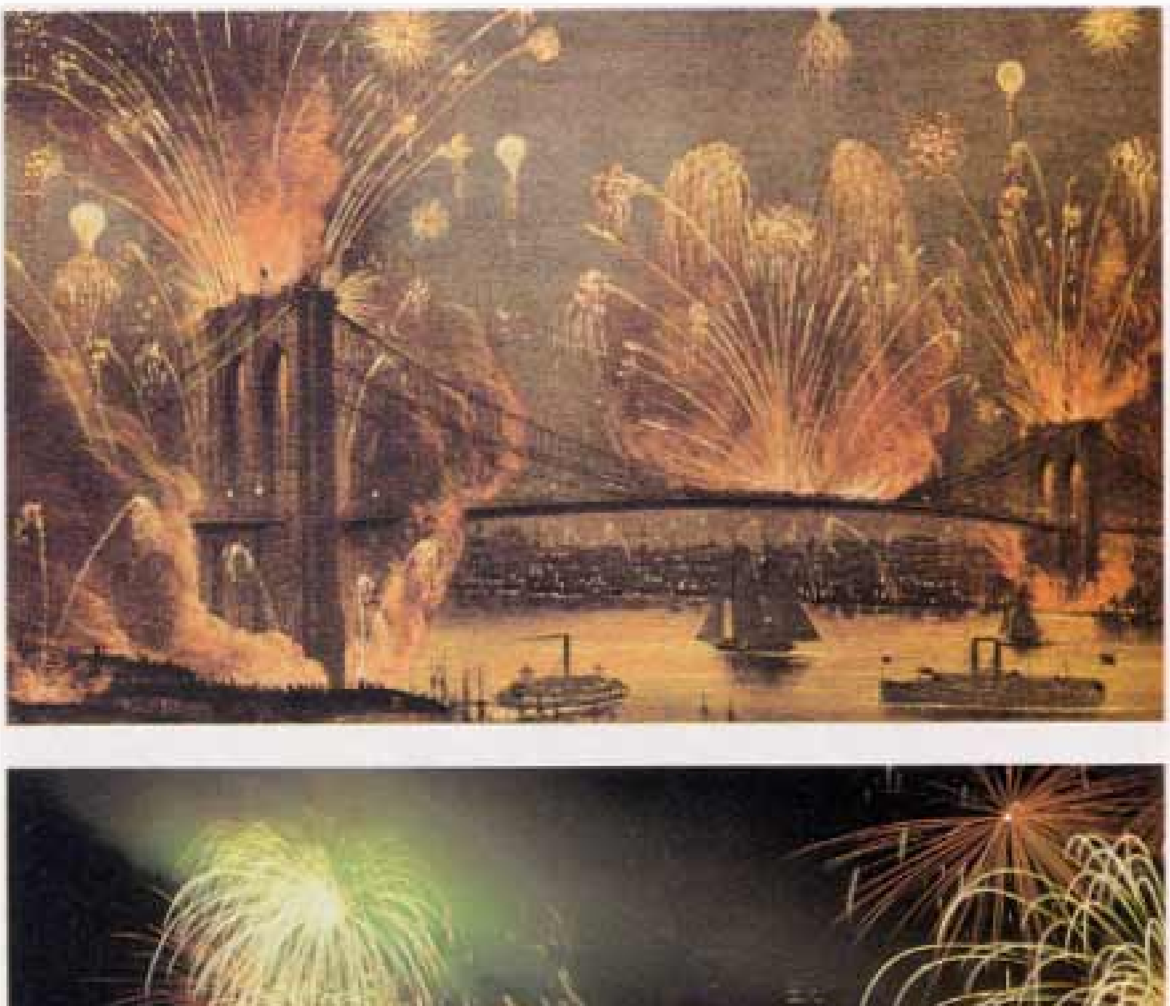


HOUSEHOLD MATCH is a specialized pyrotechnic device. A reaction between potassium chlorate oxidizer in the match and red phosphorus in the striker produces a flame that ignites the mixture of potassium chlorate and gluelike fuel in the match head. All the pyrotechnic effects—heat, smoke, light, gas and sound—are present. Some early matches were lit by dipping a potassium chlorate composition in sulfuric acid. The combination of sulfur and potassium chlorate is so sensitive to ignition that mixtures of the two were outlawed in England in 1875. Use of potassium chlorate is also restricted in fireworks in the U.S.

some source—a flame, friction, impact, spark, elevated temperature or even laser beam—breaks the chemical bonds in a pyrotechnic mixture. As a result, more stable bonds are formed and energy is released. If the energy is adequate to activate the next layer of the mixture, the reaction continues; if the energy is absorbed by the surrounding material or is insufficient to activate the next layer, the reaction dies out.

Fred L. McIntyre and his co-workers at the John C. Stennis Space Center's Hazard Test Range in Mississippi have analyzed a series of pyrotechnic compositions to determine how sensitive each is to ignition by various energy sources. These studies demonstrated that critical factors controlling sensitivity are the amount of heat generated by the reaction and the ignition temperature—the minimum temperature necessary to induce a rapid, self-propagating reaction. Ignition sensitivity is also affected by the particle size of the chemical components and by the grain size of the blended composition; fine grains ignite more readily than large ones. Ease of ignition by friction depends on the presence of abrasive materials in the mixture. Adding a lubricant, such as wax, can significantly reduce the likelihood of friction-induced ignition.

Safety is also important for the users of pyrotechnics—often children celebrating Independence Day, Bastille Day, Guy Fawkes Day, New Year's or other holidays traditionally accompanied by fireworks. In 1976 the U.S. Consumer Product Safety Commission enacted strict federal standards for consumer fireworks. The European Community nations have a wide range of safety standards that they are attempting to incorporate into a single code as part of their legal and economic unification.



CELEBRATIONS have made use of fireworks for centuries. A chromolithograph of the opening in 1883 of the Brooklyn Bridge spanning the East River recorded a particularly imaginative display (*top*). The bridge's centennial was greeted by another dazzling demonstration of pyrotechnic art (*bottom*). The 1983 display was arranged by the Gruccis, a major fireworks-producing family in the U.S.

There is no question—based on numerous conversations I have had with researchers in many fields—that many science careers were stimulated by early experiments in pyrotechnics. The need to come up with a quick explanation to parents concerning a basement filled with smoke from a successful experiment probably has also sparked more than a few legal careers.

The family-business nature of the civilian pyrotechnics industry and the classified nature of much defense-related work have made academic training in the field difficult to acquire. The only academic pyrotechnics courses in the U.S. that I am aware of are several annual, one-week seminars at Washington College in Maryland, taught by several colleagues and me. Fortunately, a number of organizations actively encourage treating pyrotechnics as a science and publish research in the field. These groups include the International Pyrotechnics Society and the more amateur-oriented Pyrotechnics Guild International. An occasional journal called *Pyrotechnica* also contains articles on current work.

The most active supporter of the civilian industry continues to be the viewing public. Since 1976 the annual consumption of fireworks in the U.S. by private individuals for family and neighborhood celebrations has doubled. The centuries-old tradition of fireworks displays is still fascinating, despite competition from rock concerts, music videos and other eye-dazzling and ear-filling forms of entertainment. Evidently modern technology has yet to find a match for the excitement one feels when the work of a master pyrotechnician explodes in the night sky with a clap of thunder and a brilliant shower of color.

FURTHER READING

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