Kirk-Othmer Encyclopedia of Chemical Technology.

PYROTECHNICS

Pyrotechnics is the field of technology that combines science and art to chemically generate heat, and from that heat create light, color, audible effects, and gas pressure for entertainment, emergency signaling, and military applications. The civilian side of pyrotechnics includes fireworks, highway flares (fusees), air bag inflators, and special effects devices for the entertainment industry. Military and aerospace pyrotechnics include a wide range of devices for illumination, signaling, obscuration, and gas generation. These devices are characterized by rugged construction and greater resistance to adverse environmental conditions with associated higher cost, reliability, and safety than most civilian pyrotechnic devices. In some ways, unlike the related technologies of explosives and propellants, pyrotechnics remains a practical discipline with an incomplete theoretical foundation, and the rigorous application of the various scientific disciplines is taking place gradually (see Explosives).

1. Principles

The usefulness of pyrotechnic reactions derives from their being exothermic (heat-releasing), self-sustaining, and self-contained. Many chemical reactions require a sustained input of energy or they occur by interaction with other substances provided from external sources; combustion of a fuel such as gasoline or wood with atmospheric oxygen is a typical example. Most pyrotechnic reactions occur independently of any external oxidizer, although in some instances the pyrotechnic effect is enhanced by interaction with the environment. Such characteristics of pyrotechnics are shared by explosives and propellants, which also involve exothermic and self-propagating reactions and, in some cases, the distinction is derived solely from the application of the device and not from the chemical nature of the reaction. Most pyrotechnic devices contain no moving parts and are small and lightweight. Compared with their mechanical analogues, pyrotechnic devices tend to be inexpensive and often are highly reliable. On the other hand, pyrotechnic devices function only once and do not normally lend themselves to reuse.

Pyrotechnics is based on the established principles of thermochemistry and the more general science of thermodynamics. There has been little work done on the kinetics of pyrotechnic reactions, largely due to the numerous chemical and nonchemical factors that affect the burn rate of a pyrotechnic mixture. Information on the fundamentals of pyrotechnics have been published in Russian (1) and English (2–6). Thermochemical data that are useful in determining the energy outputs anticipated from pyrotechnic mixtures are contained in general chemical handbooks and more specialized publications (7–9).

A pyrotechnic composition contains one or more oxidizers in combination with one or more fuels. Oxidizers used in pyrotechnics, such as potassium nitrate, KNO_3, are solids at room temperature and release oxygen when heated to elevated temperatures. The oxygen then combines with the fuel, and heat is generated by the resulting chemical reaction. Chemicals that release fluorine or chlorine on heating, such as polytetrafluoroethylene (Teflon) are also capable of serving as oxidizers, particularly with a metallic fuel. If the released heat is efficiently captured by adjacent pyrotechnic composition, further reaction occurs between oxidizer and fuel,

Table 1. Representative Oxygen Donors Used in Pyrotechnics

Compound	Formula	CAS Registry Number
ammonium perchlorate	NH_4ClO_4	[7790-98-9]
barium nitrate	$Ba(NO_3)_2$	[13465-94-6]
iron(III) oxide	Fe_2O_3	[1309-37-1]
potassium chlorate	$KClO_3$	[3811-04-9]
potassium perchlorate	$KClO_4$	[7778-74-7]
sodium nitrate	$NaNO_3$	[7631-99-4]
strontium nitrate	$Sr(NO_3)_2$	[10042-76-9]

and a self-propagating reaction ensues through the remaining mixture. The onset temperature for a rapid, self-propagating reaction between oxidizer and fuel is termed the ignition temperature of the composition. When a portion of a pyrotechnic mixture reaches this temperature through an external input of energy, such as a burning fuse, hot wire, friction, or impact, the composition undergoes a rapid chemical reaction that is self-sustaining through the remaining composition.

The most commonly used oxidizers in pyrotechnics are listed in Table 1. They are normally ionic solids such as nitrate or perchlorate salts; oxides, chlorates, and chromates are also used. The selection of oxidizer is determined by the desired heat output, reaction rate, and the physical state of the anticipated reaction products. A slower reaction occurs if the oxidizer releases its oxygen only at high temperatures, and if the oxidizer requires a net heat input (is endothermic) in its decomposition. Iron(III) oxide, Fe_2O_3, is an example of a “slow” oxidizer, since it melts at 1565°C and has a heat of decomposition of +824 kJ/mol (197 kcal/mol) (7). Potassium chlorate, $KClO_3$, in contrast, melts at approximately 356°C with the evolution of oxygen, and releases approximately −45 kJ/mol (−10.8 kcal/mol) upon decomposition into potassium chloride, KCl, and oxygen. Potassium chlorate ignites and readily reacts with a wide range of fuels, whereas iron(III) oxide can only sustain a self-propagating reaction with the most energetic fuels. Ammonium perchlorate, NH_4ClO_4, is an example of an oxidizer that liberates extensive gaseous reaction products upon its decomposition. It has found wide use as an oxidizer in the solid propellant field, since the thrust generated by a propellant is related to the amount of gas generated by the burning propellant. The solid propellant used in the booster rockets on the U.S. Space Shuttle is 70% ammonium perchlorate by weight.

Pyrotechnic fuels are selected for their heat of combination with oxygen, melting or decomposition temperature, and the physical state of their reaction products. A highly exothermic fuel that combines with oxygen at low temperature tends to be the most reactive in a pyrotechnic system. Pyrotechnic fuels include readily oxidized metals and other elements as well as organic compounds consisting of carbon and hydrogen, sometimes in combination with other elements such as nitrogen and oxygen. Organic compounds produce carbon dioxide and water as two of their primary oxidation products; these are gases above 100°C, and hence gas pressure is generated when they undergo oxidation in a pyrotechnic mixture. This may or may not be desired in the reaction products. Common pyrotechnic fuels include (*1*) metal powders, eg, aluminum, magnesium, titantium, magnesium–aluminum alloy (magnalium), and zirconium; (*2*) elemental fuels, such as carbon (charcoal), sulfur, boron, silicon, and phosphorus; and (*3*) carbon–hydrogen compounds (organic compounds), ie, starch, plastics (poly(vinyl chloride) (PVC)), epoxy, polyesters, and tree gums.

A fuel must be reasonably stable to air and moisture to be usable in pyrotechnic manufacturing. Metals such as sodium or lithium, although attractive from their low atomic masses and high heats of combustion, do not possess the required stability to be safely used in the manufacturing process and would not produce devices with acceptable long-term storage stability unless they were hermetically sealed to prevent atmospheric oxygen and moisture from slowly reacting with the fuel over time. More stable metals such as magnesium, aluminum, titanium, and zirconium do find extensive use in pyrotechnic applications. When designing pyrotechnic mixtures it must be remembered that magnesium reacts in an acidic environment, whereas aluminum is more affected in an alkaline environment. Mixtures that contain magnesium are sometimes stabilized with a few percent of an organic binder that coats and protects the magnesium particles. Similar compositions containing aluminum are more stable, except that these mixtures can undergo a base-accelerated decomposition if they get wet. Boric acid is therefore sometimes added as a stabilizer to mixtures containing a nitrate oxidizer and aluminum powder. Illuminating flare and tracer compositions contain magnesium with barium, strontium, or sodium nitrates in an organic binder, whereas more energetic photoflash compositions are typically prepared with aluminum powder and the more energetic oxidizer potassium perchlorate and used as loose powders rather than consolidated into a tube.

Other typical pyrotechnic fuels include charcoal, sulfur, boron, silicon, and synthetic polymers such as poly(vinyl alcohol) and poly(vinyl chloride). Extensive use has been made of natural products such as starches and gums, and the use of these materials continues to be substantial in the fireworks industry. Military pyrotechnics have moved away from the use of natural products due to the inherent variability in these materials depending on climatic conditions during the growth of the plants from which the compounds are derived.

Pyrotechnic mixtures may also contain additional components that are added to modify the burn rate, enhance the pyrotechnic effect, or serve as a binder to maintain the homogeneity of the blended mixture and provide mechanical strength when the composition is pressed or consolidated into a tube or other container. These additional components may also function as oxidizers or fuels in the composition, and it can be anticipated that the heat output, burn rate, and ignition sensitivity may all be affected by the addition of another component to a pyrotechnic composition. An example of an additional component is the use of a catalyst, such as iron oxide, to enhance the decomposition rate of ammonium perchlorate. Diatomaceous earth or coarse sawdust may be used to slow up the burn rate of a composition, or magnesium carbonate (an acid neutralizer) may be added to help stabilize mixtures that contain an acid-sensitive component such as potassium chlorate. Binders include such materials as dextrin (partially hydrolyzed starch), various gums, and assorted polymers such as poly(vinyl alcohol), epoxies, and polyesters. Polybutadiene rubber binders are widely used as fuels and binders in the solid propellant industry. The production of colored flames is enhanced by the presence of chlorine atoms in the pyrotechnic flame, so chlorine donors such as poly(vinyl chloride) or chlorinated rubber are often added to color-producing compositions, where they also serve as fuels.

Cost is always a factor in selecting a component for a pyrotechnic composition, as is the water-attracting ability of a substance (hygroscopicity). In general, substances that attract water from the atmosphere are avoided in pyrotechnic formulations for a variety of reasons, thereby supporting the centuries-old adage, “Keep your powder dry.”

The process of designing a pyrotechnic mixture begins with the selection of oxidizer and fuel, and proceeds to incorporate additional components to achieve the exact pyrotechnic effect and burn rate desired in the end item. It is at this point that pyrotechnics takes on the dual nature of an art and science, and experience is often the only thing that can be relied upon for the solution of a difficult problem.

The classic example of a pyrotechnic composition is black powder, a blend of potassium nitrate, sulfur, and charcoal in a 75:10:15 ratio by weight (10, 11). This composition has been used as a propellant for cannons and muskets as well as in fireworks for centuries, and is still used in the 1990s in significant amounts as a propellant, fuse powder, and bursting charge by the fireworks industry. It must be well mixed in the proper proportions to achieve a reactive powder, and even the specific charcoal selected to manufacture the black powder affects its burn behavior. Its batch-to-batch variability, depending on the mixing time, mixing energy, charcoal surface area, and residual water content, has been responsible in large part for the somewhat questionable reputation that the field of pyrotechnics has acquired over the years.

Another matter of concern in pyrotechnic formulations is the possibility of exchange reactions occurring between components. Addition of ammonium salts to compositions containing nitrate oxidizers can produce ammonium nitrate, a very hygroscopic material. The composition then becomes quite prone to pick up water and its performance deteriorates. The addition of an ammonium salt to a chlorate-based formulation can lead to the formation of the highly unstable ammonium chlorate, and spontaneous ignition may occur at room temperature. In designing a pyrotechnic composition, the pyrotechnic chemist must be careful to select components that do not undergo such adverse exchange reactions, which are often aggravated by the presence of residual moisture in the blended mixture.

2. Theoretical Considerations

The heat output of a pyrotechnic reaction is the difference between the sum of all heats of formation of the products of the reaction and the sum of the heats of formation of the reactants. If the starting and final conditions of pressure and temperature are close to those of the initial surroundings, it is permissible to use the tabulated standard heats of formation. If the reaction products are primarily solids or liquids, a moderate exothermic output is a reliable indication of a tendency to self-propagate. As long as the pyrotechnic process is represented by a primary chemical reaction, the preceding analytical methods are adequate. If, however, chemical processes take place at extreme temperatures and pressures, a large number of simultaneous reactions may exist. As the number of possible reactions increases, so does the mathematical difficulty; most calculations of chemical equilibria are performed with computers, which are programmed for the determination of the minimum free energy attainable at any given composition and temperature (12).

The ignition temperature of a given pyrotechnic mixture is largely determined by the decomposition temperature of the oxidizer and the melting point or decomposition temperature of the fuel. Ignition, or the onset of a self-propagating reaction, occurs when the oxygen from the oxidizer reacts with the fuel and produces enough heat output to rapidly activate the adjacent particles to their ignition temperature. The combination of an easily decomposed oxidizer, such as potassium chlorate, with a fuel that melts or decomposes at low temperature, such as a sulfur or sugar, produces mixtures with ignition temperatures below 200°C. A high melting oxidizer, such as iron oxide, combined with a fuel such as aluminum that does not melt until 600°C or more, results in significantly higher ignition temperatures.

The addition of sulfur or an organic compound to pyrotechnic mixtures normally improves the ignitability by providing a readily ignitable fuel. A retardation of the burn rate may also occur, however, so a minimum percentage of sensitizer should be used. The sensitivity of the mixture to spark, friction, and impact may also be affected by the addition of a second fuel. If sulfur is used, particular care must be exercised in specifying only ground and sieved crystalline material (flour of sulfur) and not sublimed sulfur (flowers of sulfur), as commonly employed in agriculture. The latter may be contaminated with sulfurous and sulfuric acids, which can make some pyrotechnic mixtures unsafe.

Once ignition is achieved, the reaction continues through the remaining composition. This propagation rate, usually referred to as the burn rate, is determined by a complex combination of chemical and physical factors. The burn rate, to a significant extent, is determined by the selection of oxidizer and fuel and the weight ratio of the oxidizer to fuel. The stoichiometric mixture, or that weight ratio corresponding to complete reaction between oxidizer and fuel, generates the maximum heat output, in kJ/g, but it is not always the fastest burning composition. Other factors affecting the burn rate include the particle sizes of the oxidizer and fuel, with finer particles usually yielding the fastest burning mixtures; the extent of homogeneity of the blended pyrotechnic composition, with burn rate increasing as the intimacy of the mixing increases; and the thermal conductivity of the mixture, ie, compositions with high thermal conductivity tend to burn faster. Metals are particularly good thermal conductors, so raising the percentage of metal fuel in a mixture, even well beyond the stoichiometric point, usually speeds up the burn rate of a composition. External temperature, ambient pressure, the extent of residual moisture in the mixture, the nature of the container holding the pyrotechnic composition, the porosity of the composition (determined by the consolidation pressure used to load the material into a tube or other container), and the surface area of the burning composition all affect the rate of burning of a pyrotechnic composition. Because of the large number of factors that affect burn rate, attempts to develop a burn rate equation for pyrotechnic compositions have not met with great success.

Many pyrotechnic reactions develop a gas-phase reaction component as they burn. A flame plume is present above the burning reaction surface as the reaction continues in the vapor phase, and the heat return from this vapor-phase reaction is another critical component of the burn rate of a pyrotechnic mixture. External pressure plays a significant role in determining the burn rate when a vapor-phase reaction component is present. High pressure tends to hold the hot gases near the burning surface, increasing the burn rate. This is the principle behind confining propellants in a chamber as they burn, leading to a high pressure and high burn rate for the propellant. In the open, propellants often are quite calm in burning performance. Not all pyrotechnic reactions, however, depend on a gas phase. Certain reactions, such as between iron powder and barium peroxide, are solid-phase reactions (3).

Light output is achieved in a pyrotechnic mixture by a combination of high flame temperature and the presence in the flame of solid or liquid particles that are heated to incandescence. A flame temperature approaching 3000°C is required for the emission of bright white light. Because the intensity of light emission from an incandescent object is proportional to temperature to the fourth power, a slight increase in flame temperature can result in a significantly brighter flame (13). Particles of magnesium, aluminum, titanium, or zirconium metal in a pyrotechnic composition cause high flame temperatures to be achieved because they are active fuels, and their solid oxidation products, such as MgO or Al_2O_3, incandesce and provide bright light output. Sparks occur if large fuel particles such as aluminum or charcoal are present in a pyrotechnic mixture. These fuel particles continue to burn in air and incandesce as they exit the pyrotechnic flame, leaving a spark-like trail.

3. Color and Sound Production

Emission of a specific color can be achieved by the presence of a specific atomic or molecular species in the vapor state in the pyrotechnic flame. The atom or molecule undergoes electronic excitation due to the elevated flame temperature, and the atom or molecule subsequently returns to its ground electronic state with the emission of a photon of light of specific wavelength. If this specific emission happens to fall in the visible region of the electromagnetic spectrum, color is perceived by onlookers. The production of color by pyrotechnic means requires the pyrotechnic composition to generate the color-emitting species as a reaction product.

Red flame color, for example, is observed if a species in the flame emits light that falls in the 650–780 nm region; visible light covers the region from $\sim 400-780$ nm. The element strontium is usually employed to produce a red pyrotechnic flame, and the primary red-emitting species is SrCl, produced in the vapor state at temperatures in the 1500°C range by a combination of Sr and Cl atoms. Strontium nitrate or strontium carbonate are the usual sources of Sr. Other color emitters include BaCl (green, from $Ba(NO_3)_2$), CuCl (blue), and atomic sodium, Na (yellow-orange) from sodium oxalate or sodium aluminum fluoride, Na_3AlF_6 (cryolite) (5, 14). Copper carbonate, copper oxide, or copper oxychloride are the usual sources of blue color. A violet hue can be achieved by a combination of SrCl (red) and CuCl (blue) in the pyrotechnic flame. Aluminum, magnesium, or titanium particles produce white sparks. Charcoal particles are used to give gold sparks.

Another unique pyrotechnic effect, a shrill whistle, can be achieved if certain pyrotechnic mixtures are pressed into narrow-diameter tubes and ignited. The escaping gas pulsing out of the tube creates the whistling phenomenon. The mixtures usually contain potassium perchlorate and a salt of an organic acid, such as sodium salicylate or potassium benzoate, all pressed into a narrow cardboard tube (5). The whistling effect is right on the verge of an explosion, and these compositions are quite dangerous to prepare and load into tubes.

4. Civilian Pyrotechnics

Fireworks are used around the world to celebrate special occasions, and the appeal of lighting up the sky with bright colors, flashes of light, and loud booms appears to be universal. Fireworks have been used for many centuries, and their origin traces back to the discovery of black powder in China or India over 1000 years ago. Black powder was used to make firecrackers and sky rockets in China, and the technology made its way to Europe where a flourishing fireworks industry then developed. The United States adopted fireworks as the traditional means of celebrating Independence Day on the 4th of July, and the tradition has continued for over 200 years. In the United States, fireworks consumption in 1994 was approximately 45,000 t with a retail sales value of approximately $300,000,000. A majority of these fireworks were imported from China, the world's principal fireworks producer. The U.S. fireworks consumption is approximately 67% consumer fireworks and 33% public display fireworks. Many other countries also have a traditional fireworks day, such as Bastille Day (July 14) in France, Guy Fawkes Day (November 5) in Great Britain, Halloween (October 31) in some parts of Canada, New Year's Eve in Germany, and Chinese New Year throughout the world in Chinese communities.

Black powder remains a key component of fireworks and research into the energetics of black powder continues to be performed (10, 11). It serves as the composition for fireworks fuses; as the propelling charge in sky rockets, Roman candles, and aerial shells; and as the bursting charge to explode aerial shells high in the air. Modern public displays are largely based on the use of mortar-fired aerial shells which explode into beautiful patterns of color high in the sky. The assembly of various types of fireworks has been described (4, 6).

4.1. Types of Fireworks

Fireworks are conveniently classified as consumer or display.

4.1.1. Consumer Fireworks

An assortment of small fireworks devices are permitted for use by private citizens in many areas in the United States and elsewhere throughout the world. These devices consist of items such as wire sparklers, fountains, Roman candles, sky rockets, mines, and small aerial shells.

Wire sparklers are wires coated with pyrotechnic composition which are hand-held and produce a gentle spray of gold sparks from iron filings. Fountains are cardboard tubes filled with chemical mixtures that produce a spray of color and sparks extending 2–5 m into the air. Roman candles are cylindrical tubes which repeatedly fire colored stars distances of 5–20 m into the air. These items typically contain 5–12 stars.

Sky rockets are tubes with a stick attached for guidance and stability and which contain a pressed black powder propellant. They rise high into the air when ignited and a burst of color or a report, an audible bang, is normally produced in the air. Alternatively, rockets may contain a different propellant that fires the device into the air with a simultaneous whistling effect. Mines are aerial items that use a black powder propelling charge to fire a burst of colored stars, whistles, or firecrackers into the air from a cardboard tube. A barrage of color and noise results. Small aerial shells are plastic or cardboard spheres that are similar in effect to the type used by professional operators at large displays. These devices are launched from a mortar tube by a black powder propelling charge. A time delay fuse burns as the sphere or canister tumbles into the air, and a burst of color is produced high in the air when a black powder bursting charge explodes, breaking the sphere open and igniting the stars that are mixed with the black powder.

4.1.2. Display Fireworks

Larger versions of the devices sold as consumer fireworks are used for public fireworks displays. The principal item used in fireworks displays is the aerial shell, a sphere or cylinder typically 8–20 cm (3–8 in.) in diameter that is launched several hundred meters into the air ($\sim$100300 m), from a mortar tube, by a propelling charge of black powder. A time fuse burns as the device climbs into the air, and a bursting charge explodes the device high in the air, lighting a shower of stars to produce a spectacular visual effect (15). Alternatively, the shell may contain an explosive charge of salute powder, which produces a loud explosion in the air. Displays also make use of large Roman candles and fountains, which can produce a waterfall-type effect if suspended upside down. Lances are small, cigarette-sized tubes that burn with specific flame colors. Pyrotechnicians attach hundreds of lances to wooden frames to create fire pictures, called set pieces. The pictures can resemble objects like the Liberty Bell or a famous person's face, or spell out messages such as "Good Night."

4.2. Theatrical Pyrotechnics or Special Effects

Many spectacular visual and audible effects are produced for stage presentations of both music and drama, and many motion pictures and television shows incorporate pyrotechnic and explosive special effects to liven up the presentation. These spectacular effects are a combination of pyrotechnics, explosives, combustion, and electronics. After the effects are filmed or videotaped, they are often enhanced by slow-motion replay and by the addition of more exciting noise. A real explosion is over in milliseconds, and hence there is a need for electronic enhancement to create a more spectacular effect on the screen.

Bullet effects or bullet hits are electrically initiated devices that simulate bullet impact through the use of various amounts of sensitive explosive composition. These explosive devices can be buried in the ground, attached to walls, or even attached with protective padding to human bodies. The explosions are triggered by firing an electric igniter, and a bullet appears to strike the intended target. Many pyrotechnic special effects resemble fireworks in much of their chemistry and intended effect. However, because the audience is often much closer to special effect devices than they would be to a fireworks display, greater control needs to be taken in manufacturing special effects to ensure that the height of the flame and the maximum distance that sparks fly are closely controlled. These effects must be set up and fired by trained professionals with extensive experience.

4.3. Model Rockets and Missiles

Model rockets are another type of pyrotechnic device that have been quite popular since the appearance of the Russian satellite Sputnik in the 1950s. These items are most often sold as kits with modular, preassembled, solid propellant engines. The engines have traditionally been constructed of nonmetallic casings, clay nozzles, and a compressed black powder charge, which is ignited by an electric match. The actual burn time of the propellant is generally less than a second, and the rocket can be propelled quite a distance into the air ($\sim$200 m). Parachutes are often deployed at the height of flight, and the rocket body is recovered and reused. The concept of prepackaging model rocket motors provided a significant element of safety to the hobby of model rocketry, because it eliminated the need for individuals to blend and load their own propellant mixtures, a potentially dangerous operation.

Model rocket engines have appeared in the 1990s that use solid rocket propellant composition similar to the higher technology propellants used in military rockets and missiles. These propellants use ammonium perchlorate in combination with a rubber-like binder. They produce a higher percentage of gaseous products than does black powder, and the use of these new engines has helped advance the hobby of model rocketry into a mature science (16). Many rocket enthusiasts are adults who began firing black powder rockets as children and have continued to pursue rocketry as their avocation into adulthood.

4.4. Other Civilian Devices

Pyrotechnic devices also serve an assortment of civilian uses, primarily for signaling. Highway flares, often known as fusees, are made chiefly of strontium nitrate mixed with sawdust, wax, sulfur, and potassium perchlorate and contained in a waterproof cardboard tube. A small quantity of a safety-match composition also is incorporated and, upon ignition by friction, the device burns for up to 30 minutes with a distinctive red flame. Other hand-held and aerial devices are used for marine distress signals, and some type of distress signal must be carried on boats in intercoastal waterways under U.S. Coast Guard regulations. Noisemaking pyrotechnic devices are also used to a limited extent in agriculture to discourage birds and other pests from frequenting fruit orchards and freshly planted fields.

The air bag industry has become one of the principal users of pyrotechnic compositions in the world. Most of the current air bag systems are based on the thermal decomposition of sodium azide, NaN_3, to rapidly generate a large volume of nitrogen gas, N_2. Air bag systems must function immediately (within 50 ms) upon impact, and must quickly deploy a pulse of reasonably cool, nontoxic, unreactive gas to inflate the protective cushion for the driver or passenger. These formulations incorporate an oxidizer such as iron oxide to convert the atomic sodium that initially forms into sodium oxide, Na_2O. equation 1 represents the reaction.

$$6\ NaN_3 + Fe_2O_3 \longrightarrow 3\ Na_2O + 2\ Fe + 9\ N_2 \qquad (1)$$

The actual formulations used by the various companies engaged in the highly competitive air bag business are proprietary, and contain numerous additives to modify the actual performance of the air bag compositions. Many more changes are likely in this new industry.

4.5. Regulations

The manufacture, transportation, storage, and use of pyrotechnics are all very highly regulated fields, and the volume and scope of the regulations covering the industry, both military and civilian, has increased enormously since the 1980s. The transportation of all commercial pyrotechnic articles, for both consumer and military use, is under the control of the U.S. Department of Transportation (DOT). All pyrotechnic devices must be officially approved for transportation by DOT, and this approval process involves testing to determine the appropriate classification of the device, as well as its suitability for transportation from a sensitivity point of view. Pyrotechnic devices are classed as “Explosives” for transportation purposes (17).

The U.S. Treasury Department’s Bureau of Alcohol, Tobacco and Firearms (BATF) regulates the licensing (qv) and storage of all civilian explosives, including pyrotechnic devices. Consumer fireworks are exempt from most BATF regulations, because they are subject to regulations of the U.S. Consumer Product Safety Commission (CPSC). The CPSC rules cover the labeling, construction, performance, and explosive content of fireworks intended for sale to consumers (18). States and local governments may enact stricter regulations governing consumer fireworks than those adopted by CPSC. The U.S. Occupational Safety and Health Administration (OSHA) regulates the manufacturing of pyrotechnics from an employee safety point of view. Additional U.S. Department of Defense regulations cover the manufacturing of military pyrotechnics.

5. Military Pyrotechnics

Pyrotechnics have been used for military purposes for many centuries as propellants, explosive charges, time fuses, and for illumination. There are still many uses of pyrotechnic devices in military applications, where they provide portability, storage stability, simplicity of operation, safety, and the reliability required for military scenarios. The devices must be capable of surviving rough handling, weather extremes, and extended storage, yet reliably perform when called on to function.

Pyrotechnic devices are used for light generation in flares, tracers, and flash cartridges; for smoke generation for signaling and obscuration; for heat production for time delay components, incendiary applications, and ignition; and for gas-generation applications. The propellants used in many military devices are also essentially pyrotechnic compositions in nature, containing an oxidizer and fuel designed to burn at a high rate with the generation of a large quantity of hot gas to produce significant thrust. Military pyrotechnics are required to meet rigorous standards of performance, reliability, and storage lifetime, and the materials of construction are generally substantially more sturdy than those used for civilian pyrotechnics.

Many aspects of the performance of military pyrotechnics are measured and analyzed by modern instrumental techniques such as spectrophotometers for light intensity studies, replacing the qualitative, visual evaluations that were formerly used for acceptance of these devices. Military pyrotechnics are also experiencing a shift away from a concentration on the visible region of the electromagnetic spectrum, and are moving into the generation and obscuration of the infrared and microwave/millimeter regions, as modern techniques such as heat-seeking missiles, thermal imaging systems, and night vision equipment have dramatically altered the battlefield scenario. Pyrotechnic devices, such as screening smoke units, have had to adjust with these changes in technology to remain viable and effective. There will undoubtedly be more changes in pyrotechnics as modern warfare becomes more and more instrumental rather than visual in nature.

Military illuminating flares have been based for many years on the energetic reaction between sodium nitrate and magnesium metal. One of the primary reactions is equation 2. This high candlepower composition is blended with an

$$2\ NaNO_3 + 5\ Mg \longrightarrow Na_2O + 5\ MgO + N_2 \qquad (2)$$

organic binder to produce a mixture with good mechanical strength, and the mixture is then consolidated into a tube to produce a long-burning effect rather than a flash of light. A typical composition contains 53–58 wt % magnesium powder, 36–40 wt % sodium nitrate, and 4–8 wt % binder, such as a polyester. Thermodynamic data for flare reactions are given in Reference 13. The intense light emission is a combination of atomic emission from sodium atoms and incandescence from solid particles, such as magnesium oxide, present in the flame. The mixtures are usually prepared to be quite fuel (magnesium) rich in formulation. The excess magnesium, for which there is no sodium nitrate with which to react, vaporizes in the high temperature flame ($>3000^\circ C$) and vigorously reacts with atmospheric oxygen at the edge of the flame, yielding additional energy and candlepower. The relatively low boiling point ($\sim 1100^\circ C$) of magnesium metal allows this process to occur efficiently.

Military flare technology has concentrated in recent years on the development and production of decoy flares to protect aircraft against heat-seeking missiles. These flares, which emit a considerable amount of infrared radiation, use a composition based on magnesium metal and polytetrafluoroethylene (PTFE), which is perhaps better known by one of its trade names, Teflon. Here, Teflon serves as the oxidizer, releasing fluorine atoms that energetically combine with magnesium to form magnesium fluoride. These flares ignite and undergo the reaction shown as equation 3. This reaction is quite exothermic and generates hot carbon particles which emit considerable infrared radiant energy. The flame signature resembles that of a jet engine.

$$2n\ Mg + (C_2F_4)_n \longrightarrow 2n\ MgF_2 + 2n\ C \qquad (3)$$

The intensity of a flare is largely determined by its flame temperature, which depends on the stability of the reaction products. The higher the decomposition temperature of the oxide, the higher the flame temperature. Hydrogen, carbon, boron, silicon, and phosphorus form oxides that dissociate at comparatively low temperatures. A flare temperature greater than 3000 K is required to generate gray-body radiation, which is optimum for the spectral sensitivity of the human eye. Metallic fuels such as magnesium, aluminum, zirconium, and titanium are necessary to achieve these high temperatures.

Military signal flares are designed to burn with clearly distinguishable colors, and the chemistry of these compositions is quite similar to that used for color effects in civilian pyrotechnics (14). They normally contain magnesium metal as a fuel to achieve high candlepower output. Standard colors are red, green, and yellow (Table 2). Photoflash bombs are explosive devices that are used in night photography and that, for time intervals as short as 0.1 s, provide intense light output. Flash charges are loosely packed powdered mixtures

Table 2. Color Flare Compositions[a]

Ingredient	Wt %
Red	
magnesium	24.4
potassium perchlorate	20.5
strontium nitrate	34.7
poly(vinyl chloride)	11.4
asphaltum	9.0
Green	
magnesium	21.0
potassium perchlorate	32.5
barium nitrate	22.5
poly(vinyl chloride)	12.0
copper powder	7.0
binder	5.0
Yellow	
magnesium	30.3
potassium perchlorate	21.0
barium nitrate	20.0
sodium oxalate	19.8
asphaltum	3.9
binder	5.0

[a]Ref. 14.

of aluminum powder with potassium perchlorate and barium nitrate, and initiation is by an explosive charge. Flash compositions are among the most hazardous to manufacture and are processed by remote control in heavy-walled bays. With advances in the technology of low light photography, the need for these devices is diminishing. These flash mixtures are also useful for simulating explosions when packaged into smaller units as projectile ground-burst simulators for training purposes.

5.1. Smoke-Generating Devices

Smoke generators are used by the military for daytime obscuration and signaling. For field use where portable stable systems are required, pyrotechnic devices are often employed. The primary composition since the 1940s has been HC smoke, which generates a cloud of zinc chloride, $ZnCl_2$, smoke by a series of reactions between hexachloroethane, C_2Cl_6(HC), zinc oxide, and aluminum (3) (eq. 4–6). The zinc regenerated in

$$3\ ZnO + 2\ Al \longrightarrow 3\ Zn + Al_2O_3 \qquad (4)$$

$$3\ Zn + C_2Cl_6 \longrightarrow 3\ ZnCl_2 + 2\ C \qquad (5)$$

$$C + ZnO \longrightarrow Zn + CO \qquad (6)$$

equation 6 then reacts with C_2Cl_6, etc. This mixture is used in smoke grenades and large smoke pots, and it produces a dense, gray-white cloud that is largely zinc chloride. Concerns about the toxicity of the smoke from HC mixtures has led to efforts to find a replacement, but it has proven to be a difficult challenge to find a composition that can equal the obscuring efficiency of the HC mixture.

Signaling smokes may be white or colored. White signal smoke has traditionally been derived from red phosphorus or an HC mixture. New smokes based on the sublimation of terephthalic acid (TA) have been developed by the U.S. military to replace HC smoke for training purposes. Both red phosphorus and HC smokes generate high temperatures and significant flames during their operation, and neither of these are desirable in a training situation; the TA smokes are far better because they generate little if any external flame and function at much lower reaction temperatures.

Grenades and smoke marker devices that produce highly visible plumes of brightly colored smoke are used by the military for signaling and marking purposes. The production of a distinct color is critical in these devices, and the color is produced by the sublimation of an organic dye which, because of its low sublimation temperature, evaporates and recondenses in air as a brilliantly colored smoke cloud. The mixtures must be cool-burning to minimize decomposition of the dye, and are composed of potassium chlorate with sulfur or sugar (qv) as the fuel. They also contain sodium bicarbonate or magnesium carbonate to act as an acid neutralizer, generate carbon dioxide gas to assist in expelling the dye from the combustion zone, and slow the burn rate (5). Some of the organic dyes formerly used in these devices have been replaced due to carcinogenicity concerns (see DYES, NATURAL). Standard military smokes are red, violet, green, and yellow. Orange smoke is widely used in the civilian pyrotechnics industry for marine distress signaling.

5.2. Tracer Munitions

Tracer bullets guide the direction of the fire, aid in range estimation, mark target impact, and act as incendiaries. Tracers can, through preselected tracer colors, also serve for nighttime identification of the combatants. Red strontium-containing tracers are more visible under adverse atmospheric conditions, therefore these are preferred although green tracers based on barium salts also are used. Daylight visibility can be enhanced by increasing the fraction of magnesium in the tracer composition. With the increased use of night vision systems for pilots and ground artillery personnel, interest in tracers with reduced light output (dim tracers) has increased; such devices are readily observable with night vision equipment but almost invisible to others. Conversely, the light output would not overwhelm night vision systems the way standard, high intensity tracer output can.

5.3. Incendiary Devices

Incendiary devices are used to initiate destructive fires in a variety of targets. Small-arms incendiaries are used primarily for starting fires in aircraft fuels. Whereas they are highly effective against subsonic aircraft, such as helicopters, the problem of defeating supersonic aircraft by incendiary action alone is more difficult owing to the high flash point of jet fuels. Most small-arms incendiary compositions consist of a metallic fuel such as a magnesium–aluminum alloy, and an oxidizer such as barium nitrate. The use of pyrophoric fragment generators such as zirconium, titanium, or depleted uranium as incendiary components of projectiles has been the subject of intensive study (19). The reason some metals ignite and burn progressively when fractured is uncertain. Generally, these metals have higher densities than do their oxides, so that the oxides flake from the metal during combustion, thereby exposing fresh metallic surface to oxygen attack.

5.4. Special Gas Generators

A special category of pyrotechnic system with military and aerospace applications is the cartridge-actuated device (CAD) which is also called the propellant-actuated device (PAD) (20). The CAD produces mechanical movement for closing electrical switches, opening or closing valves, cutting cables, or the performance of other mechanical work. They usually contain a small quantity of a gas-generating mixture which is ignited electrically. Many of these devices are used in aerospace systems.

6. Ignition

Pyrotechnic devices are initiated by some type of external energy input. This can range from a match lighting a piece of black powder-containing fuse to a battery sending a surge of current through a circuit, creating a hot spot on a narrow, high resistance section of wire that is coated with a thermally sensitive material (see Batteries). Alternatively, impact can be used to ignite a primer, as in a shotgun shell, or the friction generated by rubbing two surfaces together can create a hot spot; a highway flare uses this technique. Lasers (qv), high intensity beams of light, have been investigated more and more as another potentially reliable way to ignite pyrotechnic devices. When very rapid ignition is required, such as propellant in a gun, the method of ignition is usually not pyrotechnic but relies instead on a sensitive explosive mixture. The choice of the ignition method depends on the permissible ignition delay. Igniters containing primary explosives function in microseconds, whereas purely pyrotechnic igniters require milliseconds.

Within a given pyrotechnic device there may be several components such as a propelling charge, a delay column, and the main pyrotechnic effect (perhaps a flare). Each of these components must sequentially undergo ignition by the output from the preceding component in the pyrotechnic train. To ensure reliable ignition transfer, a family of pyrotechnic compositions known as ignition compositions, primes, or first fires has been developed. A small quantity of ignition composition is coated, pressed, or otherwise held in contact with the material to be ignited. The ignition mixture is readily ignited by the energy input from the fuse, delay column, or propellant and then transfers its energy to the next composition, assuring a reliable device. Ignition compositions tend to be relatively slow burning rather than explosive, and tend to generate hot particles as reaction products. These particles spray the next pyrotechnic composition with high temperature particulate matter and produce smooth, reliable ignition of more-difficult-to-light compositions.

Igniter compositions are formulated for specific desired response times, ignition sensitivities, and gas output (21). These mixtures are often rather sensitive to ignition, and require caution in their manufacturing. Examples of igniter materials are mixtures of aluminum, boron, magnesium, silicon, titanium, or zirconium with ammonium or potassium perchlorate, barium or potassium nitrate, barium or lead chromate, and cupric or lead oxides. Representative igniter compositions are shown in Table 3. A traditional igniter is black powder, which is an efficient flame carrier because of the high fraction of hot solid particles in its combustion products.

6.1. Delay Elements

Compositions and characteristics of some delay compositions are listed in Table 4. Many of these contain lead, barium, and chromium compounds, and there is a need for new delay compositions that are more environmentally compatible yet have the excellent reliability and performance properties of the current compositions. In some pyrotechnic devices, a precise time delay is required between the operating stages of the device. An example is the several-second delay designed into hand grenades to provide a delay between the release of the safety pin and the functioning of the grenade. Delay elements are self-contained pyrotechnic devices consisting of an initiator, a pressed column of pyrotechnic composition, and an output charge. Delays are either obturated or vented. An obturated element contains all of the reaction products and, therefore, it is not affected by ambient pressure. Obturation is an aid in protecting other components of the hardware from the effects of unwanted smoke and debris, but it also tends to increase the burn rate of the composition. Vented delays are used if large amounts of gaseous products must be disposed of and if the device is used where the effect of changes in

Table 3. Representative Ignition Compositions

Composition	Ingredients	Wt %
MTV	magnesium	54.0
	Teflon	30.0
	Viton A[a]	16.0
A1A	zirconium	65.0
	iron(III) oxide	25.0
	diatomaceous earth	10.0
B/KNO_3	potassium nitrate	70.7
	boron	23.7
	polyester[a]	5.6
black powder	potassium nitrate	75.0
	charcoal	15.0
	sulfur	10.0

[a]Binder.

Table 4. Standard Delay Compositions[a]

Component	Composition	Wt %
lead tetroxide	Pb_3O_4	85
silicon	Si	15
binder	[b]	additional 2%
barium chromate	$BaCrO_4$	90
boron	B	10
barium chromate	$BaCrO_4$	40
potassium perchlorate	$KClO_4$	10
tungsten	W	50
lead chromate	$PbCrO_4$	37
barium chromate	$BaCrO_4$	30
manganese	Mn	33

[a]Ref. 5.
[b]Nitrocellulose.

ambient pressure can be ignored. Delay elements based on black powder are necessarily vented and their burn rates are affected by the ambient pressure.

7. Safety Concerns

Safety concerns permeate all aspects of pyrotechnics. Although pyrotechnic materials have less of an explosive output than the energetic materials used for military and civilian blasting applications, the sensitivity of pyrotechnics to ignition from flame or spark is considerably greater than for many of the high explosives. Hence, great caution is needed in the manufacture of pyrotechnic mixtures to avoid possible ignition sources.

Wherever possible, operations involving the mixing and processing of pyrotechnic compositions should be performed remotely and monitored by video camera. Where this is not possible, the protection of personnel should include shielding for the eyes, face, and hands as well as the use of antistatic clothing. Rubber and plastic gloves may present a hazard when used for handling flammable materials because they may melt and stick to damaged skin. Suede leather gloves are preferable as they are wettable and washable (2).

Because pyrotechnic compositions contain their own oxygen, suffocation methods of fire fighting are not effective. Instead, the temperature of the burning material must be brought down below the ignition point of the material. A water deluge is perhaps the best way to accomplish this, as evaporating water is a very effective heat remover. However, this method must be used with great care if burning metal fuels such as magnesium are involved in the fire. An insufficient amount of water actually contributes to the violence of the fire by reacting with the burning metal to generate hydrogen gas, a violently reactive material. Chlorinated hydrocarbons should also be used only with great caution to fight pyrotechnic fires, because metal fuels can also react with those liquids.

Many pyrotechnic mixtures potentially can be ignited by electrostatic discharge during the manufacturing process. Loose pyrotechnic composition is considerably more sensitive to static than is consolidated material. The risk of electrostatic discharge can be minimized by grounding and bonding materials, containers, and personnel. Pyrotechnic processing is generally performed in a humidity range from 45–60%. These values allow a conductive moisture layer to form on work surfaces, which can effectively dissipate static charge accumulations without being too humid such that the component chemicals pick up excessive amounts of water from the atmosphere.

As an additional safety precaution, water must never be used in the blending of mixtures containing zinc or magnesium, nor should it be used with titanium or zirconium powder unless water is present in excess. Otherwise an exothermic reaction between the metal and water might occur. The danger of a dust explosion is present when fine particle size fuels are processed. Of particular concern is the handling of zirconium powder (<10 μm dia), which may be pyrophoric in air. Specific standard operating procedures must be established for each pyrotechnic operation, and personnel must be instructed in the importance of strictly following these procedures. In designing a pyrotechnic facility, it is advisable to assume that an ignition can occur at each stage of the manufacturing process at some point during the lifetime of the plant. The facility should be designed to minimize the consequences to both personnel and the physical plant if an ignition does occur. Separation of plant areas and the minimization of in-process material in each area are two key points of plant safety (qv) (3). All finished devices and all composition awaiting further stages of the manufacturing process must be held in storage magazines where no other manufacturing activities are performed. It is highly unlikely that an incident will begin in a storage magazine, since no work is being performed on the stored materials. Hence, separating the stored materials from work-in-progress helps to minimize the consequences of any event that might occur in manufacturing.

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JOHN A. CONKLING
American Pyrotechnic Association

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