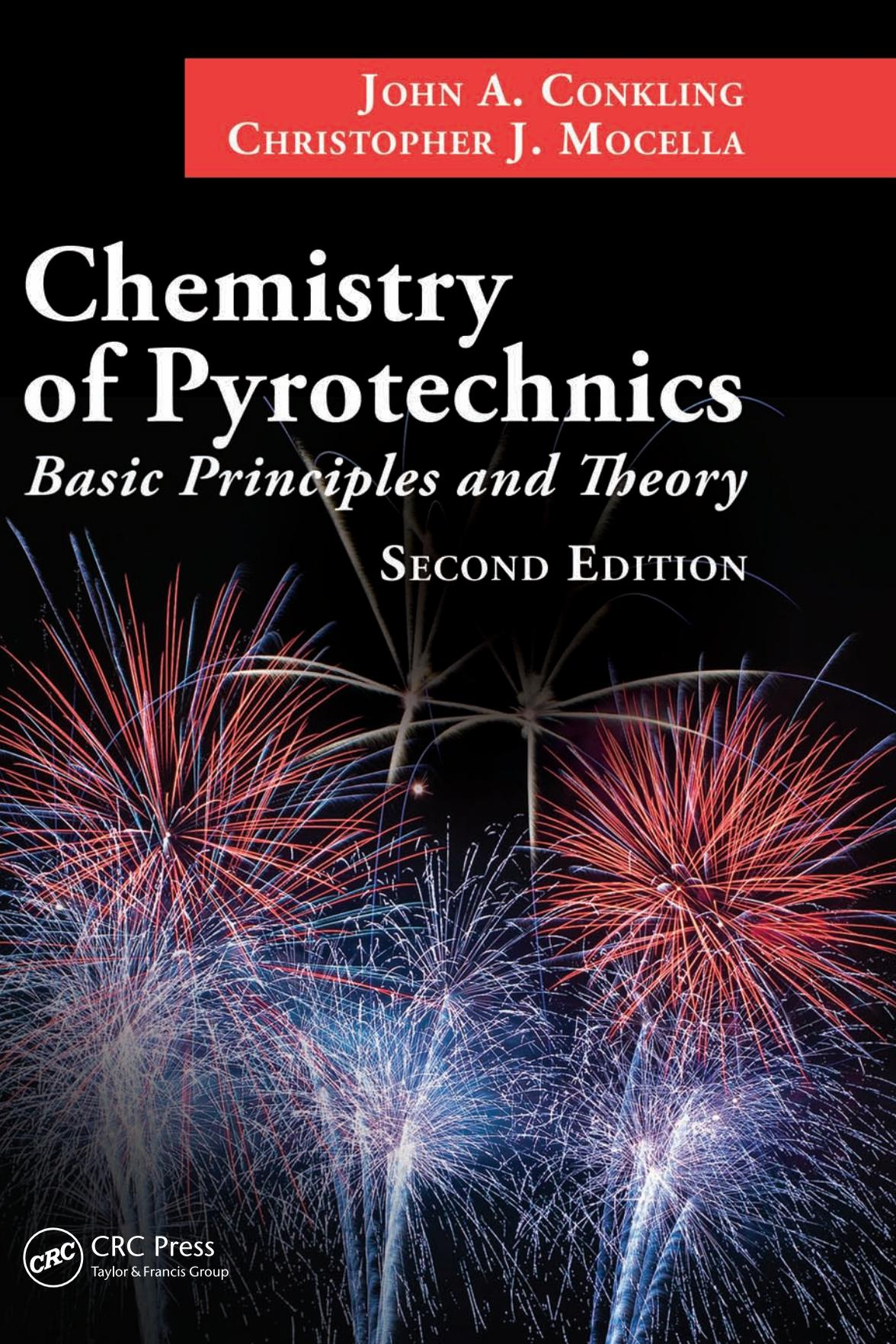


JOHN A. CONKLING
CHRISTOPHER J. MOCELLA

Chemistry of Pyrotechnics

Basic Principles and Theory

SECOND EDITION



 CRC Press
Taylor & Francis Group

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Cover photo by Rob Stowers, courtesy of Pyrotecnico. Red, white, and blue bursts highlight a 4th of July fireworks spectacular.

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Preface to the Second Edition—2010

In the twenty-five years that have passed since the first edition of this book was published, the world of pyrotechnics and high-energy materials has continued to undergo significant changes. The changes have been driven primarily by concerns for safety—of personnel working with energetic materials and of the communities located near facilities producing energetic materials—as well as concerns for the environment. One result of the pressure for change has been the promulgation of new government regulations placing restrictions on the materials that may be used in energetic mixtures, mandating numerous training programs, and initiating other actions, such as OSHA's Process Safety Management standard, intended to eliminate accidents and incidents. And almost all of the personnel who entered the field of energetic materials in the 1950s and 1960s have now retired and taken with them their years of hands-on, practical knowledge in the preparation of energetic mixtures.

The International Pyrotechnics Seminars have grown in frequency and significance since the first edition of this book was published in 1985. There is now at least one seminar a year, either in Colorado or a non-United States location, and the proceedings from these seminars continue to be a great source of information regarding ongoing pyrotechnic research. In addition, the International Symposium on Fireworks (ISF) continues to be held every other year in Canada or elsewhere, and these sessions always produce an interesting blend of technical papers.

The Pyrotechnics Guild International (PGI) has matured into a respected group of pyrotechnics enthusiasts and researchers who are making significant contributions in the area of fireworks technology.

A new journal, appropriately named the *Journal of Pyrotechnics*, has provided a vehicle for the prompt publication of research and review papers in the broad field of pyrotechnics.

On the negative side, we in the United States continue to lack any organized, broad-range academic programs covering the science of energetic materials. The New Mexico Institute of Technology is offering a program in explosive technology, and this is a great first step. More and more, the field of pyrotechnics is interacting with and adapting to changing technology in areas such as obscuration science and low-signature flame emission. Greater academic interest in the science of pyrotechnics would be a valuable asset for this country.

I thank my numerous colleagues and coworkers over the past twenty-five years for their interesting discussions, helpful comments, and constructive criticism. First on the list is Joseph Domanico, my friend and colleague with the Summer Pyrotechnic Seminar program at Washington College since 1984—Joe is truly a unique individual with a broad knowledge of the field of energetic materials.

I also thank Chris Mocella, Washington College 2001, for his assistance with, and contributions to, the second edition of this book. Chris also participates as an instructor in the Summer Pyrotechnic Seminars at Washington College, and has become a valuable member of the team.

The thank-you list includes Tom Shook and Loy Aikman at Pine Bluff Arsenal, who got me involved in the military side of pyrotechnics two decades ago. Another special acknowledgment goes to David Pier of MP Associates, with whom I have enjoyed debating a wide variety of topics covering many aspects of energetic material for many years. Other friends and colleagues who have contributed to my education include the late Fred McIntyre and another former Washington College chemistry student, Jeff Johnson, with Orion Safety Products. I also thank the American Pyrotechnics Association for allowing me time to pursue my scientific interests for many years, and to TNT Fireworks and Orion Safety Products for allowing me to assist them with interesting projects since my retirement from the APA. More thanks go to the participants in my Summer Pyrotechnic Seminar programs for the past twenty-seven years, and to my friends at the Bureau of Alcohol, Tobacco, and Firearms, and Judy LeDoux and Debra Satkowiak in particular, for allowing me to assist them with training for their personnel.

Finally, I must acknowledge the importance of my wife, Sandra, to this project, without whose persistent encouragement this second edition would have been delayed even more. Aiding her in this motivational effort have been my two children, Melinda Conkling Hart and John A. Conkling Jr., who in addition have presented us with four wonderful Texas grandchildren—John Maxey Hart, Edward Austin Hart Jr., Julia Valliant Conkling, and the newest arrival, John A. Conkling III. Maybe one of them will go on to a career in this fascinating field.

This book continues to stress basic chemical principles, rather than serve as a how-to guide for pyrotechnics. There are detailed published works covering many areas of energetic materials. This book is intended as a bridge to allow people to transition with confidence from a knowledge of chemistry to an ability to apply chemical principles and logic to energetic materials. Discussion of the historical past of the field of pyrotechnics is, regrettably, kept to a minimum. The history of this field, particularly the work in the twentieth century, is another book waiting for someone to pursue, but there should be no doubt in anyone's mind that pyrotechnics—like any other field of science—can only grow and expand as a science by building on past accomplishments in the field. Everyone's goal must continue to be to make the field of energetic materials as productive and useful and as safe as possible.

John A. Conkling
Chestertown, Maryland

Preface to the First Edition—1985

Everyone has observed chemical reactions involving pyrotechnic mixtures. Beautiful 4th of July fireworks, highway distress signals, solid fuel boosters for the Space Shuttle, and the black powder used by muzzle-loading rifle enthusiasts all have a common technical background.

The chemical principles underlying these high-energy materials have been somewhat neglected in the twentieth century by academic and industrial researchers. Most of the recent work has been goal-oriented rather than fundamental in nature (e.g., produce a deeper green flame). Many of the significant results are found in military reports, and chemical fundamentals must be gleaned from many pages of test results.

Much of today's knowledge is carried in the heads of experienced personnel. Many of these workers acquired their initial training during World War II, and they are presently fast approaching (if not already past) retirement age. This is most unfortunate for future researchers. Newcomers have a difficult time acquiring the skills and the knowledge needed to begin productive experiments. A background in chemistry is helpful, but much of today's modern chemistry curriculum will never be used by someone working in pyrotechnics and explosives. Further, the critical education in how to safely mix, handle, and store high-energy materials is not covered at all in today's schools and must be acquired in "on-the-job" training.

This book is an attempt to provide an introduction to the basic principles of high-energy chemistry to newcomers and to serve as a review for experienced personnel. It can by no means substitute for the essential "hands on" experience and training necessary to safely work in the field, but I hope that it will be a helpful companion. An attempt has been made to keep chemical theory simple and directly applicable to pyrotechnics and explosives. The level approaches that of an introductory college course, and study of this text may prepare persons to attend professional meetings and seminars dealing with high-energy materials and enable them to intelligently follow the material being presented. In particular, the International Pyrotechnic Seminars, hosted biannually in the United States by the Illinois Institute of Technology Research Institute in conjunction with the International Pyrotechnics Society, have played a major role in bringing researchers together to discuss current work. The Proceedings of the nine seminars held to date contain a wealth of information that can be read and contemplated by persons with adequate introduction to the field of high-energy chemistry.

I would like to express my appreciation to Richard Seltzer of the American Chemical Society and to Dr. Maurits Dekker of Marcel Dekker, Inc. for their encouragement and their willingness to recognize pyrotechnics as a legitimate branch of modern chemistry. I am grateful to Washington College for a sabbatical leave in 1983

that enabled me to finalize the manuscript. I would also like to express my thanks to many colleagues in the field of pyrotechnics who have provided me with data as well as encouragement, and to my 1983 and 1984 Summer Chemistry Seminar groups at Washington College for their review of draft versions of this book. I also appreciate the support and encouragement given to me by my wife and children as I concentrated on this effort.

Finally, I must acknowledge the many years of friendship and collaboration that I enjoyed with Joseph H. McLain, former Chemistry Department Chairman and subsequently President of Washington College. It was his enthusiasm and encouragement that dragged me away from the norbornyl cation and physical organic chemistry into the fascinating realm of pyrotechnics and explosives. The field of high-energy chemistry lost an important leader when Dr. McLain passed away in 1981.

1 Introduction



BLACK POWDER GRANULES: (See color insert following page 112) Black powder granules are the first commercial energetic material, and have remained an article of commerce for over one thousand years. This unique blend of potassium nitrate (saltpeter), charcoal, and sulfur (brimstone) has served as an explosive, a propellant, and a component in pyrotechnic devices such as safety fuse and squibs. (Photo by Tim Wade and Dennis King, courtesy of MP Associates.)

Welcome to the world of energetic materials. Few people plan to spend their professional careers in this field of science and technology, but there is an old saying that “once you smell the smoke,” you are hooked.

This book is an introduction to the basic principles and theory of pyrotechnics. Much of the material is also applicable to the closely related areas of propellants and explosives. The term *high-energy chemistry* will be used to refer to all of these fields. Explosives rapidly release large amounts of energy, and explosives engineers take advantage of this energy and the associated shock and pressure to do work. Propellants are designed to burn quite rapidly under the confinement of a rocket engine or a gun barrel, but many propellants burn rather mildly in the open. They are formulated to maximize the volume of hot gas produced as the propellant rapidly burns. Pyrotechnic mixtures, in general, react more slowly, and the heat generated

TABLE 1.1
Classes of High-Energy Reactions

Class	Approximate Reaction Velocity	Example
Burning	Millimeters/second	Delay mixtures, colored smoke compositions
Deflagration	Meters/second	Rocket propellants, confined black powder
Detonation	>1 kilometer/second	Dynamite, TNT

by the burning chemical mixture is used to produce combinations of light, color, smoke, heat, and noise for a wide range of applications.

The chemical reactions involved are of the electron-transfer, or oxidation-reduction, type. The mixtures to be studied are almost always solids at room temperature, and are designed to function in the absence of external oxygen. Table 1.1 illustrates the reaction rates to be dealt with, which range along a continuum from very slow burning to “instantaneous” detonations with rates greater than a kilometer per second. Please note that *detonation* refers to a specific, shock-propagated process for the reaction of an energetic material—the term *detonation* is *not* synonymous with *ignition* or *explosion*. A detonation is an explosion, but so are high-rate deflagrations (especially when the material is confined).

It is important to recognize early on that the same material may vary dramatically in its reactivity, depending on its method of preparation and the conditions under which it is used. Black powder is an excellent example of this variability, and it is quite fitting that it serves as the first example of a high-energy material due to its historical significance.^{1,2} Black powder is an intimate mixture of potassium nitrate (~75% by weight), charcoal (~15%), and sulfur (~10%), and its unique properties and characteristics continue to intrigue researchers even today.³⁻⁵ A reactive black powder is no simple material to prepare, and is a classic example of the “art” of manufacturing pyrotechnics. If one gently mixes the proper ratio of three components briefly, a powder is produced that is difficult to light and burns quite slowly. The same ingredients in the same proportions—when thoroughly mixed, moistened, and ground with a heavy stone wheel to achieve a high degree of homogeneity—become a mixture that readily ignites and burns rapidly. Particle size, purity of the starting materials, mixing time, and a variety of other factors, including the type of wood used to prepare the charcoal, are all critical in producing high-performance black powder. Also, deviations from the 75/15/10 ratio of ingredients will lead to substantial changes in performance. Much of the early history of modern Europe is related to the availability of high-quality black powder for use in rifles and cannons. A good black powder manufacturer was essential to military success, although he usually received far less recognition and decoration than the generals who used his product in their battles.

The burning behavior of black powder illustrates how a pyrotechnic mixture can vary in performance depending on the conditions of its use. A small pile of loose

black powder can be readily ignited by the flame of a match, producing an orange flash and a puff of smoke, but almost no noise. The same powder, tightly sealed in a strong paper tube but still in loose condition, will explode upon ignition by means of a fuse, rupturing the container with an audible noise. Black powder spread in a thin trail will quickly burn along the trail, a property used in making early fuses. Finally, if the powder is compressed in a tube, one end is left open, and that end is then constricted to partially confine the hot gases produced when the powder is ignited, a rocket-type device is produced. This varied behavior, depending on confinement, is quite typical of pyrotechnic mixtures and illustrates why one must be quite specific in giving instructions for preparing and using the materials discussed in this book.

Black powder is also a good example to use to illustrate the dramatic effect that moisture can have on pyrotechnic compositions. Damp powder is difficult to light, and burns quite slowly—if at all—if ignition is successful. “Keep your powder dry” is still among the best pieces of advice for anyone making or using pyrotechnic materials, and hygroscopic chemicals—those that tend to rapidly pick up moisture in a humid environment—tend to be avoided by pyrotechnic formulators.

Why should someone working in pyrotechnics and related areas bother to study the basic chemistry involved? Throughout the four-hundred-year modern history of the United States, many black powder factories have been constructed and put into operation. Although smokeless powder and other new materials have replaced black powder as a propellant and delay mixture in many applications, there is still a sizable demand for black powder in both the military and civilian pyrotechnic industries. How many black powder factories are operating in the United States today? Exactly one. The remainder have been destroyed by explosions or closed because of the probability of one occurring. In spite of a demand for the product, manufacturers are reluctant to engage in the production of the material because of the history of problems with accidental ignition during the manufacturing process. Why is black powder so sensitive to ignition? What can the chemist do to minimize the hazard? Can one alter the performance of black powder by varying the ingredients and their percentages, using theory as the approach rather than trial and error?

Black powder is not unique in its properties, however. High-energy materials like propellants and pyrotechnics are all designed to release energy in brief periods of time when an ignition stimulus is applied. New formulations continue to be developed, and new materials continue to be investigated for possible use in novel compositions. A pyrotechnic formulation consisting largely of magnesium powder and polytetrafluoroethylene (PTFE; also known as Teflon®) is used to produce decoy flares for the protection of military aircraft from heat-seeking missiles. This material has acquired a black-powder-like reputation in recent years. Virtually every manufacturer of this material has suffered an incident producing a magnesium-Teflon composition, and the need to understand the basic science of the material has received much attention.^{6,7} It is this type of problem and its analysis that I hope can be addressed a bit more thoroughly and scientifically with an understanding of the fundamental concepts presented in this book. If one accident can be prevented as a consequence of someone’s better insight into the chemical nature of high-energy materials, achieved through the study of this book, then the effort that went into its preparation was worthwhile.

A BRIEF HISTORY

The use of chemicals, and chemical mixtures, to produce heat, light, smoke, noise, and motion has existed for several thousand years, originating most likely in China or India. India has been cited as a particularly good possibility due to the natural deposits of saltpeter (potassium nitrate, KNO_3) found there.⁸

Much of the early use of chemical energy involved military applications. “Greek fire,” first reported in the seventh century A.D., was probably a blend of sulfur, organic fuels, and saltpeter that generated flames and dense fumes when ignited. It was used in a variety of incendiary ways in both sea and land battles and added a new dimension to military science.⁸

At some early time, most likely prior to 1000 A.D., an observant scientist recognized the unique properties of a blend of potassium nitrate, sulfur (brimstone), and charcoal, and black powder was developed as the first modern high-energy composition.

The Chinese were involved in pyrotechnics at an early date and had developed rockets by the tenth century.⁸ Fireworks followed, including firecrackers, and Chinese firecrackers became a popular item in the United States when trade was begun between the United States and China in the 1800s. Family correspondence passed down to me shows that my great-great-grandfather, a merchant ship captain also named John Alexander Conkling, included “firecrackers” on his personal shopping list for a voyage to Canton, China (now Guangdong, China), in the 1830s. I was not aware of this until after I had become involved in the field of pyrotechnics, but I was pleased to learn that the Conkling family was among the first importers of Chinese fireworks into the United States.

Chinese fireworks remain popular in the United States today, along with an assortment of other types of pyrotechnic articles that produce a wide assortment of visible and audible effects. The Japanese also produce beautiful fireworks, but curiously, they do not appear to have developed the necessary technology until fireworks were brought to Japan around 1600 A.D. by an English visitor.⁹ Many of the advances in fireworks technology over the past several centuries have come from these two Asian nations, and China today is the world’s primary supplier of both consumer and display fireworks.

The use of pyrotechnic and propellant mixtures for military purposes in rifles, rockets, flares, and cannons developed simultaneously with the civilian applications, such as fireworks. Progress in both areas followed advances in modern chemistry, as new chemical compounds were isolated and synthesized and became available commercially to the pyrotechnician. Berthollet’s discovery of potassium chlorate in the 1780s resulted in the ability to produce brilliant flame colors using pyrotechnic compositions, and color was added to the effects of sparks, noise, and motion previously available using potassium nitrate-based compositions.

The harnessing of electricity led to the manufacturing of magnesium and aluminum metals by electrolysis in the latter part of the nineteenth century, and bright white sparks and whiter light could then be produced. Strontium, barium, and copper compounds capable of producing vivid red, green, and blue flames also became commercially available during the nineteenth century, and modern pyrotechnic technology really took off.

Simultaneously, the discovery of nitroglycerine in 1846 by Sobrero in Italy, and Nobel's subsequent work with dynamite, led to the development of a new generation of true high explosives that were far superior to black powder for many blasting and explosives applications. These materials released their chemical energy through the detonation process, at rates much faster—and with greater accompanying blast pressure and shock—than the deflagration process by which propellants and pyrotechnics react upon ignition. The development of modern smokeless powder in the latter part of the nineteenth century—based on nitrocellulose and nitroglycerine—led to the demise of black powder as the main propellant for guns of all types and sizes.

Although black powder has been replaced in most of its former uses by newer and more energetic materials, it is important to recognize the role black powder has played in modern civilization. Tenney Davis, addressing this issue in his classic book on the chemistry of explosives, wrote: “The discovery that a mixture of potassium nitrate, charcoal, and sulfur is capable of doing useful work is one of the most important chemical discoveries or inventions of all times ... the discovery of the controllable force of gunpowder, which made huge engineering achievements possible, gave access to coal and to minerals within the earth, and brought on directly the age of iron and steel and with it the era of machines and of rapid transportation and communication.”¹⁰ Black powder remains a viable energetic material today; it ignites readily and reliably and is quite stable in storage if kept dry, and it is commercially available in a range of grain sizes, from fine powder to granules the size of kernels of corn. Black powder is also fascinating because it is one of the very few materials produced by the chemical industry that is still made today using essentially the same materials and manufacturing process as was used five hundred years ago.

Explosives are widely used today throughout the world for mining, excavation, demolition, and military purposes. Pyrotechnics are also widely used by the military for signaling, obscuration, and training simulators. Military technology is constantly striving to keep pace with advances in other areas of technology, such as thermal detection and night vision equipment. Civilian applications of pyrotechnics are many and varied, ranging from the common match to highway warning flares (fusees) to ever-popular fireworks and the spectacular special effects used to enhance movies, rock concerts, professional wrestling matches, sporting events, and theme park shows.

The fireworks industry remains perhaps the most visible example of pyrotechnics to the general public, and also remains a major user of traditional black powder. This industry provides the pyrotechnician with the opportunity to fully display his skill at producing colors and other brilliant visual effects. The use of fireworks in the United States has not diminished. There has been a steady growth in consumption of fireworks from an estimated 30 million pounds in 1976 to over 230 million pounds in 2007, according to data compiled by the American Pyrotechnics Association.¹¹

Fireworks form a unique part of the cultural heritage of many countries.¹² In the United States, fireworks have traditionally been associated with Independence Day—the Fourth of July. In England, large quantities are set off in commemoration of Guy Fawkes Day (November 5), while the French use fireworks around Bastille Day (July 14). In Germany, the use of fireworks by the public is limited to one hour per year—from midnight to 1 a.m. on January 1, but it is reported to be quite a

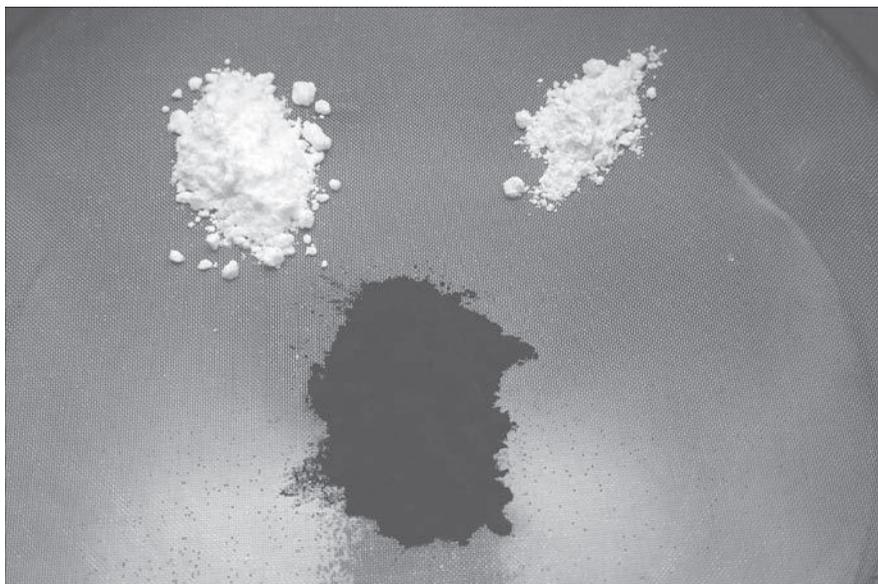
celebration. Much of the Chinese culture is associated with the use of firecrackers to celebrate New Year's and other important occasions, and this custom has carried over to the Chinese communities throughout the world. The brilliant colors and booming noises of fireworks appear to have a universal appeal to our basic senses, eliciting "oohs" and "aahs" from spectators regardless of where the fireworks are displayed worldwide.

To gain an understanding of how these beautiful effects are produced, we will begin with a review of some basic chemical principles and then proceed to discuss various pyrotechnic systems.

REFERENCES

1. J. Kelly, *Gunpowder*, New York: Basic Books, 2004.
2. B. Buchanan, Ed., *Gunpowder—The history of an international technology*, Bath, UK: Bath University Press, 1996.
3. M. E. Brown and R. A. Rugunanan, A temperature-profile study of the combustion of black powder and its constituent binary mixtures, *Propellants, Explosives, Pyrotechnics*, 14, 69 (1989).
4. G. Hussain and G. J. Rees, Combustion of black powder. Part IV. Effect of carbon and other parameters, *Propellants, Explosives, Pyrotechnics*, 17, 1 (1992).
5. I. Von Maltitz, Our present knowledge of the chemistry of black powder, *Journal of Pyrotechnics*, 14, 27 (2001).
6. N. Kubota and C. Serizawa, Combustion processes of Mg/TF pyrotechnics, *Propellants, Explosives, Pyrotechnics*, 12, 145 (1987).
7. T. Kuwahara, S. A. Matsuo, and N. Shinozaki, Combustion and sensitivity characteristics of Mg/TF pyrolants, *Propellants, Explosives, Pyrotechnics*, 22, 198 (1997).
8. U.S. Army Material Command, *Engineering design handbook: Theory and application*, Military Pyrotechnic Series, Part 1, Washington, DC, 1967 (AMC Pamphlet 706-185).
9. T. Shimizu, *Fireworks—The art, science and technique*, Tokyo: T. Shimizu, 1981.
10. T. L. Davis, *The chemistry of powder and explosives*. New York: John Wiley & Sons, 1941.
11. American Pyrotechnics Association, www.americanpyro.com.
12. G. Plimpton, *Fireworks: A history and celebration*, New York: Doubleday, 1984.

2 Basic Chemical Principles



BLACK POWDER COMPONENTS: (See color insert following page 112) Potassium nitrate (white), charcoal (black), and sulfur (yellow) are blended for hours to produce a homogeneous blend that has the reactivity associated with high-quality black powder. Purity of the starting chemicals, the right ratio of the three components by weight, and the proper mixing process are all necessary for a successful manufacturing process. (Photo by Tim Wade and Dennis King, courtesy of MP Associates.)

Most chemistry courses do not directly discuss energetic materials—explosives, propellants, and pyrotechnics. However, these materials all involve “chemistry in action” and produce their energetic output through chemical reactions. Many of the principles and logical thought processes that are taught in Chem 101 directly apply to what will be covered in this book. Pyrotechnics are not magic, and the pyrotechnic chemist is no longer viewed as a wizard. When you are working in this field, and things seem to be making no sense, it’s time to go back to the basics of science.

ATOMS AND MOLECULES

To understand the chemical nature of pyrotechnics and other energetic mixtures, one must begin at the atomic level. Two hundred years of elegant experiments and complex calculations have led to our present picture of the atom as the fundamental

TABLE 2.1
Properties of the Subatomic Particles

Particle	Location	Charge	Mass, amu ^a	Mass, grams
Proton	In nucleus	+1	1.007	1.673×10^{-24}
Neutron	In nucleus	0	1.009	1.675×10^{-24}
Electron	Outside nucleus	-1	0.00549	9.11×10^{-28}

^a amu = atomic mass unit, where 1 amu = 1.66×10^{-24} grams.

building block of matter. An atom consists of a small, dense nucleus containing positively charged *protons* and neutral *neutrons*, surrounded by a large cloud of light, negatively charged *electrons*. Table 2.1 summarizes the properties of these subatomic particles.

A particular *element* is defined by its *atomic number*—the number of protons in the nucleus (which will equal the number of electrons surrounding the nucleus in a neutral atom). For example, iron is the element of atomic number 26, meaning that every iron atom will have twenty-six protons in its nucleus. Chemists use a one- or two-letter symbol for each element to simplify communication; iron, for example, is given the symbol Fe, from the old Latin word for iron, *ferrum*. The sum of the protons plus neutrons found in the nucleus is called the *mass number*. For some elements, only one mass number is found in nature. Fluorine (atomic number 9, mass number 19) is an example of such an element. Other elements are found in nature in more than one mass number. Iron is found as mass numbers 56 (91.52%), 54 (5.90%), 57 (2.245%), and 58 (0.33%). These different mass numbers of the same element are called *isotopes*, and vary in the number of neutrons found in the nucleus, and therefore vary in their mass as well. *Atomic weight* refers to the average mass found in nature of all the atoms of a particular element; the atomic weight of iron is 55.847. For calculation purposes, these atomic weights are used for the mass of a particular element. Table 2.2 contains symbols, atomic numbers, and atomic weights for the elements.

Chemical reactivity, and therefore pyrotechnic and explosive behavior, is determined primarily by the tendency for each element to gain or lose electrons during a chemical reaction. Calculations of theoretical chemists, with strong support from experimental studies, suggest that electrons in atoms are found in orbitals, or regions in space where they possess the lowest possible energy—close to the nucleus but away from other negatively charged electrons. As electrons are placed into an atom, energy levels close to the positive nucleus are occupied first, and the higher energy levels are then successively populated. Extra stability appears to be associated with completely filled levels, termed *shells*. Elements with completely filled shells include helium (atomic number 2), neon (atomic number 10), argon (atomic number 18), and krypton (atomic number 36). These elements all belong to a group called the *inert*

TABLE 2.2
Symbols, Atomic Weights, and Atomic Numbers of the Elements

Element	Symbol	Atomic Number	Atomic Weight, amu ^a
Actinium	Ac	89	[227] ^b
Aluminum	Al	13	26.9815386
Americium	Am	95	[243]
Antimony	Sb	51	121.760
Argon	Ar	18	39.948
Arsenic	As	33	74.92160
Astatine	At	85	[210]
Barium	Ba	56	137.327
Berkelium	Bk	97	[247]
Beryllium	Be	4	9.012182
Bismuth	Bi	83	208.98040
Bohrium	Bh	107	[272]
Boron	B	5	10.811
Bromine	Br	35	79.904
Cadmium	Cd	48	112.411
Cesium	Cs	55	132.9054519
Calcium	Ca	20	40.078
Californium	Cf	98	[251]
Carbon	C	6	12.0107
Cerium	Ce	58	140.116
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.9961
Cobalt	Co	27	58.933195
Copernicium	CN	112	[285]
Copper	Cu	29	63.546
Curium	Cm	96	[247]
Darmstadtium	Ds	110	[281]
Dubnium	Db	105	[268]
Dysprosium	Dy	66	162.500
Einsteinium	Es	99	[252]
Erbium	Er	68	167.259
Europium	Eu	63	151.964
Fermium	Fm	100	[257]
Fluorine	F	9	18.9984032
Francium	Fr	87	[223]
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.723
Germanium	Ge	32	72.64
Gold	Au	79	196.966569
Hafnium	Hf	72	178.49
Hassium	Hs	108	[270]
Helium	He	2	4.002602
Holmium	Ho	67	164.93032

(continued)

TABLE 2.2 (CONTINUED)
Symbols, Atomic Weights, and Atomic Numbers of the Elements

Element	Symbol	Atomic Number	Atomic Weight, amu ^a
Hydrogen	H	1	1.00794
Indium	In	49	114.818
Iodine	I	53	126.90447
Iridium	Ir	77	192.217
Iron	Fe	26	55.845
Krypton	Kr	36	83.798
Lanthanum	La	57	138.90547
Lawrencium	Lr	103	[262]
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.9668
Magnesium	Mg	12	24.3050
Manganese	Mn	25	54.938045
Meitnerium	Mt	109	[276]
Mendelevium	Md	101	[258]
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.96
Neodymium	Nd	60	144.242
Neon	Ne	10	20.1797
Neptunium	Np	93	[237]
Nickel	Ni	28	58.6934
Niobium	Nb	41	92.90638
Nitrogen	N	7	14.0067
Nobelium	No	102	[259]
Osmium	Os	76	190.23
Oxygen	O	8	15.9994
Palladium	Pd	46	106.42
Phosphorus	P	15	30.973762
Platinum	Pt	78	195.084
Plutonium	Pu	94	[244]
Polonium	Po	84	[209]
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.90765
Promethium	Pm	61	[145]
Protactinium	Pa	91	231.03588
Radium	Ra	88	[226]
Radon	Rn	86	[222]
Rhenium	Re	75	186.207
Rhodium	Rh	45	102.90550
Roentgenium	Rg	111	[280]
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	[267]
Samarium	Sm	62	150.36

TABLE 2.2 (CONTINUED)
Symbols, Atomic Weights, and Atomic Numbers of the Elements

Element	Symbol	Atomic Number	Atomic Weight, amu ^a
Scandium	Sc	21	44.955912
Seaborgium	Sg	106	[271]
Selenium	Se	34	78.96
Silicon	Si	14	28.0855
Silver	Ag	47	107.8682
Sodium	Na	11	22.98976928
Strontium	Sr	38	87.62
Sulfur	S	16	32.065
Tantalum	Ta	73	180.94788
Technetium	Tc	43	[98]
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92535
Thallium	Tl	81	204.3833
Thorium	Th	90	232.03806
Thulium	Tm	69	168.93421
Tin	Sn	50	118.710
Titanium	Ti	22	47.867
Tungsten	W	74	183.84
Ununhexium	Uuh	116	[293]
Ununoctium	Uuo	118	[294]
Ununpentium	Uup	115	[288]
Ununquadium	Uuq	114	[289]
Ununtrium	Uut	113	[284]
Uranium	U	92	238.02891
Vanadium	V	23	50.9415
Xenon	Xe	54	131.293
Ytterbium	Yb	70	173.054
Yttrium	Y	39	88.90585
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.224

Source: Based on the 2005 table in Weizer, M. E. *Pure Appl. Chem.*, 78, 2051–2066, 2006. <http://IUPAC.org/publications/pac/78/11/2051/>

^a mu = atomic mass unit, where 1 amu = 1.66×10^{-24} grams.

^b Value enclosed in brackets is the mass number for the longest-lived isotope.

^c Elements 112 through 118 are currently under review.

gases, and their virtual lack of any chemical reactivity provides support for the theory of filled-shell stability—the atoms do not wish to gain, lose, or share electrons.

Other elements show varying tendencies to obtain a filled shell by the sharing of electrons with other atoms, or by the actual gain or loss of electrons to form charged species, called *ions*. For example, sodium (symbol Na, atomic number 11) readily loses one electron to form the sodium ion, Na⁺, with ten electrons. By losing one

electron, sodium has acquired the same number of electrons as the inert gas neon, and it has become a very stable chemical species. Fluorine (symbol F, atomic number 9) readily acquires one additional electron to become the fluoride ion, F^- . This is another ten-electron species and is quite stable. Other elements display similar tendencies to gain or lose electrons to acquire inert gas electron configurations by becoming positive or negative ions. Many chemical species found in nature are *ionic compounds*. These are usually found as crystalline solids composed of interpenetrating lattices of positive and negative ions held together by electrostatic attraction between these oppositely charged particles. Table salt, or sodium chloride, is an ionic compound consisting of sodium and chloride ions, Na^+ and Cl^- , and one uses the formula NaCl to represent the one-to-one ionic ratio. The attractive forces holding the solid together are called *ionic bonds*.

Hence, if one brings together a good electron donor (such as a sodium atom) and a good electron acceptor (such as a fluorine atom), one might expect a chemical reaction to occur. Electrons are transferred and an ionic compound (sodium fluoride, NaF) is produced. A three-dimensional solid lattice of sodium and fluoride ions is created, where each sodium ion is surrounded by fluoride ions, and each fluoride ion is in turn surrounded by sodium ions. Another very important aspect of such a relation is the fact that *energy* is released as the product is formed. This release of energy associated with the formation of the reaction products becomes very important in the consideration of the chemistry of pyrotechnics and explosives.

In addition to forming ions by electron transfer, atoms may *share* electrons with other atoms as a means of acquiring filled shells (and their associated stability). The simplest illustration of this is the combination of two hydrogen atoms (symbol H, atomic number 1) to form a hydrogen molecule:



The sharing of electrons between two atoms is called a *covalent bond*. Such bonds owe their stability to the interaction of the shared electrons with *both* positive nuclei. The nuclei will be separated by a certain distance—termed the *bond distance*—that maximizes the nuclear-electron attractions balanced against the nuclear-nuclear repulsive forces. A *molecule* is a neutral species of two or more atoms held together by covalent bonds.

The element *carbon* (atomic number 6, symbol C) is almost always found in nature covalently bonded to other carbon atoms or to a variety of other elements (most commonly H, O, and N). Due to the presence of carbon-containing compounds in all living things, the chemistry of carbon compounds is known as *organic chemistry*. Most high explosives are organic compounds. Trinitrotoluene (TNT), for example, consists of C, H, N, and O atoms, with a molecular formula for $C_7H_5N_3O_6$. When TNT detonates, it produces a mixture of stable, small molecules such as N_2 , CO_2 , and H_2O as reaction products. We will encounter other organic compounds in our study of fuels and binders in energetic mixtures.

Covalent bonds can also form between dissimilar elements, such as hydrogen and chlorine:



By this combination, both atoms now have filled-shell electronic configurations and a hydrogen chloride molecule is formed. The sharing here is not exactly equal, however, for chlorine is a stronger electron attractor than hydrogen. The chlorine end of the molecule is slightly electron rich; the hydrogen end is electron deficient. This behavior can be noted using the Greek letter delta, δ , as the symbol for partial, as in



The bond that is formed in hydrogen chloride is termed *polar covalent*, and a molecule possessing these partial charges is referred to as *polar*. The relative ability of atoms of different elements to attract electron density is indicated by the property termed *electronegativity*. A scale ranking the elements was developed by Nobel Laureate Linus Pauling. The electronegativity sequence for some of the more common covalent-bond-forming elements is given in Table 2.3. Using this sequence, one can assign partial charges to atoms in a variety of molecules; the more electronegative atom in a given bond will bear the partial negative charge, leaving the other atom with a partial positive charge.

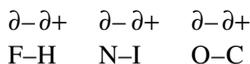


TABLE 2.3
Electronegativity Values for Some Common Elements

Element	Pauling Electronegativity Value
Fluorine, F	4.0
Oxygen, O	3.5
Nitrogen, N	3.0
Chlorine, Cl	3.0
Bromine, Br	2.8
Carbon, C	2.5
Sulfur, S	2.5
Iodine, I	2.5
Phosphorous, P	2.1
Hydrogen, H	2.1

Source: L. Pauling, *The Nature of the Chemical Bond*, Ithaca, NY: Cornell University, 1960.

TABLE 2.4
Boiling Points of Several Small Molecules

Compound	Formula	Boiling Point (°C at 1 atmosphere pressure)
Methane	CH ₄	-164
Carbon dioxide	CO ₂	-78.6
Hydrogen sulfide	H ₂ S	-60.7
Water	H ₂ O	+100

These partial charges, or *dipoles*, can lead to intermolecular attractions that play an important role in such physical properties as melting point and boiling point, and they are quite important in determining solubility as well. The boiling point of water, 100°C, is quite high when compared to values of other small molecules, as shown in Table 2.4. The high boiling point for water can be attributed to strong intermolecular attractions (called *dipole–dipole interactions*) of the type shown in Figure 2.1.

The considerable solubility of polar molecules and many ionic compounds in water can be explained by dipole–dipole or ion–dipole interactions between dissolved species and the solvent, water, as shown in Figure 2.2.

The degree of solubility of solid compounds in water, as well as in other solvents, is determined by the competition between attractions in the solid state between molecules or ions and the solute–solvent attractions that occur in solution. A solid that is more attracted to itself than to the solvent molecules will not dissolve. A general

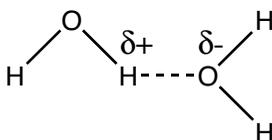


FIGURE 2.1 Intermolecular attractions (dipole–dipole interactions) of water. Note that the partially-positive hydrogen atoms are attracted to the partially-negative oxygen atoms (“opposites attract”)

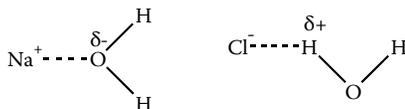


FIGURE 2.2 Dipole–dipole interactions between water and solvated NaCl (sodium chloride, or table salt). Note that the positive sodium ion is attracted to the partially-negative oxygen atom, and the negative chloride ion is attracted to the partially-positive hydrogen atom.

rule of solubility is likes dissolve likes—a polar solvent such as water is most effective as dissolving polar molecules (such as sugar) and ionic compounds. A nonpolar solvent such as gasoline is most effective at dissolving other nonpolar species, such as motor oil, but it is a poor solvent for ionic species such as sodium chloride or potassium nitrate.

THE MOLE CONCEPT

Out of the atomic theory developed by John Dalton and other chemistry pioneers in the nineteenth century grew a number of important concepts essential to an understanding of all areas of chemistry, including pyrotechnics and explosives. The basic features of the atomic theory are:

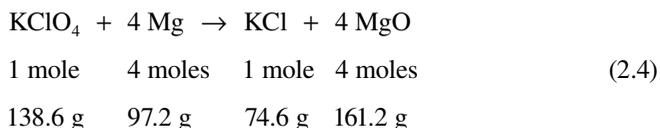
1. The atom is the fundamental building block of matter, and consists of positive, negative, and neutral subatomic particles. Approximately ninety naturally occurring elements are known to exist (additional elements have been synthesized in the twentieth century in the laboratory using high-energy nuclear reactions, but these unstable species are not found in nature).
2. Elements may combine to form more complex species called *compounds*. The *molecule* is the fundamental unit of a compound and consists of two or more atoms joined together by chemical bonds.
3. All atoms of the same element are identical in terms of the number of protons and electrons contained in the neutral species. Atoms of the same element may vary in the number of neutrons, and therefore may vary in mass.
4. The chemical reactivity of an atom depends on the number of electrons; therefore, the reactivity of all atoms of a given element should be the same, and reproducible, anywhere in the world.
5. Chemical reactions consist of the combination or recombination of atoms, in fixed ratios, to produce new species.
6. A relative scale of atomic weights (as the weighted average of all forms, or isotopes, of a particular element found in nature) has been developed. The base of this scale is the assignment of a mass of 12.0000 to the isotope of carbon containing six protons, six neutrons, and six electrons. An atomic weight table can be found in Table 2.2.
7. As electrons are placed into atoms, they successively occupy higher energy levels, or shells. Electrons in filled levels are unimportant as far as chemical reactivity is concerned. It is the outer, partially filled level that determines chemical behavior. Hence, elements with the same outer-shell configuration display markedly similar chemical reactivity. This phenomenon is called *periodicity*, and an arrangement placing similar elements in a vertical column has been developed—the *periodic table*. The alkali metals (lithium, sodium, potassium, rubidium, and cesium) are one family of the periodic table; they all have one reactive electron in their outer shell. The halogens (fluorine, chlorine, bromine, and iodine) are another common family; they all have seven electrons in their outer shell and readily accept an eighth electron to form a filled level.

The mass of one atom of any element is infinitesimal and is impossible to measure on any existing balance. A more convenient mass unit was needed for laboratory work, and the concept of the *mole* emerged, where 1 mole of an element is a quantity equal to the atomic weight in grams. One mole of carbon, for example, is 12.01 grams, and 1 mole of iron is 55.85 grams. The actual number of atoms in 1 mole of an element has been determined by several elegant experimental procedures to be 6.02×10^{23} ! This quantity is known as *Avogadro's number*, in honor of one of the pioneers of atomic theory. One can then see that 1 mole of carbon atoms (12.01 grams) will contain exactly the same number of atoms as 1 mole (55.85 grams) of iron. Using the mole concept, the chemist can now go into the laboratory and weigh out equal quantities of atoms of various elements.

The same concept holds for molecules. One mole of water (H_2O) consists of 6.02×10^{23} molecules and has a mass of 18.0 grams. It contains 1 mole of oxygen atoms and two moles of hydrogen atoms covalently bonded to make water molecules. The *molecular weight* of a compound is the sum of the respective atomic weights, taking into account the number of atoms of each element that comprise the molecule. For ionic compounds, a similar concept termed *formula weight* is used. The formula weight of sodium nitrate, NaNO_3 , is therefore:

$$\text{Na} + \text{N} + 3 \text{ O's} = 23.0 + 14.0 + 3(16.0) = 85.0 \text{ g/mole} \quad (2.3)$$

These concepts permit the chemist to examine chemical reactions and determine the mass relationships that are involved. For example, consider the simple pyrotechnic reaction



In a balanced chemical equation, the number of atoms of each element on the left-hand, or reactant, side will equal the number of atoms of each element on the right-hand, or product, side. The above equation states that 1 mole of potassium perchlorate (KClO_4 , a *reactant*) will react with 4 moles of magnesium metal to produce 1 mole of potassium chloride (KCl) and 4 moles of magnesium oxide (MgO).

In mass terms, 138.6 grams (or pounds, tons, etc.) of potassium perchlorate will react with 97.2 grams (or any other mass unit) of magnesium to produce 74.6 grams of KCl and 161.2 grams of MgO. This mass ratio will always be maintained regardless of the quantities of starting material involved. If 138.6 grams (1.00 mole) of KClO_4 and 48.6 grams (2.00 moles) of magnesium are mixed and ignited, only 69.3 grams (0.50 mole) of the KClO_4 will react, completely depleting the magnesium. Remaining as excess starting material will be 0.50 mole (69.3 grams) of KClO_4 —there is no magnesium left for it to react with! The products formed in this example would be 37.3 grams (0.50 mole) of KCl and 80.6 grams (2.00 moles) of MgO, plus the 69.3 grams of excess KClO_4 .

The preceding example also illustrates the *law of conservation of mass*. In any normal chemical reaction (excluding nuclear reactions), the mass of the starting

materials will always equal the mass of the products (including the mass of any excess reactant). Two hundred grams of KClO_4/Mg mixture will produce 200 grams of products (which includes any excess starting material).

The formula for the preceding illustration involved KClO_4 and Mg in a 138.6-to-97.2 mass ratio. The balanced mixture—with neither material present in excess—should then be 58.8% KClO_4 and 41.2% Mg by weight. The study of chemical weight relationships of this type is referred to as *stoichiometry*. A mixture containing exactly the quantities of each starting material corresponding to the balanced chemical equation is referred to as a *stoichiometric mixture*. Such balanced compositions are frequently associated with maximum performance in high-energy chemistry and will be referred to from time to time in subsequent chapters.

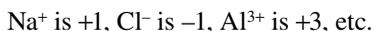
ELECTRON-TRANSFER REACTIONS

OXIDATION-REDUCTION THEORY

A major class of chemical reactions involves the transfer of one or more electrons from one species to another. This process is referred to as an *electron-transfer* or *oxidation-reduction reaction*, where the species undergoing electron loss is said to be *oxidized*, while the species acquiring electrons is *reduced*. Pyrotechnics, propellants, and explosives belong to this chemical reaction category.

The determination of whether or not a species has undergone a loss or gain of electrons during a chemical reaction can be made by assigning oxidation numbers to the atoms of the various reacting species and products, according to the following simple rules:

1. Except in a few rare cases, hydrogen is always +1 and oxygen is always -2. Metal hydrides and peroxides are the most common exceptions. This rule is applied first—it has highest priority, and the rest are applied in decreasing priority.
2. Simple ions have their charge as their oxidation number. For example,



The oxidation number of an element in its standard state (either as a monatomic atom such as metallic iron, Fe , or combined with itself to form a diatomic molecule, as in N_2 or O_2) is 0.

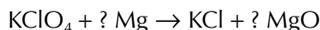
3. In a polar covalent molecule, the more electronegative atom in a bonded pair is assigned all of the electrons shared between the two atoms. For example, in H-Cl , the chlorine atom is assigned both bonded electrons, making it identical to Cl and giving it an oxidation number of -1. The hydrogen atom therefore has an oxidation number of +1 (in agreement with rule 1 as well).
4. In a neutral molecule, the sum of the oxidation numbers will be 0. For an ion, the sum of the oxidation numbers on all the atoms will equal the net charge of the ion.

Examples

NH_3 (ammonia): The three hydrogen atoms are all +1 by rule 1. The nitrogen atom will therefore be -3 by rule 4.

CO_3^{2-} (the carbonate ion): The three oxygen atoms are all -2 by rule 1. Since the ion has a net charge of -2 , the oxidation number of carbon will be $3(-2) + x = -2$, $x = +4$ by rule 4.

For the reaction



the oxidation numbers on the various atoms are:

KClO_4 : This is an ionic compound, consisting of the potassium ion, K^+ , and the perchlorate ion, ClO_4^- . The oxidation number of potassium in K^+ will be +1 by rule 2. In ClO_4^- , the four oxygen atoms are all -2 , making chlorine atom +7, by rule 4.

Mg: Magnesium is present in elemental form as a reactant, making its oxidation number 0 by rule 2.

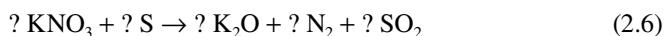
KCl: This is an ionic compound made up of K^+ and Cl^- ions, with respective oxidation numbers of +1 and -1 by rule 2.

MgO: This is another ionic compound. Oxygen will be -2 by rule 1, leaving the magnesium ion as +2.

Examining the various changes in oxidation number that occur as the reaction proceeds, one can see that potassium and oxygen are unchanged in going from reactants to products. Magnesium, however, undergoes a change from 0 to +2, corresponding to a loss of two electrons per atom—it has lost electrons, or been *oxidized*. Chlorine undergoes an oxidation number change from +7 to -1 , or a *gain* of 8 electrons per atom—it has been *reduced*. In a balanced oxidation-reduction reaction, the electrons lost must equal the electrons gained; therefore, four magnesium atoms (each losing two electrons) are required to reduce one chlorine atom from the +7 (as ClO_4^-) to -1 (as Cl^-) state. The equation is now balanced!

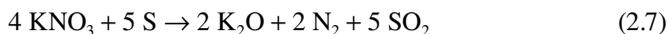


Similarly, the equation for the reaction between potassium nitrate and sulfur can be balanced if one assumes, or has determined by laboratory analysis, that the products are potassium oxide, sulfur dioxide, and nitrogen gas:



Again, analysis of the oxidation numbers reveals that potassium and oxygen are unchanged, with values of +1 and -2 , respectively, on both sides of the equation.

Nitrogen changes from a value of +5 in the nitrate ion (NO_3^-) to 0 in elemental/molecular form as N_2 . Sulfur changes from 0 in elemental form to a value of +4 in SO_2 . In this reaction, then, sulfur is oxidized and nitrogen is reduced. To balance the equation, four nitrogen atoms, each gaining five electrons, and five sulfur atoms, each losing four electrons, are required. This results in twenty electrons gained and twenty electrons lost—they're balanced. The balanced equation is, therefore,



The ratio by weight of potassium nitrate and sulfur corresponding to a balanced—or stoichiometric—mixture will be $4(101.1) = 404.4$ grams (4 moles) of KNO_3 and $5(32.1) = 160.5$ grams (5 moles) of sulfur. This equals 72% KNO_3 and 28% S by weight.

THE PYRO VALENCE METHOD—A SIMPLE YET POWERFUL TECHNIQUE

The ability to balance oxidation-reduction equations can be quite useful in working out weight ratios for mixtures that should theoretically yield optimum pyrotechnic or explosive performance. An understanding of the oxidation number concept discussed in the previous section is valuable because it provides insight into which elemental species are directly related to the gain and loss of electrons.

However, for the practicing pyrotechnic researcher, the ability to quickly balance oxidation-reduction equations (or oxidizer/fuel ratios), as well as the ability to rapidly determine if a given composition is oxidizer rich, fuel rich, or stoichiometric, can be quite valuable. While it is quite likely that some pyrotechnic reactions occurring quite rapidly at high temperature will yield a complex mixture of reaction products, it is also likely that one reaction pathway will account for a majority of the products, and this is usually the pathway that will yield the most stable reaction products. It is always possible to carry out a laboratory analysis of the reaction products to confirm that you have identified the primary reaction that is occurring between an oxidizer and a fuel.

It is possible to rapidly perform these types of calculations using a method based on oxidation numbers (valences) put forward by Jain.² The use of this Pyro Valence method can be of great value in the analysis of a large variety of quantitative problems associated with explosive, propellant, and pyrotechnic systems.

The Pyro Valence approach is based on the concept of oxidation numbers, but concentrates on the oxidation numbers of each element in its most stable product form. Each element in an energetic mixture is assigned a valence, which is the most common oxidation number of that element as a reaction *product*. An initial assumption in the Pyro Valence approach is that each element will react to form its normal, or most stable, oxidation state as a reaction product. Hence, any nitrogen present in a reactant is assumed to form N_2 . Any chlorine is assumed to form Cl^- , any magnesium will form Mg^{2+} , and it is initially assumed that all carbon atoms will go to CO_2 . Hydrogen will be present in reaction products as H^+ , usually as either H_2O

TABLE 2.5
Pyro Valences for Elements Used to Calculate Valence for a
Molecule or Formula Unit of Ionic Compound or Polymer

Element	Pyro Valence	Assumed Product
Aluminum, Al	+3	Al ₂ O ₃
Barium, Ba	+2	BaO
Boron, B	+3	B ₂ O ₃
Calcium, Ca	+2	CaO
Carbon, C	+4	CO ₂
Chlorine, Cl	-1	HCl, KCl, other metal chlorides
Chromium, Cr	+3	Cr ₂ O ₃
Fluorine, F	-1	HF, MgF ₂ , other metal fluorides
Hydrogen, H	+1	H ₂ O
Iron, Fe (in oxidizer)	0	Fe
Iron, Fe (as a fuel)	+3	Fe ₂ O ₃
Magnesium, Mg	+2	MgO
Nitrogen, N	0	N ₂
Oxygen, O	-2	H ₂ O, metal oxides
Potassium, K	+1	K ₂ O, KCl
Silicon, Si	+4	SiO ₂
Sulfur, S	+4	SO ₂
Titanium, Ti	+4	TiO ₂
Zirconium, Zr	+4	ZrO ₂

or HCl. The valences for these elements are therefore 0 for N (since the oxidation number of N in N₂ is 0), -1 for Cl (since the oxidation number of Cl as Cl⁻ is -1), +2 for Mg, and +4 for C going to CO₂, where C would have an oxidation number of +4. A list of Pyro Valences for common elements used in pyrotechnic materials is given in Table 2.5.

To continue with the Pyro Valence approach, you then add up all of the atomic valences for a chemical compound, to obtain the molecular or compound valence. KClO₄ will have a net valence of -8, obtained by adding up four O's at -2 each, one Cl at -1, and one K at +1 (since K remains K⁺ on the product side, as KCl). Any species under the Pyro Valence system that has a net negative valence (such as KClO₄ at -8) will have oxidizing ability—it has one or more elements in the compound that want to gain electrons (the Cl atom in KClO₄, for example). A list of net valences for some of the common oxidizers is given in Table 2.6.

Similarly, any species with a net positive Pyro Valence has reducing ability, or is a fuel. A metal fuel such as aluminum (Al) will have a valence of +3, since it will lose three electrons to produce Al³⁺ product (usually in the form of Al₂O₃). An organic compound such as a simple sugar, with formula C₆H₁₂O₆, will have a net valence of 6(+4) + 12(+1) + 6(-2) for the C, H, and O atoms that are present. This adds up to a net +24, indicating that sugar—even though it contains six oxygen atoms per

TABLE 2.6
Pyro Valences for Some Common Pyrotechnic Oxidizers

Oxidizers	Valence	Products
Potassium nitrate, KNO_3	-5	K_2O , N_2 , oxide/fuel
Potassium perchlorate, KClO_4	-8	KCl , oxide/fuel
Potassium chlorate, KClO_3	-6	KCl , oxide/fuel
Ammonium perchlorate, NH_4ClO_4	-5	N_2 , H_2O , HCl , oxide
Barium nitrate, $\text{Ba}(\text{NO}_3)_2$	-10	BaO , N_2 , oxide/fuel
Iron(III) oxide, Fe_2O_3	-6	Fe , oxide/fuel
Barium chromate, BaCrO_4	-3	BaO , Cr_2O_3 , oxide
Red lead oxide, Pb_3O_4	-8	Pb (valence = -2 if PbO is formed)
Ammonium nitrate, NH_4NO_3	-2	N_2 , H_2O , oxide

molecule—is still a net fuel. Net Pyro Valences for some common fuels and explosive compounds are given in Table 2.7.

Once Pyro Valences have been assigned to all reactant species, we can proceed to balance an equation by the use of the concept that in a balanced equation, the sum of the oxidizing valences will equal the sum of the reducing valences, and the net, overall valence will be zero. This is the equivalent of saying that the number of electrons lost will equal the number of electrons gained—electrons are neither created nor destroyed, they just move from one atomic species to another during a chemical reaction.

TABLE 2.7
Pyro Valences of Some Common Fuels and Explosives

Compound	Valence	Reaction Products
Fuel oil, $-(\text{CH}_2-\text{CH}_2)-$ (unit mass = 28 grams/mole)	+12 per unit	CO_2 , H_2O
Glucose, $\text{C}_6\text{H}_{12}\text{O}_6$	+24	CO_2 , H_2O
Polyvinyl chloride, $-(\text{CH}_2-\text{CHCl})-$ (unit mass = 62.5 grams/mole)	+10 per unit	CO_2 , HCl , H_2O
TNT, $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$	+21	CO_2 , H_2O , N_2
RDX, $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$	+6	CO_2 , H_2O , N_2
EGDN, ethylene glycol dinitrate $\text{C}_2\text{H}_4\text{N}_2\text{O}_6$	0! (stoichiometric)	CO_2 , H_2O , N_2
Nitroglycerine, $\text{C}_3\text{H}_5\text{N}_3\text{O}_9$	-1 (O rich)	CO_2 , H_2O , N_2
Sodium azide, NaN_3	0	Na , N_2 (extra energy can be obtained if the sodium metal product is oxidized to Na^+ by an oxidizer)

Note: Some elemental fuels may be found in the table of elements.

For example, consider ammonium perchlorate, NH_4ClO_4 :

$$\begin{aligned} \text{Total valence} &= 0 + 4(+1) + (-1) + 4(-2) = -5 \\ &\quad \text{N} \quad 4 \text{ H's} \quad \text{Cl} \quad 4 \text{ O's} \end{aligned}$$

Since the total valence is a net negative value (-5), ammonium perchlorate will be an oxidizing species.

Now, let's look at a simple sugar such as glucose, $\text{C}_6\text{H}_{12}\text{O}_6$:

$$\begin{aligned} \text{Total valence} &= 6(+4) + 12(+1) + 6(-2) = +24 \\ &\quad 6 \text{ C's} \quad 12 \text{ H's} \quad 6 \text{ O's} \end{aligned}$$

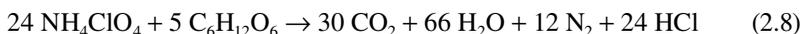
Since the net molecular Pyro Valence is positive, glucose will be a fuel.

And suppose you then wanted to balance the equation for the reaction between glucose and ammonium perchlorate. The key to balancing an equation by the Pyro Valence method is to remember that the oxidizing valences will equal the reducing valences, or the sum of the valences will equal zero.

BALANCING AN EQUATION

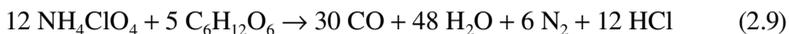
To balance an energetic equation, determine the coefficients (smallest whole number ratio) that will produce equal valences.

For ammonium perchlorate, or AP (-5) and glucose (+24), you will need twenty-four APs and five glucoses in the balanced equation. There are no smaller factors for the numbers 24 and 5. Put these coefficients in for the reactants, and you've balanced the equation. You can then work out how many moles of each product will form, if you so desire.



Note: This method assumes that all N winds up as N_2 , and all Cl winds up as HCl. All the C atoms in the fuel are assumed to go to CO_2 , all the H atoms go to H_2O or HCl, and all the N atoms become N_2 . Upon inspection, the equation is balanced!

Note: The Pyro Valence method works equally well if one wishes to calculate the stoichiometric mixture for a composition where carbon monoxide (CO) is the assumed product formed by the carbon atoms in the fuel. To do this, use +2 as the valence for carbon in the calculations, and the net valence for glucose will be +12. The balanced equation will be



IS A CHEMICAL COMPOUND FUEL OR OXYGEN RICH?

The Pyro Valence procedure also provides a very easy way to calculate if a specific molecule or compound is fuel rich, oxygen rich, or stoichiometric. Consider, for example, the compound trinitrotoluene, better known as TNT, with a molecular

formula of $C_7H_5N_3O_6$. TNT is a powerful explosive, but is it oxygen balanced? The Pyro Valence method provides an easy, quick way to tell. Simply add up the atomic valences multiplied by the number of atoms of each element found in the molecule:

$$\begin{aligned} \text{TNT's Pyro Valence} &= 7(+4) + 5(+1) + 3(0) + 6(-2) = +21 \\ &7 \text{ C's} \quad 5 \text{ H's} \quad 3 \text{ N's} \quad 6 \text{ O's} \end{aligned}$$

Because of the large, positive valence, we can see that TNT is a very fuel-rich explosive—more energy should theoretically be obtainable if TNT is combined with an oxygen-rich explosive, to better utilize TNT's fuel capacity. When TNT is detonated, a large cloud of dark smoke is produced, due to a significant amount of atomic carbon being formed. In theory, then, we would expect a candidate molecular explosive that has a significant number of positive and negative valences that add up close to zero to be of great interest.

The molecular nitramine explosive HMX (so dubbed for "his Majesty's Explosive), with molecular formula $C_4H_8N_8O_8$, has a positive valence total of +24 (4 C's and 8 H's) and a negative valence total of -16 (8 O's), for a net molecule valence of +8 (fuel rich). If carbon monoxide (CO) is the product from the carbons, however, we have valences of +16 and -16, for a molecule Pyro Valence of *zero*. Perhaps this has something to do with the high detonation velocity of HMX—over 9,000 meters/second.

WHAT ABOUT METHYLAMMONIUM PERCHLORATE, $CH_3NH_3ClO_4$?

Ammonium perchlorate, NH_4ClO_4 , is a good oxidizer, with a Pyro Valence of -5. A similar compound, methylammonium perchlorate, might be considered for use in energetic mixtures as well, and it might be assumed initially that methylammonium perchlorate (MAP) will also serve as an oxidizer. However, the replacement of a H atom by a CH_3 group significantly alters the nature of the compound, as shown by the valence calculation below:

$$\begin{aligned} \text{Valence} &= 1(+4) + 6(+1) + 0 + 1(-1) + 4(-2) = +1 \text{ (a net fuel!)} \\ &1 \text{ C} \quad 6 \text{ H's} \quad 1 \text{ N} \quad 1 \text{ Cl} \quad 4 \text{ O's} \end{aligned}$$

The calculation shows that the compound is actually now slightly fuel rich, and very close to stoichiometric. If you combined MAP with a fuel, hoping to get a violent reaction, you would probably be disappointed—MAP is already fuel rich with carbon dioxide as the product.

A logical question to ask at this point is: Are there any energetic compounds that are actually internally stoichiometric going to CO_2 as the carbon product, or have a net valence of 0? What about ethylene glycol dinitrate (EGDN)—a material used in many dynamites for low-temperature applications? EGDN has a molecular formula of $C_2H_4N_2O_6$. Its Pyro Valence will be

$$2(+4) + 4(+1) + 2(0) + 6(-2) = 0 \text{—a stoichiometric explosive going to } CO_2!$$

In actual practice, EGDN is a good explosive, but it does not rise dramatically above other explosives in terms of its performance. Its net valence of 0 is as much a chemical curiosity as anything; other explosives are capable of very rapid, energetic reactions even if they deviate somewhat from internal stoichiometry. If you wish to enhance the performance of an explosive compound, however, the ideal material to add would be an oxidizer or a fuel—whichever one will bring the overall system closer to oxygen balance.

WEIGHT RATIO CALCULATIONS

The Pyro Valence approach provides a simple procedure for calculating the weight of any fuel needed to react with a given oxidizer, in stoichiometric proportions. The ammonium nitrate–fuel oil (ANFO) system, widely used as a commercial blasting agent, provides a good example. We will assume that fuel oil can be represented by CH_2 , which is the repeating unit that makes up the vast majority of a fuel oil molecule.

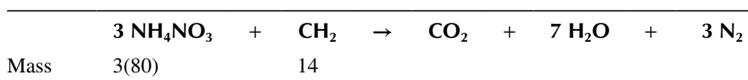
The valence for ammonium nitrate (NH_4NO_3) is

$$2(0) + 4(+1) + 3(-2) = -2 \text{ (oxidizer)}$$

The valence for a hydrocarbon unit (CH_2) is

$$1(+4) + 2(+1) = +6 \text{ (fuel) (per 14 grams or 1 } \text{CH}_2 \text{ unit)}$$

The balanced equation will therefore require three ANs for each CH_2 unit by the valence method, or



Ammonium nitrate has a formula weight of 80, while the CH_2 fragment has a mass of 14. The mass ratio for the above-balanced equation is, therefore,

$$3(80):14 = 240:14, \text{ or } 94.5:5.5$$

which is almost the exact ratio found in the ANFO explosives. This ratio (the stoichiometric ratio) maximizes the energy output from the system by fully utilizing all the available oxygen and all the available fuel.

Note: It is highly likely that a pyrotechnic reaction will yield more than a single set of reaction products, due to the possibility of multiple reactions occurring and competing at high reaction temperatures and very fast reaction rates. The thermodynamically favored reaction will have competition from other reaction pathways, but the stoichiometry that is predicted using the Pyro Valence approach represents a good starting point in the development of a new formulation.

Once the initial composition has been prepared and its reaction rate measured, vary the oxidizer/fuel ratio up and down in small increments and observe the effect on the reaction rate. This will give you an insight into the effect of small changes in composition on the reactivity of the composition, as well as an indication of whether you are close to the actual stoichiometric point for the primary reaction that is occurring when the test material is ignited.

Remember, you can always perform a chemical analysis of the reaction products to verify if your proposed primary reaction is, in fact, the one that is taking place. That is the beauty of chemistry—theory can usually be confirmed or disproved by a trip to the lab.

ANALYZING A MIXTURE

Analyzing a mixture by the Pyro Valence method consists of calculating the valence for a given *mass* (which is typically assumed to be 100 grams for calculation purposes) of the mixed composition. This is accomplished by first calculating the number of *moles* of each component in 100 grams of the mixture, using the molecular or formula weight of each component. The actual number of moles of each species in 100 grams is then multiplied by the appropriate valence to calculate the fractional valence for each component. These individual valences are then summed up to give the net valence for 100 grams of composition. If this sum is negative, the mixture is oxygen rich; if it is positive, the composition is fuel rich; and if the net valence is 0, the mixture is stoichiometric.

Consider an 80:20 mixture (by weight) of potassium perchlorate and titanium (KClO_4/Ti). Assume that you have 100 grams for calculation purposes. You do not need to balance the equation to perform this analysis.

	KClO_4	+	Ti	→	KCl	+	TiO_2
M, mass (grams)	80		20				
FW, formula weight (grams/mole)	138.6		47.9				
Number of moles (g/FW)	0.577		0.418				
Valence (per FW)	-8		+4				
Valence for the mass used	-4.62		+1.67				

$$\text{Sum} = -2.95 \text{ (number of moles} \times \text{valence/FW)}$$

The sum of the Pyro Valences in this mixture is -2.95 ; therefore, this mixture is oxidizer rich, and the addition of more titanium should yield an even more reactive formulation. If the valences had added up to zero, the mix would have been stoichiometric.

THREE-COMPONENT SYSTEMS

The analysis is essentially identical for systems with more than two components, and provides a very simple means of determining the oxygen balance of even complex

mixtures. Again, the one assumption that must be made involves what reaction products will form, for this determines the Pyro Valence of each reacting element. Once this has been done, calculate the number of moles of each component in 100 grams of mix, calculate the valences for each component, and see if the sum is negative (oxidizer rich) or positive (fuel rich). In this example, we will use polymethylmethacrylate (PMMA) as a fuel/binder. PMMA is a polymer consisting of a chain of $C_5H_8O_2$ units; calculations for polymers can be performed on the monomer unit, since the use of the appropriate formula weight cancels out any discrepancy and greatly simplifies calculations with polymers. Let's analyze a mixture that is 60/35/5 $KClO_4$ /Ti/PMMA by weight.

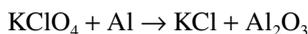
	$KClO_4$	+ Ti	+ $C_5H_8O_2$	→	KCl	+ CO_2	+ H_2O	+ TiO_2
Weight	60	35	5		Grams per 100 grams of mixture			
FW	138.5	47.9	100		Grams per mole			
Moles	0.433	0.731	0.050		Grams/formula weight			
Valence/mole	-8	+4	+24		Valence of each species			
Valence/formula	-3.46	+2.92	+1.20		Number of moles × valence/mole			

Sum = +0.66 (mixture is fuel rich)

There is just no easier way to analyze complex mixtures to determine if they are oxidizer rich, fuel rich, or stoichiometric! While there are computer programs that can perform detailed calculations on energetic mixtures, the Pyro Valence method gives you some quick insight into the fundamental nature of an energetic system, and suggests the effect that various chemical additives might have on the system. Below are a few exercises using the Pyro Valence method.

PYRO VALENCE EXERCISES

1. Calculate the stoichiometric composition for the potassium perchlorate-aluminum system:



2. Determine whether the following composition is fuel or oxidizer rich:

Potassium Perchlorate	Glucose	Polyvinyl Chloride (PVC)
$KClO_4$	$C_6H_{12}O_6$	$-(C_2H_3Cl)-$
65	25	10 (parts by weight)

3. Develop the stoichiometric mixture for potassium perchlorate/glucose/PVC for a composition that contains 5% PVC by weight.

4. A delay system consisting of barium chromate (BaCrO_4), potassium perchlorate (KClO_4), and molybdenum (Mo) is desired containing 10% KClO_4 . What would be the stoichiometric mixture? Reaction products are assumed to be BaO , Cr_2O_3 , KCl , and MoO_3 .
5. Develop the stoichiometric ratio for the ammonium perchlorate (NH_4ClO_4)–sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) system. The formula weight for AP is 117.5; the molecular weight of sucrose is 342.

Solutions and Answers to the Exercises

1. Complete the reaction:



Calculate/look up Pyro Valences of the oxidizer and fuel:

$$\text{KClO}_4 \quad V = +1 - 1 + 4(-2) = -8$$

$$\text{Al} \quad V = +3$$

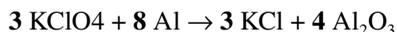
Balance oxidizer and fuel valences:

$$\text{KClO}_4 \quad -8 \times 3 = -24$$

Three KClO_4 's are needed to balance the valences of 8 Al's

$$\text{Al} \quad +3 \times 8 = +24$$

So the balanced equation is



Note: Four moles of Al_2O_3 contains 8 moles of aluminum atoms. The mass relationship is therefore:

$$3 \text{KClO}_4: \quad 8 \text{Al}$$

$$3 (138.5): \quad (8 \times 27) \text{ grams}$$

$$415.5: \quad 216 \text{ grams}$$

The % KClO_4 in the stoichiometric (balanced) mix is

$$\% \text{KClO}_4 = 415.5 / (415.5 + 216) = .658 \times 100 = 65.8\%$$

The aluminum percent is $216 / (415.5 + 216) = 0.342 \times 100 = 34.2\%$.

Check: The sum of the percents should equal 100% if you've done everything right.

2. Is a composition fuel or oxidizer rich?

	KClO_4	$\text{C}_6\text{H}_{12}\text{O}_6$	$-(\text{C}_2\text{H}_3\text{Cl})-$
A. Parts by weight	65	25	10
B. Formula weight	138.5	180	62.5 (per monomer unit)
C. Number of moles (A/B)	0.47	0.14	0.16
D. Pyro Valence	-8	+24	+10
E. Net valence (C \times D)	-3.8	+3.3	+1.6

Pyro Valence sum (net valence) = +1.1, so mix is fuel rich

3. Develop the stoichiometric mixture for potassium perchlorate/glucose/PVC that contains 5% PVC by weight. This problem gives you an opportunity to use that algebra you never thought you'd need again.

Let x = grams of glucose in 100 grams of the mix. Since there are 5 grams of PVC (5%), you will therefore have $95 - x$ grams of potassium perchlorate. The weights are therefore:

	KClO_4	$\text{C}_6\text{H}_{12}\text{O}_6$	$-(\text{C}_2\text{H}_3\text{Cl})-$
Grams	$95 - x$	x	5
A. Number of moles	$(95 - x)/138.5$	$x/180$	$5/62.5$
B. Pyro Valence	-8	+24	+10
C. Net valence (A \times B)	$\frac{-8(95 - x)}{138.5}$	$\frac{+24(x)}{180}$	$\frac{+10(5)}{62.5}$

For a stoichiometric mix, the total valence = 0. Therefore:

$$\text{Valence}(\text{KClO}_4) + \text{Valence}(\text{C}_6\text{H}_{12}\text{O}_6) + \text{Valence}(\text{PVC}) = 0$$

Set the sum of the net valences in (C) equal to 0 and solve for x .

$$x = 24.5 = \text{number of grams of glucose in the stoichiometric mixture}$$

Therefore, number of grams of $\text{KClO}_4 = 95 - x = 95 - 24.5 = 70.5$ grams. The balanced mixture is as follows:

KClO_4	Glucose	PVC
70.5%	24.5%	5%

4. Molybdenum delay system, 10% KClO_4 . Calculate the percents in the stoichiometric mixture: First, let x = grams Mo in 100 grams of mixture.

The percents (grams/100 grams) are as follows:

	BaCrO ₄	KClO ₄	Mo
Grams	90 - x	10	x
A. Formula weight	253.3	138.5	95.9
B. Pyro Valence	-3	-8	+6*
C. Number of moles in mix	$\frac{90-x}{253.3}$	$\frac{10}{138.5}$	$\frac{x}{95.9}$
D. Net valence (B × C)			

For a stoichiometric mix, the sum of all valences will = 0, so the sum of the entries in line D is set = 0:

$$-3 \frac{90-x}{253.3} + -8 \frac{10}{138.5} + 6 \frac{x}{95.9} = 0$$

Solve this equation for x (or get a ninth-grader taking algebra to work it out for you!). You should get $x = 22.1$, which is the number of grams of Mo in the stoichiometric mixture.

The stoichiometric mix is, therefore,

BaCrO ₄	KClO ₄	Mo
67.9	10.0	22.1 (parts by weight)

* Note that the Pyro Valence of Mo is obtained by analysis of the formula of the reaction product, MoO₃. Mo in this compound has an oxidation number of +6, and the valence is therefore +6 for Mo metal.

5. This one is about as messy as they get! The valence for ammonium perchlorate is +5 (oxidizer); the valence for sucrose is -48 (-48 - 22 + 22). The balanced equation is therefore:



Weights: 48(117.5):5(342) grams

5,640:1,710

76.7%:23.3% by weight

ADDITIONAL PYRO VALENCE PROBLEMS

1. A flare composition is 15% KClO₄, plus it contains strontium nitrate (a second oxidizer) and magnesium (fuel). What will be the composition of the stoichiometric mixture? Assume that Sr(NO₃)₂ forms SrO, N₂, and oxygen.

The magnesium will form MgO, and KClO_4 will form KCl and oxygen (which combines with Mg and Sr).

Answer: 15% KClO_4 , 47.3% $\text{Sr}(\text{NO}_3)_2$, 37.7% Mg.

2. A flare mixture contains 45% $\text{Ba}(\text{NO}_3)_2$, 35% Mg, and 20% polyvinyl chloride (PVC, $\text{C}_2\text{H}_3\text{Cl}$ polymer). Is this mixture fuel rich or fuel lean?

Answer: Net valences for 100 grams are -1.72 for barium nitrate, $+2.88$ for Mg, and $+3.20$ for PVC. Sum of all valences is $+4.36$, so the mixture is fuel rich.

3. Ferric oxide (Fe_2O_3) and boron (B) make an interesting low-toxicity delay mixture. What is the composition of the stoichiometric mixture, assuming that the reaction products are Fe and B_2O_3 ? Valences are -6 for ferric oxide and $+3$ for boron.

Answer: 88.1% Fe_2O_3 , 11.9% B.

4. Aluminized ammonium nitrate–fuel oil (aluminized ANFO) is a popular commercial explosive. If a mixture contains 5% Al by weight, what weights of ammonium nitrate (valence = -2) and fuel oil will make up the stoichiometric mixture? Assume that ammonium nitrate forms N_2 , $2 \text{H}_2\text{O}$, and evolves 1 O atom per formula unit. Also assume that fuel oil can be represented by $-\text{CH}_2-$, with a molecular weight of 14 and a valence of $+6$.

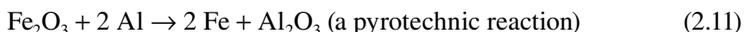
Answer:

	NH_4NO_3	Al	$-\text{CH}_2-$
Grams	$95 - x$	5	x

Stoichiometric mixture: Ammonium nitrate, 91.0%; Al, 5.0%; fuel oil, 4.0%.

ELECTROCHEMISTRY

If one takes a spontaneous electron-transfer reaction and *separates* the materials undergoing oxidation and reduction, a battery is created by allowing the electron transfer to occur through a good conductor such as a copper wire. By proper design, electrical energy associated with reactions of this type can be harnessed. The fields of electrochemistry (e.g., batteries) and pyrotechnics (e.g., fireworks) are actually very close relatives. The reactions involved in the two areas can look strikingly similar:



In both fields of research, one is looking for inexpensive, high-energy electron donors and acceptors that will readily yield their energy on demand yet be quite stable in storage.

It is interesting to note that many of the energetic materials used in the fields of explosives and pyrotechnics owe their high energy potential to the use of electrochemistry in the manufacturing process. Through electrolysis or electrochemical processes, modern technology converts Mg^{2+} to Mg metal, and converts chloride ions (Cl^-) to ClO_3^- (chlorate) and ClO_4^- (perchlorate) by the passage of an electric current through molten material in a reaction vessel. We do not find these materials in any significant quantity in nature—any that might be created by lightning or other high-energy natural processes usually convert quickly to their lower-energy forms (Mg^{2+} , Cl^-) by electron-transfer reactions with naturally occurring chemical species. Magnesium metal, for example, will react with water to form $\text{Mg}(\text{OH})_2$ and hydrogen gas, H_2 . Iron metal, formed from Fe^{3+} by a high-energy process in a blast furnace, all too quickly reverts to rust (Fe_2O_3) when exposed to air and moisture.

Many high-energy explosive molecules such as nitroglycerine and trinitrotoluene (TNT) similarly owe their stored energy to electrochemical processes, or the energy stored in these energetic species has its origin in solar and biochemical processes.

Therefore, in many ways, a pyrotechnic device is quite similar to a battery. Both provide packaged energy consisting of an electron donor and an electron acceptor. In a battery, we cause the energy contained within the chemical species to be released by closing a circuit and allowing a flow of electrons to occur, and work is performed in the process. With a pyrotechnic system, we intimately blend the electron donor and electron acceptor, and require that an energy input (for example, friction, impact, or the flame and sparks from a burning piece of fuse) be imposed on the system to initiate the electron-transfer reaction. Once the reaction begins, it generates sufficient energy to become self-sustaining, and no further external energy input (such as the flame from a fuse) is required.

Electrochemists have developed extensive tables listing the relative tendencies of materials to donate or accept electrons, and these tables can be quite useful to the pyrotechnic chemist in a search for new materials. Chemicals are listed in order of decreasing tendency to gain electrons, and are all expressed as *half-reactions* in the reduction direction, with the half-reaction



arbitrarily assigned a value of 0.000 volts. All other species are measured relative to this reaction, with more readily reducible species having positive voltages (also called *standard reduction potentials*), and less readily reducible species showing negative values. Species with sizable negative potentials should then, logically, be the best electron *donors*, and a combination of a good electron donor with a good electron acceptor should produce a battery of high voltage. Such a combination will also be a potential candidate for a pyrotechnic system. One must bear in mind, however, that most of the values listed in the electrochemistry tables are for reactions in solution, rather than for solids, so direct calculations can't be made for pyrotechnic systems. Some good ideas for candidate materials can be obtained, however.

A variety of materials of pyrotechnic interest and their standard reduction potentials at 25°C are listed in Table 2.8. Note the large positive values associated with

TABLE 2.8
Standard Reduction Potentials

Half-Reaction	Standard Potential at 25°C, in volts ^a
$F_2 + 2e^- \rightarrow 2 F^-$	2.87
$CO_3^{2-} + e^- \rightarrow CO_2^-$	1.8
$PbO_2 + 4 H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4(s) + 2 H_2O$	1.69
$MnO_4^- + 8 H^+ + 5e^- \rightarrow Mn^{2+} + 4 H_2O$	1.49
$PbO_2 + 4 H^+ + 2e^- \rightarrow Pb^{2+} + 2 H_2O$	1.46
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14 H^+ + 6e^- \rightarrow 2 Cr^{3+} + 7 H_2O$	1.33
$O_2 + 4 H^+ + 4e^- \rightarrow 2 H_2O$	1.23
$Br_2 + 2e^- \rightarrow 2 Br^-$	1.07
$NO_3^- + 4 H^+ + 3e^- \rightarrow NO + 2 H_2O$	0.96
$Hg^{2+} + 2e^- \rightarrow Hg$	0.85
$Ag^+ + e^- \rightarrow Ag$	0.8
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$I_2 + 2e^- \rightarrow 2I^-$	0.54
$Cu^+ + e^- \rightarrow Cu$	0.52
$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$	0.36
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Cu^{2+} + e^- \rightarrow Cu^+$	0.15
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.15
$2 H^+ + 2e^- \rightarrow H_2$	0
$Fe^{3+} + 3e^- \rightarrow Fe$	-0.04
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25
$CO^{2+} + 2e^- \rightarrow CO$	-0.29
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.359
$PbI_2 + 2e^- \rightarrow Pb + 2I^-$	-0.365
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.4
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.4
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.41
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$2 H_2O + 2e^- \rightarrow H_2(g) + 2 OH^-$	-0.83
$V^{2+} + 2e^- \rightarrow V$	-1.18
$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37

^a R. C. Weast (ed.), *CRC Handbook of Chemistry and Physics*, 75th ed., Boca Ration, FL: CRC Press, 1994.

certain oxygen-rich negative ions, such as the chlorate ion (ClO_3^-), and the large negative values associated with certain active metal fuels such as aluminum (Al).

THERMODYNAMICS

There are a vast number of possible reactions that the chemist working in the explosives and pyrotechnics field can write between various electron donors (fuels) and electron acceptors (oxidizers). Whether a particular reaction will occur and thereby be of possible use depends on two major factors:

1. Whether the reaction is *spontaneous*, or will actually occur if the oxidizer and fuel are mixed together
2. The *rate* at which the reaction will proceed, or the time required for complete reaction to occur

Spontaneity is determined by a quantity known as the *free energy change*, ΔG . Δ is the symbol for the uppercase Greek letter delta and stands for “change in.”

The thermodynamic requirement for a reaction to be spontaneous (at constant temperature and pressure) is that the products are of lower free energy than the reactants, or that ΔG —the change in free energy associated with the chemical reaction—be a negative value. Two quantities comprise the free energy of a system at a given temperature. The first is *enthalpy*, or heat content, represented by the symbol H. The second is the *entropy*, represented by the symbol S, which may be viewed as the randomness or disorder of the system. The free energy of a system, G, is equal to $H - TS$, where T is the temperature of the system on the Kelvin, or absolute, scale. (To convert from Celsius to Kelvin temperature, add 273 to the Celsius value.) The free energy change accompanying a chemical reaction at constant temperature is therefore given by

$$\Delta G = G(\text{products}) - G(\text{reactants}) = \Delta H - T\Delta S \quad (2.13)$$

For a chemical reaction to be spontaneous, or energetically favorable, it is desirable that ΔH , or the enthalpy change, be a negative value, corresponding to the liberation of heat by the reaction. Any chemical process that liberates heat is termed *exothermic*, while a process that absorbs heat is called *endothermic*. ΔH values for many high-energy reactions have been experimentally determined as well as theoretically calculated. The typical units for ΔH , or *heat of reaction*, are calories/mole or calories/gram. The International System of Units (SI System) calls for energy values to be given in *joules*, where 1 calorie = 4.184 joules. Most thermochemical data acquired prior to the 1980s are found with the calorie as the unit, and it will be used in this book in most instances. Some typical ΔH values for pyrotechnics are given in Table 2.9.

$$1 \text{ kilocalorie} = 1,000 \text{ calories}$$

$$1 \text{ calorie} = 4.184 \text{ joules, for conversion purposes}$$

TABLE 2.9
Typical ΔH Values for High-Energy Reactions

	Composition (% by weight)	ΔH (kcal/gram) ^a	Application
KClO ₄	60	2.24	Photoflash
Mg	40		
NaNO ₃	60	2.00	White light
Al	40		
Fe ₂ O ₃	75	0.96	Thermite (heat)
Al	25		
KNO ₃	75	0.66	Black powder
C	15		
S	10		
KClO ₃	57	0.61	Red light
SrCrO ₃	25		
Shellac	18		
KClO ₃	35	0.38	Red smoke
Lactose	25		
Red dye	40		

^a A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Moscow, 1964. (Translated as Report FTD-HC-23-1704-74 by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.) All values represent heat *released* by the reaction.

It is also favorable to have the entropy change, ΔS , be a positive value, making the $-\Delta S$ term in Equation (2.1) a negative value. A positive value for ΔS corresponds to an increase in the randomness or disorder of the system when the reaction occurs. The entropies of the various states of matter show the following trend:

$$S(\text{solid}) < S(\text{liquid}) \ll S(\text{gas})$$

Therefore, a process of the type solids \rightarrow gas (common to many high-energy systems) is particularly favored by the change in entropy occurring upon reaction. Reactions that evolve heat *and* form gases from solid starting materials should be favored thermodynamically and fall in the spontaneous category. Chemical processes of this type will be discussed in subsequent chapters.

HEAT OF REACTION

It is possible to calculate a heat of reaction for a high-energy system by assuming what the reaction products will be, and then using available thermodynamic tables of

heats of formation. Heat of formation is the heat associated with the formation of a chemical compound from its constituent elements. For example, for the reaction



ΔH is -400.5 kcal/mole of $\text{ Al}_2\text{O}_3$, and this value is therefore the heat of formation (ΔH_f) of aluminum oxide ($\text{ Al}_2\text{O}_3$). The reaction of 2.0 moles (54.0 grams) of aluminum with 1.5 moles of oxygen gas (48.0 grams) to form $\text{ Al}_2\text{O}_3$ (1.0 mole, 102.0 grams) will liberate 400.5 kcal of heat—a sizable amount! Also, to *decompose* 102.0 grams of $\text{ Al}_2\text{O}_3$ into 54.0 grams of aluminum metal and 48.0 grams of oxygen gas, one must put 400.5 kcal of heat *into* the system—an amount equal in magnitude but opposite in sign from the heat of formation. The heat of formation of any *element* in its standard state at 25°C will therefore be 0 using this system.

A chemical reaction can be considered to occur in two steps:

1. Decomposition of the starting materials into their constituent elements
2. Subsequent reaction of these elements to form the desired products

The *net* heat change associated with the overall reaction can then be calculated from:

$$\Delta H (\text{reaction}) = \Sigma \Delta H_f (\text{products}) - \Sigma \Delta H_f (\text{reactants})$$

where Σ = “the sum of.” This equation sums up the heats of formation of all of the products from a reaction, and then subtracts from that value the heat required to dissociate all of the starting materials into their elements. The difference between these two values is the net heat change, or heat of reaction. The heats of formation of a number of materials of interest to the high-energy chemist may be found in Table 2.10. All values given are for a reaction occurring at 25°C (298 K).

Example 1

Consider the following reaction, balanced using the oxidation numbers or Pyro Valence method:

Reaction	KClO₄	+	4 Mg	→	KCl	+	4 MgO
Grams	138.6		97.2		74.6		161.2
Heat of formation (kcal/mole × number of moles)	-103.4		4 (0)		-104.4		4 (-143.8)

$$\begin{aligned} \Delta H (\text{reaction}) &= \Sigma \Delta H_f (\text{products}) - \Sigma \Delta H_f (\text{reactants}) \\ &= [-104.4 + 4(-143.8)] - [-103.4 + 4(0)] \\ &= -576.2 \text{ kcal/mole KClO}_4 \\ &= -2.44 \text{ kcal/gram of stoichiometric mixture (obtained by dividing} \\ &\quad -576.2 \text{ kcal by } 138.6 + 97.2 = 235.8 \text{ grams of starting material)} \end{aligned}$$

TABLE 2.10
Standard Heats of Formation at 25°C

Compound	Formula	ΔH_f (kcal/mole) ^a
Oxidizers		
Ammonium nitrate	NH_4NO_3	-87.4
Ammonium perchlorate	NH_4ClO_4	-70.58
Barium chlorate (hydrate)	$\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$	-184.4
Barium chromate	BaCrO_4	-345.6
Barium nitrate	$\text{Ba}(\text{NO}_3)_2$	-237.1
Barium peroxide	BaO_2	-151.6
Iron oxide (red)	Fe_2O_3	-197.0
Iron oxide (black)	Fe_3O_4	-267.3
Lead chromate	PbCrO_4	-217.7 ^b
Lead oxide (red lead)	Pb_3O_4	-171.7
Lead peroxide	PbO_2	-66.3
Potassium chlorate	KClO_3	-95.1
Potassium nitrate	KNO_3	-118.2
Potassium perchlorate	KClO_4	-103.4
Sodium nitrate	NaNO_3	-111.8
Strontium nitrate	$\text{Sr}(\text{NO}_3)_2$	-233.8
Fuels		
Elements		
Aluminum	Al	0
Boron	B	0
Iron	Fe	0
Magnesium	Mg	0
Phosphorous (red)	P	-4.2
Silicon	Si	0
Titanium	Ti	0
Organic Compounds^c		
Lactose (hydrate)	$\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$	-651
Shellac	$\text{C}_{16}\text{H}_{24}\text{O}_5$	-227
Hexachloroethane	C_2Cl_6	-54
Starch (polymer)	$(\text{C}_6\text{H}_{10}\text{O}_5)_n$	-227 (per unit)
Anthracene	$\text{C}_{14}\text{H}_{10}$	+32
Polyvinyl chloride (PVC)	$(-\text{CH}_2\text{CHCl}-)_n$	-23 (per unit) ^b
Reaction Products		
Aluminum oxide	Al_2O_3	-400.5
Barium oxide	BaO	-133.4
Boron oxide	B_2O_3	-304.2
Carbon dioxide	CO_2	-94.1
Carbon monoxide	CO	-26.4

TABLE 2.10 (CONTINUED)
Standard Heats of Formation at 25°C

Compound	Formula	ΔH_f (kcal/mole) ^a
Chromium oxide	Cr ₂ O ₃	-272.4
Lead oxide (litharge)	PbO	-51.5
Magnesium oxide	MgO	-143.8
Nitrogen	N ₂	0
Phosphoric acid	H ₃ PO ₄	-305.7
Potassium carbonate	K ₂ CO ₃	-275.1
Potassium chloride	KCl	-104.4
Potassium oxide	K ₂ O	-86.4
Potassium sulfide	K ₂ S	-91.0
Silicon dioxide	SiO ₂	-215.9
Sodium chloride	NaCl	-98.3
Sodium oxide	Na ₂ O	-99.0
Strontium oxide	SrO	-141.5
Titanium dioxide	TiO ₂	-225
Water	H ₂ O	-68.3
Zinc chloride	ZnCl ₂	-99.2

^a R. C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, 75th ed., CRC Press, Boca Raton, FL, 1994.

^b U.S. Army Material Command, *Engineering Design Handbook: Properties of Materials Used in Pyrotechnic Compositions*, Military Pyrotechnics Series, Part Three, Washington, DC, 1863 (AMC Pamphlet 706-187).

^c A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Moscow, 1964. (Translated as Report FTD-HC-23-1704-74 by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)

Example 2

Reaction	4 KNO₃	+	5 C	→	2 K₂O	+	2 N₂	+	5 CO₂
Grams	404.4		60		188.4		56		220
Heat of formation	4(-118.2)		5(0)		2(-86.4)		2(0)		5(-94.1)

$$\begin{aligned}
 \Delta H(\text{reaction}) &= \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants}) \\
 &= [2(-86.4) + 0 + 5(-94.1)] - [4(-118.2) + 5(0)] \\
 &= -643.3 - (-472.8) \\
 &= -170.5 \text{ kcal/equation as written (4 moles KNO}_3\text{)} \\
 &= -42.6 \text{ kcal/mole KNO}_3 \\
 &= -0.37 \text{ kcal/gram of stoichiometric mixture} \\
 &\quad (-170.5 \text{ kcal per 464.4 grams})
 \end{aligned}$$

RATES OF CHEMICAL REACTIONS

The preceding section discussed how the chemist can make a thermodynamic determination of the spontaneity of a chemical reaction. However, even if these calculations indicate that a reaction should be quite spontaneous (the value for ΔG is a large, negative number), there is no guarantee that the reaction will proceed rapidly when the reactants are mixed together at 25°C (298 K). For example, the reaction



has a large, negative value for ΔG at 25°C. However (fortunately), wood and oxygen are reasonably stable when mixed together at 25°C (a typical room temperature). The explanation of this thermodynamic mystery lies in another energy concept known as the *energy of activation*. This term represents the amount of energy needed to take the starting materials from their reasonably stable form at 25°C and convert them to a reactive, higher-energy excited state. In this excited state, a reaction will occur to form the anticipated products, with the liberation of considerable energy—all the energy that was required to reach the excited state plus considerably more, which will be the *net* heat of reaction. Figure 2.1 illustrates the process.

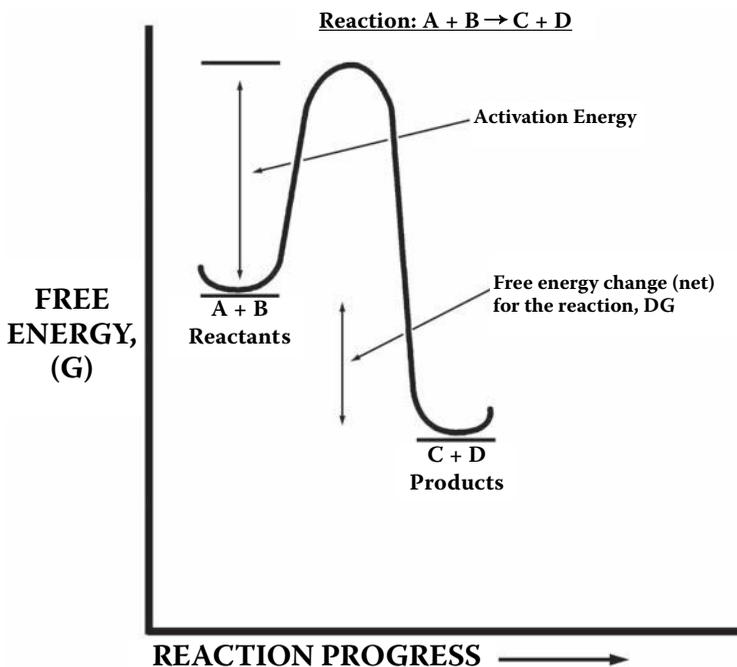


FIGURE 2.3 The free energy, G , of a chemical system as reactants A and B convert to products C and D. A and B must first acquire sufficient energy (activation energy) to be in a reactive state. As products C and D are formed, energy is released and the final energy level is reached. The *net* energy change, ΔG , corresponds to the difference between the energies of the products and reactants. The *rate* at which a reaction proceeds is determined by the energy barrier that must be crossed—the activation energy.

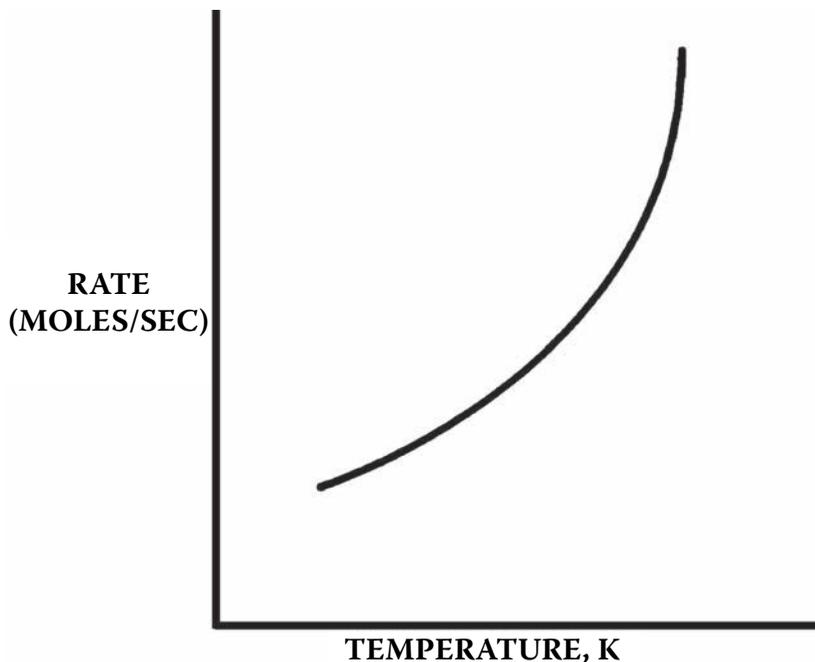


FIGURE 2.4 The effect of temperature on reaction rate. As the temperature of a chemical system is increased, the rate at which that system reacts to form products increases exponentially.

The rate of a chemical reaction is determined by the magnitude of this required activation energy, and rate is a temperature-dependent phenomenon. As the temperature of a system is raised, an exponentially greater number of molecules will possess the necessary energy of activation. The reaction rate will therefore increase accordingly in an exponential fashion as the temperature rises. This is illustrated in Figure 2.4. Much of the pioneering work in this area of reaction rates was done by the Swedish chemist Svante Arrhenius, and the equation describing this rate-temperature relationship is known as the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (2.16)$$

where:

k = the rate constant for a particular reaction at temperature T (this is a constant representing the speed of the reaction, and is determined experimentally)

A = a temperature-independent constant for the particular reaction, termed the preexponential factor

E_a = the activation energy for the reaction

R = a universal constant known as the ideal gas constant

T = temperature, in Kelvin

If the natural logarithm (\ln) of both sides of Equation (2.3) is taken, one obtains:

$$\ln k = \ln A - E_a/RT \quad (2.17)$$

Therefore, if the rate constant, k , is measured at several temperatures and $\ln k$ vs. $1/T$ is plotted, a straight line should be obtained, with slope of $-E_a/R$. Activation energies can be obtained for chemical reactions through such experiments. The Arrhenius equation, describing the rate-temperature relationship, is of considerable significance in the processes leading to the ignition of pyrotechnics and explosives, and it will be referred to in subsequent chapters.

One other significant point that can be gleaned from the rate-temperature relationship is the fact that warm energetic materials (propellants and pyrotechnics in particular) will have a lower energy of activation hill to climb to undergo ignition than cold energetic materials, and therefore warm compositions will ignite easier and exhibit faster burn rates upon ignition. Numerous studies over the years have demonstrated this phenomenon. The ambient temperature for materials from rocket propellant to highway flares will affect their performance, and this must be considered when comparing performance tests that have been run under different temperature conditions.

ENERGY-RICH BONDS

Certain covalent chemical bonds (such as N–O and Cl–O) are frequently encountered in the high-energy field. Bonds between two highly electronegative atoms tend to be less stable than ones between atoms of differing electronegativity. The intense competition for the electron density in a bond such as Cl–O is believed to be responsible for at least some of this instability. A modern chemical bonding theory known as the molecular orbital theory predicts inherent instability for some common high-energy species. The azide ion, N_3^- , and the fulminate (or isocyanate) ion, NCO^- , are examples of species whose unstable behavior is explainable using this approach.⁴

In structures such as the nitrate ion, NO_3^- , and the perchlorate ion, ClO_4^- , a highly electronegative atom has a large, positive oxidation number (+5 for N in NO_3^- , +7 for Cl in ClO_4^-). Such large positive numbers indicate electron deficiency. It is therefore not surprising that structures with such bonding arrangements are particularly reactive as electron acceptors (oxidizers). It is for similar reasons that many of the nitrated carbon-containing (organic) compounds, such as nitroglycerine and TNT, are so unstable (Figure 2.5). The nitrogen atoms in these molecules want to accept electrons to relieve bonding stress, and the carbon atoms found in the same molecules are excellent electron donors.

In addition, if you assign partial charges to the atoms in many of these molecules, using Pauling's electronegativity concept, you wind up with many situations where adjacent carbon atoms bear partial positive charges. This has a destabilizing, bond-weakening effect on the molecular structure that is often reflected in causing the molecule to decompose at lower temperature or be more shock sensitive. Nitroglycerine (Figure 2.5) is a good example—the three carbon atoms all possess partial positive charges due to the presence of a highly electronegative nitrate group on each carbon. The adjacent positively charged carbons will have a repelling effect on each other, thereby explaining—at least in part—the extremely sensitive nature of nitroglycerine to impact and shock.

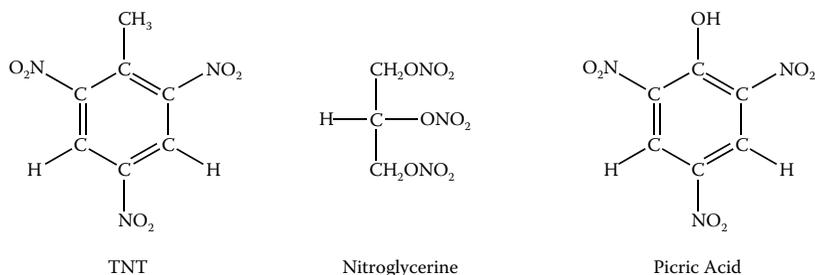


FIGURE 2.5 Many unstable organic compounds are used as explosives. These molecules contain internal oxygen, usually bonded to nitrogen, and undergo intramolecular oxidation-reduction to form stable products—carbon dioxide, nitrogen, and water. The mixing of oxidizer and fuel is achieved at the molecular level, and *fast* rates of decomposition can be obtained.

Two very stable gaseous (high-entropy) chemical species, N₂ and CO₂, are produced upon the decomposition reaction of most nitrated carbon-containing compounds, helping to ensure a large, negative value for ΔG for the process (therefore making it spontaneous). These considerations make it mandatory that anyone working with nitrogen-rich carbon-containing compounds or with nitrate, perchlorate, and similar oxygen-rich negative ions must use extreme caution in the handling of these materials until their properties have been fully examined in the laboratory. Elevated temperatures should also be avoided when working with potentially unstable materials, because of the rate-temperature relationship that is exponential in nature. A nonexistent or sluggish process can become an explosion when the temperature of the system is sharply increased.

STATES OF MATTER

With few exceptions, the high-energy chemist deals with materials that are in the solid state at normal room temperature. This provides for dimensional stability when the materials are loaded into end items, and this is very helpful in ensuring long storage lifetimes for energetic devices. Solids mix very slowly with one another, and hence they tend to be more sluggish in their reactivity than mixtures of gases, where a homogeneous state can be reached very quickly. Liquids also reach a homogeneous state quickly, provided the liquids are miscible. Rapid reactivity with solid systems is usually associated with the formation, at higher temperatures, of liquid or gas states. Species in these states can diffuse into one another more rapidly, leading to accelerated reactivity.

In pyrotechnics, the solid-to-liquid transition appears to be of considerable importance in initiating a self-propagating reaction in many systems. The oxidizing agent is frequently the key component in such mixtures, and a ranking of common oxidizers by increasing melting point bears a striking resemblance to the reactivity sequence for these materials (Table 2.11). The other significant factor here is that many of the common oxidizers used in pyrotechnics begin to undergo decomposition with the

TABLE 2.11
Melting Points of Some Common Oxidizers

Oxidizer	Formula	Melting Point, °C ^a
Potassium nitrate	KNO ₃	334
Potassium chlorate	KClO ₄	356
Barium nitrate	Ba(NO ₃) ₂	592
Potassium perchlorate	KClO ₄	610
Strontium nitrate	Sr(NO ₃) ₂	570
Lead chromate	PbCrO ₄	844
Iron oxide	Fe ₂ O ₃	1,565

^a R. C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, 75th ed., Boca Raton, FL: CRC Press, 1994.

evolution of oxygen gas as they approach their melting point, and thereby facilitate the ignition process; this will be discussed in more detail in Chapter 5.

A change of state also involves an energy change. Going from solid to liquid, or liquid to gas, normally requires a net input of energy into a system. Both the liquid state and the solid state are held together by attractive forces between the atoms, molecules, or ions making up the material. These attractive forces must be broken or weakened to go from solid to liquid, and must be completely overcome for the liquid state to convert to vapor. The reverse of these directions (i.e., water vapor condensing to liquid water) is associated with an exothermic process, as the attractive forces interact and release energy.

While a phase change is under way, a system will remain at constant temperature (e.g., the melting of ice at 0°C and 1 atm pressure, or the boiling of water at 100°C and 1 atm pressure). This is a very significant factor in the ignition process for an energetic material, since no temperature rise will occur while a phase change is under way. Hence, water-wet pyrotechnic composition (or wet wood in your fireplace) cannot get warmer than 100°C (212°F) until all of the water present has been driven off. If the ignition temperature of the material exceeds this temperature, ignition will not occur until the water has been removed and the temperature of the material rises to its ignition point. For the wood in your fireplace, the ignition temperature is near the infamous value of Fahrenheit 451, the ignition temperature of cellulose/paper made famous by Ray Bradbury in the book of that title.

GASES

On continued heating, a pure material passes from the solid to liquid to vapor state, with continued absorption of heat. The volume occupied by the vapor is much greater than that of the solid and liquid phases. One mole (18 grams) of water occupies approximately 18 milliliters (0.018 liters) as a solid or liquid. One mole of water vapor, however, at 100°C (373 K) occupies approximately 30.6 liters at normal atmospheric

pressure. The volume occupied by a gas can be estimated using the *ideal gas equation* (Equation [2.18]).

$$V = nRT/P \quad (2.18)$$

where:

V = volume occupied by the gas, in liters

n = number of moles of gas

R = a constant, 0.0821 liter-atm/deg-mole

T = temperature, in K

P = pressure, in atmospheres

This equation is obeyed quite well by the inert gases (helium, neon, etc.) and by small diatomic molecules such as H₂ and N₂. Molecules possessing polar covalent bonds tend to have strong intermolecular attractions and usually deviate from ideal behavior—producing lower than expected pressures for a specified temperature. Equation (2.18) remains a fairly good estimate of volume and pressure even for these polar molecules, however. Using the ideal gas equation, one can readily estimate the pressure produced during ignition of a confined high-energy composition.

For example, assume that 200 milligrams (0.200 grams) of black powder is confined in a volume of 0.1 milliliter. Black powder burns to produce approximately 50% gaseous products and 50% solids. Approximately 1.2 moles of permanent gas is produced per 100 grams of powder burned (the gases are mainly N₂, CO₂, and CO).⁵ Therefore, 0.200 grams should produce 0.0024 moles of gas, at a temperature near 2,000 K. The expected pressure is

$$P = \frac{(0.0024 \text{ mole})(0.0821 \text{ liter} - \text{atm/deg} - \text{mole})(2000 \text{ deg K})}{(0.0001 \text{ liter})} = 3941 \text{ atm!}$$

Needless to say, the casing will rupture and an explosion will be observed. Burning a similar quantity of a good quality black powder in the open, where little pressure accumulation occurs, will produce a slower, less violent (but still quite vigorous) reaction and no explosive effect. This significant dependence of burning behavior on degree of confinement is an important characteristic of pyrotechnic mixtures, and distinguishes them from true high explosives, where confinement plays a relatively minor role in determining detonation velocity.

LIQUIDS

Gas molecules are widely separated, traveling at high speeds while colliding with other gas molecules and with the walls of their container. Pressure is produced by these collisions with the walls and depends upon the number of gas molecules present as well as their kinetic energy. Their speed, and therefore their kinetic energy, increases with increasing temperature.

As the temperature of a gas system is lowered, the speed of the molecules decreases. When these lower-speed molecules collide with one another, attractive forces between the molecules become more significant, and a temperature will be

reached where *condensation* occurs—the vapor state converts to liquid. Dipole–dipole attractive forces are most important in causing condensation, and the molecules with substantial partial charges, resulting from polar covalent bonds, typically have high condensation temperatures. (Condensation temperature will be the same as the boiling point of a liquid, approached from the opposite direction.)

The liquid state has a minimum of order, and the molecules have considerable freedom of motion. A drop of food coloring placed in water demonstrates the rapid diffusion that can occur in the liquid state. The solid state will exhibit no detectable diffusion. If this experiment is tried with a material such as iron, the liquid food coloring will merely form a drop on the surface of the metal.

At the liquid surface, molecules can acquire high vibrational and translational energy from their neighbors, and one will occasionally break loose to enter the vapor state. This phenomenon of vapor above a liquid surface is termed vapor pressure, and will lead to gradual evaporation of a liquid unless the container is covered. In this case, an *equilibrium* is established between the molecules entering the vapor state per minute and the molecules recondensing on the liquid surface. The pressure of gas molecules above a liquid in a confined system (such as a half-empty water bottle with the cap on) is a constant for a given material at a given temperature, and is known as the *equilibrium vapor pressure*. It increases exponentially with increasing temperature. When the vapor pressure of a liquid is equal to the external pressure acting on the liquid surface, boiling occurs. For solids and liquids to undergo sustained burning, the presence of a portion of the fuel in the vapor state is required.

THE SOLID STATE

The solid state is characterized by definite structure and volume. The observed structure will be the one that maximizes favorable interactions between the atoms, ions, or molecules making up the solid state. The preferred packing arrangement begins at the atomic or molecular level and is regularly repeated throughout the solid, producing a highly symmetrical, three-dimensional form called a *crystal*. The network produced is termed the *crystalline lattice*.

Solids lacking an ordered, crystalline arrangement are termed *amorphous* materials, and resemble rigid liquids in structure and properties. Glass (SiO_2) is the classic example of an amorphous solid. Such materials typically soften on heating, rather than showing a sharp melting point.

In the crystalline solid state, there is little vibrational or transitional freedom, and hence diffusion into a crystalline lattice is slow and difficult. As the temperature of a solid is raised by the input of heat, vibrational and transitional motion increases. At a particular temperature—termed the melting point—this motion overcomes the attractive forces holding the lattice together and the liquid state is produced. The liquid state, on cooling, returns to the solid state as crystallization occurs and heat is released by the formation of strong attractive forces.

The types of solids, categorized according to the particles that make up the crystalline lattice, are listed in Table 2.12.

TABLE 2.12
Types of Crystalline Solids

Type of Solid	Units Comprising Crystal Lattice	Attractive Force	Examples
Ionic	Positive and negative ions	Electrostatic attraction	KNO ₃ , NaCl
Molecular	Neutron molecules	Dipole–dipole attractions, plus weaker, nonpolar forces	CO ₂ (dry ice), sugar
Covalent	Atoms	Covalent bonds	Diamond (carbon)
Metallic	Metal atoms	Dispersed electrons attracted to numerous metal atom nuclei	Fe, Al, Mg

The type of crystalline lattice formed by a solid material depends on the size and shape of the lattice units, as well as on the nature of the attractive forces. Six basic crystalline systems are possible:⁷

1. Cubic: Three axes of equal length, intersecting at all right angles.
2. Tetragonal: Three axes intersecting at right angles; only two axes are equal in length.
3. Hexagonal: Three axes of equal length in a single plane intersecting at 60° angles; a fourth axis of different length is perpendicular to the plane of the other three.
4. Rhombic: Three axes of unequal length, intersecting at right angles.
5. Monoclinic: Three axes of unequal length, two of which intersect at right angles.
6. Triclinic: Three axes of unequal length, none of which intersect at right angles.

To this point, our model of the solid state has suggested a placement of every lattice object at the proper site in order to create a perfect three-dimensional crystal. Research into the actual structure of solids has shown that crystals are far from perfect, containing a variety of types of defects. Even the purest crystals modern chemistry can create contain large numbers of impurities and “misplaced” ions, molecules, or atoms in the lattice. These inherent defects can play an important role in the reactivity of solids by providing a mechanism for the transport of electrons and heat through the lattice. They also can greatly enhance the ability of another substance to diffuse into the lattice, thereby again affecting reactivity.⁸

A commonly observed phenomenon associated with the presence of impurities in a crystalline lattice is a depression in the melting point of the solid, with the solid → liquid transition occurring over a broad range rather than displaying the sharp melting point at higher temperature that is observed with a purer material. Melting behavior thereby provides a convenient means of checking the purity of solids, a property that can be quite useful to quality assurance laboratories examining incoming shipments of chemicals for use in manufacturing energetic mixtures.

TABLE 2.13
Thermal Conductivity Values for Solids

Material	Thermal Conductivity ($\times 10^3$), cal/s-cm- $^{\circ}$ C
Copper	910
Aluminum	500
Iron	150
Glass	2.3
Oak wood	0.4
Paper	0.3
Charcoal	0.2

Source: R. L. Tuve, *Principles of Fire Protection Chemistry*, Boston: National Fire Protection Association, 1976.

An important factor in the ignition and propagation of burning of pyrotechnic compositions is the conduction of heat along a column of the mixture. Hot gases serve as excellent heat carriers and can be a significant burn rate factor in porous compositions, but frequently the heat must be conducted by the solid state, ahead of the reaction zone. Heat can be transferred by molecular motion as well as by free, mobile electrons.⁷ The thermal conductivity values of some common materials are given in Table 2.13. Examining this table, one can readily see how the presence of a small quantity of metal powder in a pyrotechnic composition can greatly increase the thermal conductivity of the mixture, and thereby increase the burning rate by preheating the column of burning material ahead of the actual reaction zone.

ACIDS AND BASES

An *acid* is commonly described as a molecule or ion that can serve as a hydrogen ion (H^+) donor. The hydrogen ion is identical to the proton—it contains one proton in the nucleus and has no electrons surrounding the nucleus. H^+ is a light, mobile, reactive species. A *base* is a species that functions as a hydrogen ion acceptor. The transfer of a hydrogen ion (proton) from a good donor to a good acceptor is called an *acid-base reaction*. Materials that are neither acidic nor basic in nature are said to be *neutral*.

Hydrogen chloride (HCl) is a gas that readily dissolves in water. In water, HCl is called *hydrochloric acid* and the HCl molecule serves as a good proton donor, readily undergoing the reaction



to produce a hydrogen ion and a chloride ion in solution. The concentration of hydrogen ions in water can be measured by a variety of methods and provides a measure of

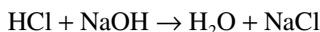
the acidity of an aqueous system. The most common measure of acidity is pH, a number representing the negative common logarithm of the hydrogen ion concentration:

$$\text{pH} = -\log [\text{H}^+] \quad (2.19)$$

If a solution also contains hydroxide ion (OH^-), a good proton acceptor, the reaction



occurs, forming water—a neutral species. The overall reaction is represented by an equation such as

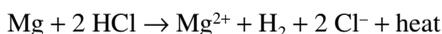


Acids usually contain a bond between hydrogen and an electronegative element such as F, O, or Cl. The electronegative element pulls electron density away from the hydrogen atom, giving it a partial positive character and making it willing to leave as H^+ . The presence of additional F, O, and Cl atoms in the molecule further enhances the acidity of the species. Examples of strong acids include sulfuric acid (H_2SO_4), hydrochloric acid (HCl), perchloric acid (HClO_4), and nitric acid (HNO_3).

Most of the common bases are ionic compounds consisting of a positive metal ion and the negatively charged hydroxide ion, OH^- . Examples include sodium hydroxide (NaOH), potassium hydroxide (KOH), and calcium hydroxide, $\text{Ca}(\text{OH})_2$. Ammonia (NH_3) is a weak base, capable of reacting with H^+ to form the ammonium ion, NH_4^+ .

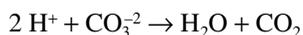
Acids catalyze a variety of chemical reactions, even when present in small quantity. The presence of trace amounts of acidic materials in many high-energy compounds and mixtures can lead to instability. The chlorate ion, ClO_3^- , is notoriously unstable in the presence of strong acids. Chlorate-containing pyrotechnic mixtures will usually ignite if a drop of concentrated sulfuric acid is added.

Many metals are also vulnerable to acids, undergoing an oxidation-reduction reaction that produces the metal ion and hydrogen gas. The balanced equation for the reaction between HCl and magnesium is



Consequently, most metal-containing compositions must be free of acidic impurities, or extensive decomposition (and possibly ignition) may occur.

As protection against acidic impurities, high-energy mixtures will frequently contain a small percentage of a neutralizer. Sodium bicarbonate (NaHCO_3) and magnesium carbonate (MgCO_3) are two frequently used materials. The carbonate ion, CO_3^{2-} , reacts with H^+ ,



to form two neutral species: water and carbon dioxide.

Boric acid (H_3BO_3)—a solid material that is a weak H^+ donor—is sometimes used as a neutralizer for base-sensitive compositions. Mixtures containing aluminum metal and a nitrate salt are notably sensitive to excess hydroxide ion, and a small percentage of boric acid can be quite effective in stabilizing such compositions.

INSTRUMENTAL ANALYSIS

Modern instrumental methods of analysis have provided scientists with a wealth of information regarding the nature of the solid state and the reactivity of solids. Knowledge of the structure of solids and an ability to study thermal behavior are essential to an understanding of the ignition behavior of high-energy materials.

X-ray crystallography has provided the crystal type and lattice dimensions for numerous solids. In this technique, high-energy x-rays strike the crystal and are diffracted in a pattern characteristic of the particular lattice type. Complex mathematical analysis can convert the diffraction pattern to the actual crystal structure. Advances in computer technology have revolutionized this field in the past few years. Complex structures, formerly requiring months or years to determine, can now be analyzed in short order. Even huge protein and nucleic acid chains can be worked out by the crystallographer.¹⁰

Thermal analysis, using either differential thermal analysis (DTA) or differential scanning calorimetry (DSC), has provided a wealth of information regarding the thermal behavior of pure solids as well as solid mixtures.¹¹ DSC has emerged as the principal technique of thermal analysis over the past several decades, although the information obtained from the two methods is quite similar. Melting points, boiling points, transitions from one crystalline form to another, and decomposition temperatures can be obtained for pure materials. Reaction temperatures can be determined via DSC for mixtures, such as ignition temperatures for pyrotechnic and explosive compositions. Thermal gravimetry (TG) monitors the weight of a sample on heating and can detect temperatures where samples lose weight through evaporation or gas evolution, or gain weight through air oxidation. When gases are evolved in such studies, they can be directly fed into a mass spectrometer or infrared spectrophotometer, and their identities can be determined to provide additional information about a material's behavior upon heating.

DSC detects the absorption or release of heat by a sample as it is heated at a constant rate from room temperature to an upper limit, commonly 500°C . Any heat-absorbing changes occurring in the sample (e.g., melting or boiling) will be detected, as will processes that evolve heat (e.g., exothermic reactions). These changes are detected by continually comparing the temperature of the sample with that of a thermally inert reference material—often an empty sample holder—that undergoes no phase changes or reactions over the temperature range being studied. Both sample and reference are placed in contact with thermocouples and heated at a constant rate. Current is applied to the electric heater to produce a linear temperature increase (typically 10 to 50 degrees/minute).⁸

If an endothermic (heat-absorbing) process occurs, the sample will momentarily become cooler than the reference material; the small temperature difference is detected by the pair of thermocouples and a deflection, termed an *endotherm*, is

produced in the plot of ΔT (temperature difference between sample and reference) versus T (temperature of the heating block). Evolution of heat by the sample will similarly produce a deflection in the opposite direction, termed an *exotherm*. The printed output produced by the instrument, a *thermogram*, is a thermal fingerprint of the material being analyzed. Thermal analysis is quite useful for determining the purity of materials; this is accomplished by examining the location and sharpness of the melting point. DSC is also useful for qualitative identification of solid materials, by comparing the thermal pattern with those of known materials. Reaction temperatures, including the ignition temperatures of high-energy materials, can be quickly (and safely) measured by thermal analysis. These temperatures will correspond to conditions of rapid heating of a confined sample, and must be recognized as such. A variety of other types of analysis, such as accelerated aging, can also be performed with thermal analysis technology.¹¹

Our understanding of the ignition phenomenon has been greatly enhanced by the use of thermal analysis to examine energetic mixtures. Analysis of the thermograms of numerous pyrotechnic mixtures has indicated that the thermal activation of one or more of the components of the mixture is required for ignition to occur. Mobility—the ability for one component to intimately mix with another—is important; oxidizer and fuel must be in intimate contact for a rapid reaction to ensue. Melting, boiling, and decomposition temperatures are therefore quite important to the ignition process. Melting exposes fresh, reactive surfaces and creates the fluid, liquid state. Intimate mixing is facilitated by melting, while vaporization allows mixing to occur at an even faster rate. We will return to this topic in Chapter 5.

The advantages of using thermal analysis to study energetic materials begin with the fact that very small sample sizes (1 mg or so) can be studied. If a material should ignite upon heating during a run, there should be no damage to the instrument. In addition, no pretreatment of the sample is typically required—it can be a powder, a slurry, a particle, or a granule.

The possible applications of thermal analysis instrumentation in energetic materials include:

1. The qualitative identification of materials and components in mixtures by solid–solid phase transition temperatures and melting points.
2. Purity determination of chemicals (quality control) by the location and sharpness of melting points determined by the use of a DSC.
3. Investigation of the ignition process for energetic mixtures—comparison of the ignition temperature to phase transitions and decomposition temperatures in the components.
4. The coupling of DSC with thermogravimetric methods to compare data by the two methods and correlate peaks in the DSC thermogram with weight gain or weight loss by TG. Gas output in TG studies can also be analyzed by other analytical methods (mass spectrometry or infrared spectroscopy) to identify gases that are evolved in the TG study.

Some representative thermograms of high-energy materials are shown in Figures 2.6 to 2.8 and 5.2 to 5.6.

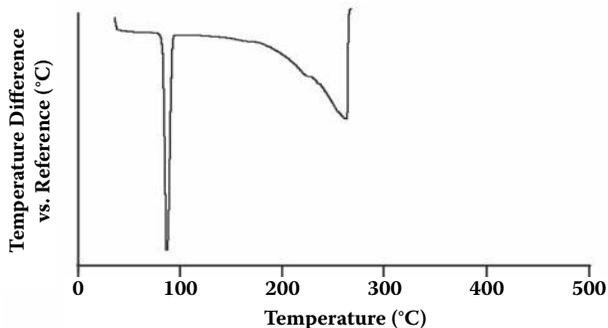


FIGURE 2.6 The differential thermal analysis (DTA) thermogram for pure 2,4,6-trinitrotoluene (TNT). The major features are an endotherm corresponding to melting at 81°C and an exothermic decomposition peak beginning near 280°C (the apparent endotherm beginning after 200°C is from the initial endothermic decomposition of the TNT sample). The x-axis represents the temperature of the heating block in degrees centigrade. The y-axis indicates the difference in temperature, ΔT , between the sample and an identically heated reference solid, typically glass beads or aluminum oxide: the reference solid only gets hot in line with the warming heating block, while the pyrotechnic composition will be cooler than the reference if melting or undergoing another endothermic change, and will be hotter than the reference upon combustion.

LIGHT EMISSION

The pyrotechnic phenomena of heat, smoke, noise, and motion are reasonably easy to comprehend. Heat results from the rapid release of energy associated with the formation of stable chemical bonds during a chemical reaction. Smoke is produced by the dispersion of many small particles during a chemical reaction. Noise is produced by the rapid generation of gas at high temperature, creating waves that travel through air at, or greater than, the speed of sound, 340 meters/second. Motion can be produced if you direct the

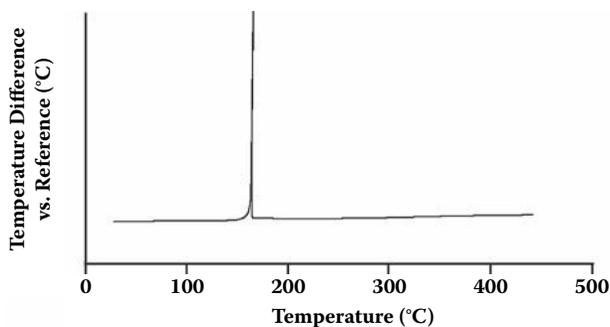


FIGURE 2.7 The differential scanning calorimetry (DSC) thermogram for pure nitrocellulose. The major feature is an exotherm corresponding to decomposition of the nitrocellulose near 160°C–170°C.

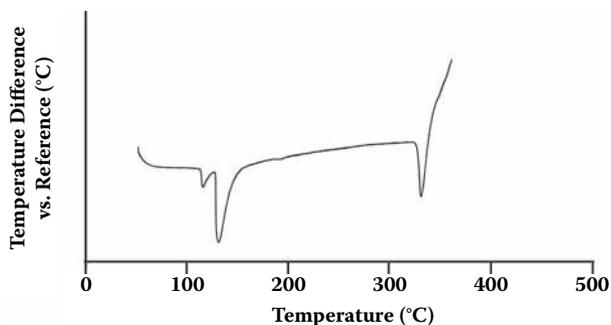


FIGURE 2.8 Black powder was the first modern high-energy mixture, and it is still used in a variety of pyrotechnic applications. It is an intimate blend of potassium nitrate (75%), charcoal (15%), and sulfur (10%). The thermogram for the mixture shows an endotherm between 105 and 119°C, corresponding to a solid–solid phase transition and melting for sulfur (two endotherms overlap into one); a strong endotherm near 130°C representing a solid–solid transition in potassium nitrate; and a final strong endotherm near 330°C representing potassium nitrate melting followed immediately by a violent exotherm where ignition of the mixture occurs.

hot gaseous products of a pyrotechnic reaction through an exit, or nozzle. The thrust that is produced can move an object of considerable mass, if sufficient propellant is used.

The theory of color and light production, however, involves the energy levels available for electrons in atoms and molecules, according to the beliefs of modern chemical theory. In an atom or molecule, there are a number of orbitals or energy levels that an electron may occupy. Each of these levels corresponds to a discrete energy value, and *only* these energies are possible. The energy is said to be *quantized*, or restricted to certain values that depend on the nature of the particular atom or molecule. We can represent these allowed electronic energies by a diagram such as Figure 2.9.

Logic suggests that an electron will occupy the lowest energy level available, and electrons will successively fill these levels as they are added to an atom or molecule. Quantum mechanics restricts all orbitals to a maximum of two electrons (these two have opposite spins and do not strongly repel one another), and hence a filling process occurs. The filling pattern for the sodium atom (sodium is atomic number 11; therefore, there will be eleven electrons in the neutral atom) is shown in Figure 2.9.

When energy is put into a sodium atom, in the form of heat or light, one means of accepting this energy is for an electron to be “promoted” to a higher energy level. The electron in this excited state is unstable, and it will tend to quickly return to the ground state with the release of an amount of energy exactly equal to the energy difference between the ground and excited states. For the sodium atom, the difference between the highest-occupied and lowest-unoccupied levels is 3.38×10^{-19} joules/atom. This energy can be lost as heat upon return to the ground state, or it can be released as a unit, or photon, of light.

Light, or electromagnetic radiation, has both wave and particle or unit character associated with its behavior. Wavelengths range from very short (10^{-12} meters) for the gamma rays that accompany nuclear decay to quite long (10 meters) for radio waves.

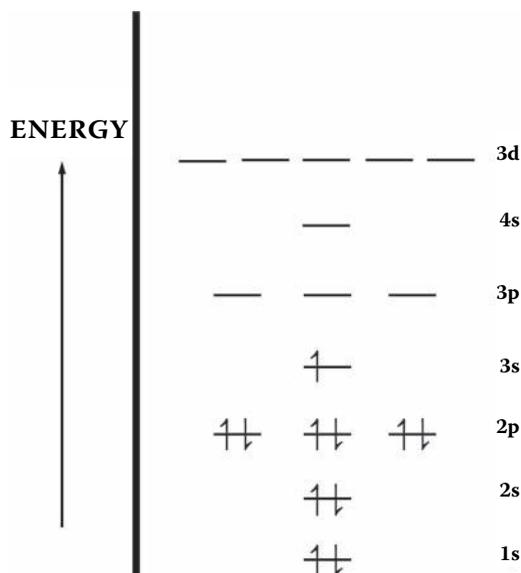


FIGURE 2.9 The energy levels of the sodium atom. The sodium atom contains eleven electrons. These electrons will successively fill the lowest available energy levels in the atom, with a maximum population of two electrons in any given orbital. The experimentally determined energy level sequence is shown in this figure, with the eleventh (and highest-energy) electron places in the 3s level. The lowest vacant level is a 3p orbital. To raise an electron from the 3s to the 3p level requires 3.38×10^{-19} joules of energy. This energy corresponds to light of 589-nanometer wavelength—the yellow portion of the visible spectrum. Sodium atoms heated to high temperature will *emit* this yellow light as electrons are thermally excited to the 3p level, and then return to the 3s level and give off the excess energy as yellow light.

All light travels at the same speed in a vacuum, with a value of 3×10^8 meters/second—the speed of light. This value can be used for the speed of light in air as well.

The wavelength of light can now be related to the frequency, or number of waves passing a given point per second, using the speed of light value:

$$\text{frequency } (\nu) = \frac{\text{speed } (c)}{\text{wavelength } (\lambda)}$$

$$(\text{waves/second}) = \frac{(\text{meters/second})}{(\text{meters/wave})}$$

The entire range of wavelengths comprising light is known as the *electromagnetic spectrum*, as shown in Figure 2.10.

We can readily tell that the light is a form of energy by staying out in the sun for too long at a time. Elegant experiments by Einstein and others clearly showed that the energy associated with light was directly proportional to the frequency of the radiation:

$$E = h(\nu) = h(c/\lambda) \quad (2.20)$$

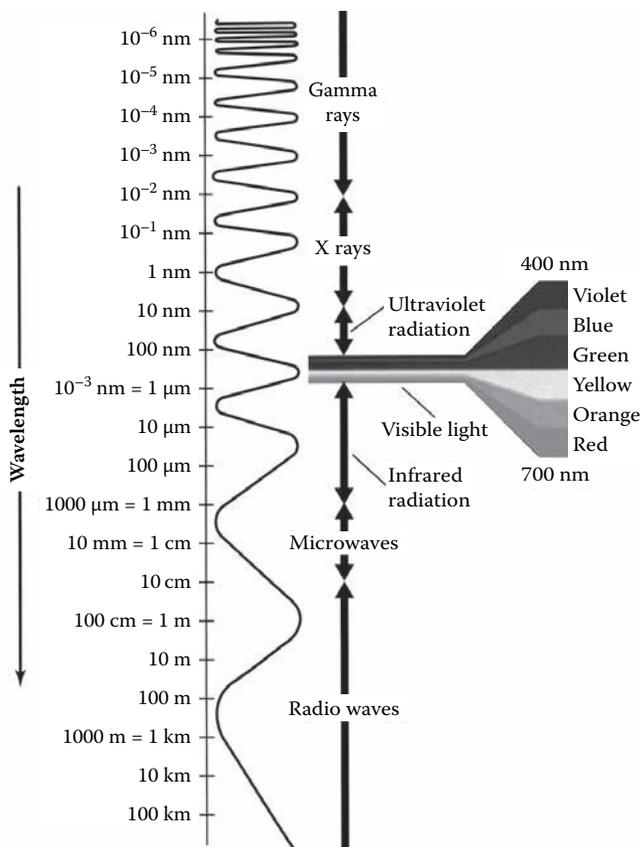


FIGURE 2.10 The electromagnetic spectrum. The various regions of the electromagnetic spectrum correspond to a wide range of wavelengths, frequencies, and energies. As wavelength decreases, energy increases, and vice versa. The radio frequency range is at the long-wavelength, low-energy end, with gamma rays at the short-wavelength, high-frequency, high-energy end. The visible region—that portion of the spectrum perceived as color by the human visual system—falls in the narrow region from 380 to 780 nanometers ($1 \text{ nm} = 10^{-9} \text{ m}$).

where:

E = the energy per light particle (photon)

h = a constant, Planck's constant, 6.63×10^{-34} joule-seconds

ν = frequency of light (in waves—cycles—per second)

c = speed of light (3×10^8 meters/second)

λ = wavelength of light (in meters)

This equation permits one to equate a wavelength of light with the energy associated with a photon of that particular radiation. For the sodium atom, the wavelength of light corresponding to the energy difference of 3.38×10^{-19} joules between the highest-occupied and lowest-unoccupied electronic energy levels should be

$$E = h(c/\lambda)$$

rearranging:

$$\begin{aligned}\lambda &= h(c/E) \\ &= \frac{(6.63 \times 10^{-34} \text{ J-sec})(3 \times 10^8 \text{ m/sec})}{(3.38 \times 10^{-19} \text{ J})} \\ &= 5.89 \times 10^{-7} \text{ meters} \\ &= 589 \text{ nm (where } 1 \text{ nm} = 10^{-9} \text{ meters)}\end{aligned}$$

Light of a wavelength of 589 nanometers falls in the yellow-orange portion of the *visible* region of the electromagnetic spectrum. The characteristic yellow-orange glow of sodium vapor lamps used to illuminate many highways results from this particular emission.

To produce this type of atomic emission in a pyrotechnic system, one must produce sufficient heat to generate atomic vapor in the flame, and then excite the atoms from the ground to various possible excited electronic states. Emission intensity will increase as the flame temperature increases, as more and more atoms are vaporized and excited. Return of the atoms to their ground state produces the light emission. A pattern of wavelengths, known as an *atomic spectrum*, is produced by each element. This pattern—a series of lines—corresponds to the various electronic transitions possible for the particular atom. The pattern is characteristic for each element and can be used for qualitative identification purposes.

MOLECULAR EMISSION

A similar phenomenon is observed when molecules are vaporized and thermally excited. Electrons can be promoted from an occupied ground electronic state to a vacant excited state; when an electron returns to the ground state, a photon of light may be emitted.

Molecular spectra are usually more complex than atomic spectra. The energy levels are more complex, and vibrational and rotational sublevels superimpose their patterns on the electronic spectrum. *Bands* are generally observed rather than the sharp lines seen in atomic spectra. Emission intensity again increases as the flame temperature is raised. However, one must be concerned about reaching too high a temperature and decomposing the molecular emitter; the light emission pattern will change if this occurs. This is a particular problem in achieving an intense blue flame. The best blue light emitter, CuCl, becomes unstable at high flame temperatures (see Chapter 8).

BLACK BODY EMISSION

The presence of solid particles in a pyrotechnic flame can lead to a substantial loss of color purity due to a complex process known as *black body radiation*. Solid particles, as they are heated to high temperature, begin to radiate in the infrared region, and give a sensation of warmth if you bring such a heated object near your skin. As

the temperature of the heated object continues to increase, the emission begins to shift into the visible region, radiating a continuous spectrum of light, much of it in the visible region—with the intensity exponentially increasing with temperature. If you are attempting to produce white light (which is a combination of *all* wavelengths in the visible region), this incandescent phenomenon is desirable.

Magnesium metal is found in many white light formulas. In an oxidizing flame, the metal is converted to the high-melting magnesium oxide, MgO, an excellent white light emitter by incandescence. Also, the high heat output of magnesium-containing compositions aids in achieving high flame temperatures. Aluminum metal is also commonly used for light production; other metals, including titanium and zirconium, are also good white light sources.

Note: Many of the white light compositions used by the military contain sodium nitrate as the oxidizer and magnesium as a fuel, with a carbon-hydrogen binder to hold the materials in a homogeneous blend. The combination of intense light emission from the vapor phase sodium atoms and the solid magnesium oxide incandescent particles produce a bright white light effect when the composition burns at a temperature above 3,000°C.¹²

The development of color and light-producing compositions will be considered in more detail in Chapter 8.

THE PYROTECHNIC LABORATORY

One question that is frequently asked with respect to the study of energetic materials deals with the type of equipment that a researcher or manufacturer should have for research as well as quality control use.

PARTICLE SIZE

Much of pyrotechnic reactivity is related to the particle sizes of the components of a given composition. Perhaps the first piece of equipment that is purchased should be a particle size analyzer for the determination of particle size, and particle size distribution, in starting chemicals to be used to manufacture energetic mixtures. This can be as simple as a set of sieves and a “shaker” apparatus, or can be a more elaborate (and expensive) piece of instrumentation (see Chapter 4).

Selection of the sample is, of course, important. The sample should be representative of the container it was taken from—tumbling of the container might be helpful prior to removing the sample to try and have a homogeneously distributed material to analyze. Carrying out several trials on the same material will also give you confidence in your results, if you get similar results from trial to trial.

It might also be helpful to have a microscope with a camera available to study and photograph the particles. Particles come as spheres, rods, plates, flakes, and other geometries; a change in the shape of your particles could affect their reactivity, as well as the sensitivity of mixtures produced with the material. If an incoming chemical changes in its particle size or shape from one shipment to the next, careful evaluation of the material is required before it is put into production.

THERMAL ANALYSIS

A thermal analysis unit, as discussed previously, is a valuable tool for both research work and quality control. It can be used for the inspection of incoming lots of chemicals, and for batch-to-batch quality control in manufacturing.

MOISTURE ANALYZER

If there is one thing that can cause significant variation from batch to batch in the production of energetic mixtures, it is water. Water is a tremendous heat sink, and slows up the burn rate of most energetic mixtures. It is also a reactive chemical, and can react over time with magnesium, zinc, and other metal fuels, leading to a slowing of the burn rate for the mixtures containing these fuels. It can also change the particle size of water-soluble components over time, as a material goes through thermal cycling. Some of the water-soluble particles dissolve at higher temperatures, and then recrystallize back out as the material cools—with a possible change in particle size. This can affect your burn rate as well. Therefore, you need to know the moisture content of pyrotechnic mixtures when they are ready to be loaded into end items.

The equipment for this analysis can be as simple as an oven and a sensitive electronic balance. Weigh the sample before and after heating in the oven, using a temperature warm enough to remove moisture from the sample, but low enough to minimize the possibility of an ignition. Obviously, small samples are desirable for this study.

HEAT OUTPUT MEASUREMENT

A bomb calorimeter is the standard device used for the measurement of the heat output, upon ignition, of an energetic mixture. A weighed sample is ignited, usually with a bit of hot wire, and the temperature rise is measured. Knowing the heat capacity of the instrument, the temperature rise can be converted into heat output. Current calorimeters on the market offer a range of options, including automated data processing and data storage.

This equipment can be used for research work to measure the heat output of new compositions, to compare the laboratory result with the theoretical heat output value. In addition, calorimetry can be used for quality-control work in manufacturing. As an example each batch of energetic material that is produced, or perhaps purchased, can be tested in the calorimeter for heat output. The new material should yield the same heat value as the previous sample of the material. If it doesn't, the reason needs to be determined before the new material is put into production. Also, a calibrated differential scanning calorimeter (DSC) can be used to determine the heats of various processes that occur in energetic materials as the sample temperature is raised.

OTHER EQUIPMENT

Depending on the specific types of energetic material that is produced at a given facility, other equipment should be on hand for quality control work, as well as research and development work. This could include light and color analysis for illuminant

and flare compositions; gas volume and pressure measurement capability, including pressure rate-of-rise measurement, for propellant production; and light obscuration equipment for obscuration (smoke) production.

REFERENCES

1. R. C. Weast (Ed.), *CRC handbook of chemistry and physics*, 75th ed., Boca Raton, FL: CRC Press, 1994.
2. S. R. Jain, Energetics of propellants, fuels, and explosives: A chemical valence approach, *Propellants, Explosives, Pyrotechnics*, 12, 188 (1987).
3. A. Shidlovskiy, *Principles of pyrotechnics*, 3rd ed., Moscow, 1964. (Translated as Report FTD-HC-23-1704-74 by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)
4. L. Pytlewski, The unstable chemistry of nitrogen, presented at Pyrotechnics and Explosives Seminar P-81, Philadelphia: Franklin Research Center, August 1981.
5. U.S. Army Material Command, *Engineering design handbook: Properties of materials used in pyrotechnic compositions*, Military Pyrotechnics Series, Part Three, Washington, DC, 1863 (AMC Pamphlet 706-187).
6. T. L. Davis, *The chemistry of powder and explosives*, New York: John Wiley & Sons, 1941.
7. U.S. Army Material Command, *Engineering design handbook: Theory and application*, Military Pyrotechnics Series, Part One, Washington, DC, 1967 (AMC Pamphlet 706-185).
8. J. H. McLain, *Pyrotechnics from the viewpoint of solid state chemistry*, Philadelphia: The Franklin Institute Press, 1980.
9. R. L. Tuve, *Principles of fire protection chemistry*, Boston: National Fire Protection Association, 1976.
10. W. J. Moore, *Basic physical chemistry*, Englewood Cliffs: Prentice Hall, NJ, 1983.
11. P. Gabbott (Ed.), *Principles and applications of thermal analysis*, Hoboken, NJ: Wiley-Interscience Publishing, 1998.
12. D. R. Dillehay, Illuminants and illuminant research, in *Pyrotechnic chemistry*, *Journal of Pyrotechnics*, Whitewater, CO, 2004, chap. 10.

3 Components of High-Energy Mixtures



HAND MIXING: (See color insert following page 112). For many centuries, many pyrotechnic compositions were gently blended by hand through a screen to produce a homogeneous material. Modern mixing equipment has removed personnel from the immediate mixing area, due to concerns over accidental ignition from friction and spark. (Photo by Tim Wade and Dennis King, courtesy of MP Associates.)

It may have begun with an early chef, somewhere in Asia, working over his cooking fire. He noticed that the saltpeter (potassium nitrate) he was using to season the evening meal caused the fire to glow more intensely when it hit the flames. Curiosity aroused, he then mixed the saltpeter with his charcoal and produced a burning mixture, but it was difficult to light. By adding a bit of brimstone (sulfur) to the mixture, the ignitability improved. After a lot of trial and error, the end result was a material that changed the world—black powder. This unique blend of potassium nitrate, charcoal, and sulfur illustrates so well how the selection of chemicals is critical to the development of a successful pyrotechnic composition.

INTRODUCTION

Compounds containing both a readily oxidized and a readily reduced component within one molecule (such as trinitrotoluene (TNT), with formula $C_7H_5N_3O_6$) or within one ionic compound (such as ammonium nitrate (NH_4NO_3)) are uncommon. Such species tend to have explosive properties. A molecule *or* ionic compound containing an internal oxidizer-reducer pair is inherently the most intimately mixed high-energy material that can be prepared. The mixing is achieved at the *molecular* (or *ionic*) level, and no migration or diffusion is required to bring the electron donor and electron acceptor together. The electron transfer reaction is *expected* to be rapid (even violent) in such species, upon application of the necessary activation energy to a small portion of the composition.

A variety of compounds possessing this *intramolecular* reaction capability are shown in Table 3.1. The output from the exothermic decomposition of these compounds is typically heat, gas, and shock. Many of these materials *detonate*—a property quite uncommon with physical mixtures, where the degree of homogeneity is considerably less and reaction times tend to be significantly longer. Many explosive molecules have the general molecular formula $C_aH_bN_cO_d$. The number and placement of the electronegative nitrogen and oxygen atoms serve to draw electron density away from carbon atoms. If the resulting partially positive carbon atoms are adjacent to one another, the carbon-carbon bond is weakened and the molecule may become shock sensitive and the result is a molecular explosive. The nitroglycerine molecule illustrates this concept well. The molecule $C_3H_5N_3O_9$ has a chain of three adjacent carbon atoms. Each carbon atom is bonded to an oxygen atom, which in turn is bonded to a nitrogen atom with two more oxygen atoms attached. The highly electronegative oxygen and nitrogen atoms (see Figure 2.5) cause a partially positive charge to exist on each carbon atom—and the resulting repulsive forces cause the carbons to

TABLE 3.1
Compounds Containing Intramolecular
Oxidation-Reduction Capability

Compound	Formula
Ammonium nitrate	NH_4NO_3
Ammonium perchlorate	NH_4ClO_4
Lead azide	$Pb(N_3)_2$
Trinitrotoluene (TNT)	$C_7H_5N_3O_6$
Nitroglycerine (NG)	$C_3H_5N_3O_9$
Mercury fulminate	$Hg(ONC)_2$

Note: These compounds readily undergo explosive decomposition when sufficient ignition stimulus is applied. A shock stimulus is frequently needed to activate the nonionic organic molecules (such as TNT); these compounds will frequently merely burn if a flame is applied.

repel each other, weakening the bonds. (Note: This is a condition that is akin to having “three cats in a bag.” If you don’t know what this means, select at random three mature tomcats and cautiously place them together in a burlap sack and observe the resulting situation. “Unstable” describes the cat situation, as well as the state of the nitroglycerine molecule.)

The high-energy chemist can greatly expand his repertoire of materials by preparing *mixtures*, combining an oxidizing material with a fuel to produce the exact heat output and burning rate needed for a particular application. Although detonations are far less likely to occur with these physical mixtures, propulsion, bright light, colors, thermal effects, hot particles, and smoke can be produced using such compositions, expanding the effects that can be achieved with high-energy materials in propellant and pyrotechnic articles. For these effects to occur, it is critical that the mixture *burn* rather than *explode*. Burning behavior is dependent upon a number of factors, and the pyrotechnician must carefully control these variables to obtain the desired performance.

Pyrotechnic mixtures “burn,” but it must be remembered that these compositions—unlike most materials that undergo combustion—supply their *own* oxygen for combustion, through the thermal decomposition of an oxygen-rich material such as potassium chlorate:



Thus, a pyrotechnic fire *cannot* be suffocated—no atmospheric oxygen is needed for these mixtures to vigorously burn. In fact, confinement can *accelerate* the burning of an energetic composition by producing an increase in pressure, holding the heat at the reactive surface and possibly leading to an explosion. Adequate venting is quite important in keeping a pyrotechnic fire from developing into a serious explosion. The only way to get a pyrotechnic fire under control is to reduce the temperature of the burning material to a value less than the ignition temperature of the composition, and the cooling material (water, perhaps, and a lot of it) must be applied very quickly to have a chance at stopping the reaction.

The selection of components for a particular energetic composition should be made using chemical logic, taking into consideration the desired heat output, burn rate, light intensity, color value, efficiency, ignitability, and physical state of the reaction products (i.e., solid vs. gas). Factors such as availability, toxicity, stability, and environmental compatibility—and, of course, cost—must also be taken into consideration. The final blend of components must produce the desired output, be safe to prepare and use, have a long storage lifetime, use readily available components that are moderate in cost, and meet toxicological and environmental requirements.

These requirements quickly reduce the field of available materials for most energetic applications. There are few, if any, “exotic” chemicals that are widely used in producing energetic materials—we will discuss iron oxide, for example, at several locations in the following chapters, but other oxidizers, such as ruthenium tetroxide (RuO_4), will not be discussed for reasons of cost, stability, and toxicity.

A variety of ingredients, each serving one or more purposes, can be used to create an effective pyrotechnic composition. These materials are discussed in varying detail in several excellent sources.¹⁻⁴

OXIDIZING AGENTS

REQUIREMENTS

Oxidizing agents are usually oxygen-rich ionic solids that decompose at moderate to high temperatures, liberating oxygen gas. These materials must be readily available in reasonably pure form, in the proper particle size, at reasonable cost. They should give a neutral reaction when wet, be stable over a wide temperature range (at least up to 100°C), and yet readily decompose to release oxygen at higher temperatures. For the pyrotechnic chemist's use, acceptable species include a variety of negative ions (anions), usually containing high-energy Cl–O or N–O bonds:

NO_3^{-1}	nitrate ion	ClO_3^{-1}	chlorate ion
ClO_4^{-1}	perchlorate ion	CrO_4^{-2}	chromate ion
O^{-2}	oxide ion	$\text{Cr}_2\text{O}_7^{-2}$	dichromate ion

The positive ions used to combine with these negatively charged anions must form stable, neutral compounds meeting several restrictions:¹

1. The oxidizer must be quite low in *hygroscopicity*, or the tendency to acquire moisture from the atmosphere. Water can cause a variety of problems in pyrotechnic mixtures, and materials that readily pick up water are usually avoided. Hygroscopicity correlates well with the size and charge of the positive ions that makes up an ionic oxidizer. Li^{+1} , Na^{+1} , Mg^{+2} , and Al^{+3} are small ions that are often associated with hygroscopic compounds. Consequently, sodium salt (e.g., sodium nitrate (NaNO_3)) is rarely employed in pyrotechnics. Lithium, magnesium, and aluminum salts are similarly avoided due to their high hygroscopicity. Potassium salts tend to have lower hygroscopicity, and are commonly used in pyrotechnics. Hygroscopicity tends to parallel water solubility, and solubility data can be used to anticipate possible moisture-attracting problems. The water solubility of the common oxidizers can be found in Table 3.2. However, it should be mentioned that large quantities of sodium nitrate *are* used by the military in combination with magnesium metal for bright white light production and illumination. In order to use sodium nitrate, however, strict humidity control is required throughout the manufacturing process to avoid moisture uptake, and the finished items must be sealed to prevent water from being picked up during storage. Only with strict manufacturing controls, along with effective packaging, can the unique light-producing properties of the sodium nitrate–magnesium system (see Chapter 8) be exploited.
2. The oxidizer's positive ion (cation) must not adversely affect the desired flame color. Sodium, for example, is an intense emitter of yellow-orange light, and its presence can ruin attempts to generate red, green, and blue flames.
3. The alkali metals (Li, Na, and K) and alkaline earth metals (Ca, Sr, and Ba) are preferred for the positive ion. These species are poor electron acceptors (and conversely, the metals are good electron donors), and they will not

TABLE 3.2
Common Oxidizers and Their Properties

Compound	Formula	Formula Weight	Melting Point, °C	Water Solubility, grams/100 ml @ 20°C ^a	Heat of Decomposition, kcal/mol	Heat of Formation, kcal/mol ^a	Grams of Oxygen Released per Gram of Oxidizer	Weight of Oxidizer Required to Evolve 1 Gram of Oxygen
Ammonium nitrate	NH ₄ NO ₃	80.0	170	118 (0°C)	—	-87.4	0.60 (total 0)	—
Ammonium perchlorate	NH ₄ ClO ₄	117.5	Decomposes	37.2 ^c	—	-70.6	-0.28	~3.5
Barium chlorate	Ba(ClO ₃) ₂ · H ₂ O	322.3	414	27 (15°C)	-28 ^b	-184.4	0.32	3.12
Barium chromate	BaCrO ₄	253.3	Decomposes	.0003 (16°C)	—	-345.6	0.095	10.6
Barium nitrate	Ba(NO ₃) ₂	261.4	592	8.7	+104 ^b	-237.1	0.31	3.27
Barium peroxide	BaO ₂	169.3	450	Very slight	+17 ^b	-151.6	0.09	10.6
Iron(III) oxide (red)	Fe ₂ O ₃	159.7	1565	Insol.	—	-197.0	0.30	3.33
Iron(II,III) oxide (black)	Fe ₃ O ₄	231.6	1594	Insol.	+266 ^b	-267.3	0.28	3.62
Lead chromate	PbCrO ₄	323.2	844	Insol.	—	-218	0.074	13.5
Lead dioxide (lead peroxide)	PbO ₂	239.2	290 (decomposes)	Insol.	—	-66.3	0.13 (total 0)	7.48
Lead oxide (litharge)	PbO	223.2	886	0.0017	—	-51.5	0.072 (total 0)	14.0
Lead tetroxide (red lead)	Pb ₃ O ₄	685.6	500 (decomposes)	Insol.	—	-171.7	0.093 (total 0)	10.7
Potassium chlorate	KClO ₃	122.6	356	7.1	-10.6 ^c	-95.1	0.39	2.55
Potassium nitrate	KNO ₃	101.1	334	31.6 ^c	+75.5 ^b	-118.2	0.40	2.53
Potassium perchlorate	KClO ₄	138.6	610	1.7 ^c	-0.68 ^c	-103.4	0.46	2.17
Sodium nitrate	NaNO ₃	85.0	307	92.1 (25°C) ^c	-111.8	-111.8	0.47	2.13
Strontium nitrate	Sr(NO ₃) ₂	211.6	570	70.9 (18°C)	-233.8	-233.8	0.38	2.63

^a R. C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, 63rd ed., Boca Raton, FL: CRC Press, 1982.

^b A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, OH, 1974.)

^c T. Shimizu, in K. Kosanke et al., *Pyrotechnic Chemistry, Journal of Pyrotechnics*, Whitewater, CO, 2004, chap. 2.

react in storage with active metal fuels such as Mg and Al. If easily reducible metal ions such as lead (Pb^{2+}) and copper (Cu^{2+}) are present in oxidizers, there is a strong possibility that a reaction such as



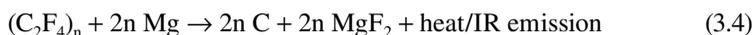
will occur over time, especially under moist conditions, replacing the energetic magnesium fuel with less reactive copper metal. The pyrotechnic performance will be greatly diminished, and spontaneous ignition might occur as the replacement reaction proceeds exothermically.

4. The compound must have an acceptable heat of decomposition. A value that is too exothermic may produce explosive or highly sensitive mixtures, while a value that is too endothermic will cause ignition difficulties, as well as poor propagation of burning. For an oxidizer such as iron(III) oxide, Fe_2O_3 , with a large, endothermic heat of decomposition, reaction will not occur with moderate-energy fuels like sulfur and sugar. A highly energetic fuel like magnesium, aluminum, or zirconium is required to extract the oxygen from iron oxide, leaving molten iron as a reaction product.
5. The compound should have as high an active oxygen content as possible. Light cations (Na^+ , K^+ , NH_4^+) are desirable while heavy cations (Pb^{2+} , Ba^{2+}) should be avoided if possible. Oxygen-rich anions, of course, are preferred. Notice the trade-off here with hygroscopicity—light positive ions tend to be hygroscopic and heavy cations reduce the active oxygen content. Logic says to shoot for the elements with medium atomic weights for use as the cation in an oxidizer.
6. Finally, all materials used in high-energy compositions should be low in toxicity, yield low-toxicity reaction products, and for all compositions developed in the twenty-first century, be environmentally green.

In addition to ionic solids, covalent molecules containing halogen atoms (primarily F and Cl) can function as oxidizers in pyrotechnic compositions, especially with active metal fuels. Examples of this are the use of hexachloroethane (C_2Cl_6) with zinc metal in white smoke compositions,



and the use of Teflon[®] (polytetrafluoroethylene) with magnesium metal in heat-producing, infrared-emitting mixtures,



In both of these examples, the metal has been oxidized—has lost electrons and increased in oxidation number—while the carbon atoms have gained electrons and been reduced. Table 3.2 lists some of the common oxidizers together with a variety of their properties. Several oxidizers are so widely used that they merit special consideration.

POTASSIUM NITRATE (KNO₃)

The oldest solid oxidizer used in high-energy mixtures, potassium nitrate (or saltpeter, as it was known for many years) remains a widely used ingredient into the twenty-first century. Its advantages are ready availability of high-purity material at reasonable cost, low hygroscopicity, and the relative ease of ignition of many mixtures prepared using it. The ignitability is related to the low (334°C) melting point of saltpeter. It has a high (39.6%) active oxygen content, and decomposes at high temperature according to the equation



This is a strongly endothermic reaction, with a heat of decomposition value of +75.5 kcal/mole of KNO₃, meaning high-energy-output fuels must be used with saltpeter to achieve rapid burning rates. When mixed with a simple organic fuel such as lactose, potassium nitrate may burn with difficulty and stop at the potassium nitrite (KNO₂) stage in its decomposition.²



With good fuels (such as charcoal and active metals), potassium nitrate will react well. Potassium nitrate has the additional property of not undergoing an explosion by itself, even when very strong initiating modes are used.²

POTASSIUM CHLORATE (KClO₃)

One of the most reactive, and certainly the most controversial, of the common oxidizers is potassium chlorate, KClO₃. It is a white, crystalline material of low hygroscopicity, with 39.2% oxygen by weight. It is prepared by electrolysis from a chloride salt in an energy-absorbing process—this energy input during manufacturing provides a means of storing energy in the oxidizer, for subsequent release during reaction with a fuel.

Potassium chlorate was used in the first successful colored-flame compositions in the mid-1800s, and it remains in use today in colored smoke compositions, firecrackers, toy pistol caps, matches, and some color-producing fireworks.

However, potassium chlorate has been involved in a number of serious accidents at fireworks manufacturing plants, and it must be treated with great care if it is used at all. Other oxidizers are strongly recommended over this material, if one can be found that will produce the desired pyrotechnic effect.

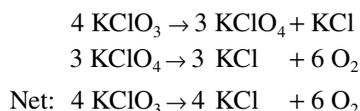
Potassium chlorate compositions are quite prone to accidental ignition, especially if sulfur or an acidic component or acidic impurity is also present. Chlorate-phosphorus mixtures are so sensitive and reactive that they can only be safely worked with when wet. The high hazard of KClO₃ mixtures was gradually recognized in the late nineteenth century, and England banned all chlorate-sulfur compositions in 1894. U.S. factories have greatly reduced their use of potassium chlorate as well, replacing it with the less sensitive potassium perchlorate in many formulas.

The Chinese, however, continue to use potassium chlorate in firecrackers and some color compositions.

Several factors contribute to the instability of potassium chlorate-containing compositions. The first is the low (356°C) melting point and low decomposition temperature of the oxidizer. Soon after melting, KClO_3 stoichiometrically decomposes according to the net equation below:



This reaction is quite vigorous, and becomes violent at temperatures above 500°C.² The actual decomposition mechanism may be more complex than it suggests. Intermediate formation of potassium perchlorate has been reported at temperatures just above the melting point, with the perchlorate then decomposing to yield potassium chloride and oxygen.⁶ The involvement of the chlorite (ClO_2^-) ion and radical has also been suggested.⁷



The decomposition reaction of potassium chlorate is rare among the common oxidizers because it is *exothermic*, with a heat of reaction value of approximately -10.6 kcal/mole.² While most other oxidizers require a net heat input for their decomposition, potassium chlorate dissociates into KCl and O_2 with the *liberation* of heat. This heat output can lead to rate acceleration, and allows the ignition of potassium chlorate-containing compositions with a minimum of external energy input (ignition stimulus). In addition, potassium chlorate is capable of sustaining propagation of burning with low-energy fuels, at low temperatures, or under conditions of poor stoichiometry where other oxidizers (iron oxide, Fe_2O_3 , for example) would not sustain the reaction.

Potassium chlorate is particularly sensitive when mixed with sulfur, a low-melting (119°C) fuel. It is also sensitive when combined with low-melting organic compounds, and low ignition temperatures are observed for most such compositions. Higher ignition temperatures are found for KClO_3 -metal mixtures, attributable to the higher melting points, oxide coatings, and rigid crystalline lattices of these metallic fuels. However, these mixtures can be quite sensitive to ignition by spark or friction because of their substantial heat output, and should still be regarded as quite hazardous. Ignition temperatures for some KClO_3 mixtures are given in Table 3.3. Note: Ignition temperatures are quite dependent upon the experimental conditions; a range of $\pm 50^\circ\text{C}$ may be observed, depending on sample size, heating rate, degree of confinement, and the experimental method that is used.⁸

Mixtures containing potassium chlorate can be quite susceptible to the presence of a variety of chemical species. Acids can have a dramatic effect—the addition of a drop of concentrated sulfuric acid (H_2SO_4) to most KClO_3 -fuel mixtures results in immediate inflammation of the composition. This dramatic reactivity has been

TABLE 3.3
Ignition Temperatures of Potassium
Chlorate-Fuel Mixtures

Fuel	Ignition Temperature of Stoichiometric Mixture, °C ^a
Lactose, C ₁₂ H ₂₂ O ₁₁	195
Sulfur	220
Shellac	250
Charcoal	335
Magnesium powder	540
Aluminum powder	785
Graphite	890

^a A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, OH, 1974.)

attributed to the formation of chlorine dioxide (ClO₂) gas, a powerful oxidizer.⁶ The presence of basic neutralizers such as magnesium carbonate and sodium bicarbonate in KClO₃ mixtures can reduce the sensitivity of chlorate-containing compositions to trace amounts of acidic impurities.

The ability of a variety of metal oxides—most notably manganese dioxide (MnO₂)—to catalyze the thermal decomposition of potassium chlorate into potassium chloride and oxygen has been known for years. Little use is made of this behavior in pyrotechnics, however, because KClO₃ is almost too reactive in its normal state and ways are not needed to *enhance* its reactivity. Materials and methods to retard its decomposition are desired instead. However, knowledge of the ability of many materials to accelerate the decomposition of KClO₃ suggests that *impurities* could be quite an important factor in determining the reactivity and sensitivity of chlorate-containing mixtures. It is vitally important that the KClO₃, as well as all other components blended with KClO₃ that are used in pyrotechnic manufacturing operations, be of the highest possible purity, and that all possible precautions be taken in storage and handling to prevent contamination of the material.

McLain has reported that potassium chlorate containing 2.8 mol% copper chlorate as an intentionally added impurity (or dopant) reacted explosively with sulfur at room temperature!⁹ A pressed mixture of potassium chlorate with “realgar” (arsenic sulfide, As₂S₂) has also been reported to ignite at room temperature.⁴

A study by Conkling and Halla investigated the relationship between the melting point of an organic fuel and the ignition temperature of a stoichiometric mixture of that compound with potassium chlorate. The results indicated that the onset of ignition was triggered by the thermal decomposition of the fuel, rather than by its melting point. A low decomposition temperature for a carbon-based compound should correspond with an increased tendency for that compound to readily undergo

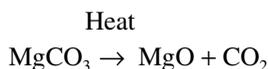
oxidation—if oxygen is available. Sugars, which tend to decompose at their melting points, were found to form mixtures with potassium chlorate that ignited at the melting/decomposition temperature of the sugar, suggesting that it might be possible to formulate mixtures with specific ignition temperatures. Carbon compounds such as benzoic acid, with stable liquid phases, ignited at higher temperatures, corresponding to their decomposition temperatures in the liquid state.¹⁰

Ammonium chlorate, NH_4ClO_3 , is an extremely unstable compound that decomposes violently at temperatures well below 100°C . If a mixture containing both potassium chlorate and an ammonium salt is prepared, there is a good possibility that an exchange reaction will occur—especially in the presence of moisture—to form some of the ammonium chlorate:



If this reaction occurs, the chance of spontaneous ignition of the mixture is likely. Therefore, any composition containing both a chlorate salt and an ammonium salt must be considered extremely hazardous. The shipping regulations of the U.S. Department of Transportation classify any such mixtures as “forbidden explosives” because of their instability.¹¹ However, compositions consisting of potassium chlorate, ammonium chloride, and organic fuels have been used, reportedly safely, for white smoke production.²

Colored smoke compositions represent a major use of potassium chlorate, and the safety record of these mixtures is excellent. An acid neutralizer (e.g., MgCO_3 or NaHCO_3) is typically added for storage stability, as well as to lower the reaction temperature through an endothermic decomposition, in the flame, of the type



The carbon dioxide gas that forms during the decomposition also aids in dispersing the volatile smoke dyes. Thus, the magnesium carbonate (or sodium bicarbonate) is playing three important roles in the performance and stability of the smoke composition: acid neutralizer, coolant, and smoke disperser.

Colored smoke mixtures also contain either sulfur or a carbohydrate as the fuel, and a volatile organic dye that sublimates from the reaction mixture to produce the colored smoke. These compositions contain a large excess of potential fuel, and their explosive properties are greatly diminished as a result. Smoke mixtures must react with low flame temperatures (500°C or less, depending on the dye that is used) or the complex dye molecules will decompose, producing black soot instead of a brilliantly colored smoke. Potassium chlorate is far and away the best oxidizer for use in these compositions.

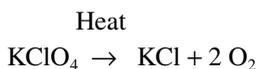
Potassium chlorate is truly a unique material. Shimizu has stated that no other oxidizer can surpass it for burning speed, ease of ignition, or noise production using a minimum quantity of composition.² It is also among the very best oxidizers for

producing colored flames, with ammonium perchlorate as its closest rival. Chlorate-containing compositions can be prepared, by altering the fuel and the fuel-oxidizer ratio, that will ignite and propagate at a wide range of reaction rates and flame temperatures for use in applications ranging from colored smoke mixtures to colored flame formulations to high-temperature flash compositions. KClO_3 is a versatile material, but the inherent dangers associated with it require that alternate oxidizers be employed wherever possible. It is just too unstable and unpredictable to be safely used by the pyrotechnician in anything but colored smoke compositions, and even here coolants and considerable care are required!

POTASSIUM PERCHLORATE (KClO_4)

This material gradually replaced potassium chlorate (KClO_3) as the principal oxidizer in civilian pyrotechnics during the twentieth century. Its safety record is far superior to that of potassium chlorate, although caution must still be used and a hazard analysis must still be conducted on all compositions and manufacturing processes, using sensitivity and output data, prior to scaling up production of any energetic material. Perchlorate mixtures, especially with a metal fuel such as aluminum, can have explosive properties, especially when present in bulk quantities and when confined.

Potassium perchlorate is a white, nonhygroscopic crystalline material with a melting point of 610°C , considerably higher than the 356°C melting point of KClO_3 . It undergoes decomposition at high temperature:



forming potassium chloride and oxygen gas. This reaction has a slightly exothermic value of $-0.68 \text{ kcal/mole}^3$ and produces substantial oxygen. The active oxygen content of KClO_4 (46.2%) is one of the highest available to the pyrotechnician.

Because of its higher melting point and less exothermic decomposition, potassium perchlorate typically produces mixtures that are less sensitive to heat, friction, and impact than those made with KClO_3 .³ Potassium perchlorate can be used to produce colored flames (such as red when combined with strontium nitrate), noise (with aluminum, in flash and sound mixtures), and light (in photoflash mixtures with magnesium). It also makes an excellent, but very spark-sensitive, ignition composition, ZPP, when blended with zirconium.

THE PERCHLORATE ISSUE—2010

When the first edition of this book was published in 1985, a widely held opinion among pyrotechnicians was that potassium perchlorate was the ideal oxidizer to use in energetic pyrotechnic compositions, and potassium nitrate was the first choice for moderately energetic systems. Similarly, ammonium perchlorate was viewed as an ideal oxidizer for propellant formulations, producing all gaseous products in its thermal decomposition.

The positive features of the perchlorate oxidizers were reasonable cost, acceptable hygroscopicity, good stability, and low toxicity, as well as availability in high purity in a wide range of particle sizes, along with excellent reactivity with a wide range of fuels. The two perchlorate oxidizers (ammonium and potassium) were widely used for a number of decades in solid rocket propellants, signal flare compositions, explosive simulators, and an assortment of other pyrotechnic applications. The fireworks manufacturing industry significantly improved its safety record as color compositions made with potassium chlorate were replaced by less sensitive and more stable potassium perchlorate formulations.

However, the excellent stability of the perchlorates—one of their strongest selling points for use in energetic compositions—has also become a great weakness for these oxidizers. Studies have indicated that perchlorate oxidizers are quite sluggish in their reaction at ambient temperatures with typical fuels (organic matter) that are found in the environment, and they appear to have considerable persistence in soil and ground water. Some microorganisms do appear to be capable of metabolizing the perchlorate ion, and research in this area continues.

The concern with perchlorates involves studies that have linked the perchlorate ion, even in low concentrations, to thyroid disorders. The perchlorate ion appears to be an ideal substitute, in size and charge (−1), for the iodide ion (I[−]). Consumption of water containing perchlorate ion appears to lead to incorporation of the perchlorate ion by acceptor sites in the thyroid gland, replacing the biologically active iodide ion, thereby possibly creating developmental problems in pregnant women and young children.¹²

The good news is that the effect appears to be preventable and reversible. The intake of foods and beverages with iodide content appears to lead to a replacement of the perchlorate ion with iodide, and this should be particularly beneficial if the supply of water that contains perchlorate is replaced with perchlorate-free material. Research into this issue is ongoing, but the issue has led manufacturers of both military and civilian devices containing perchlorate oxidizers to seek replacement materials. This has proven to be possible in some systems, and a real challenge in others, without resorting back to the use of the hazardous chlorate oxidizers.

One thing we do know is that the perchlorate ion converts in what should be a nearly quantitative manner back to the much more environmentally acceptable chloride ion upon ignition of an energetic composition, such as the reaction



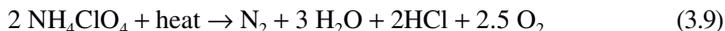
that takes place with a flame temperature in the 3,000°C range. If perchlorate-containing compositions ignite and function properly, the use of perchlorate oxidizers is of far less concern with respect to environmental contamination.

Obviously, then, the major opportunity for ground contamination with perchlorate occurs at manufacturing sites. As a result, manufacturers of propellants and pyrotechnics have proceeded to take appropriate measures and institute best management practices to prevent the release of perchlorate materials into groundwater systems, while research is under way to find replacement formulations that are perchlorate-free, as well as to better determine hazardous exposure levels for humans.¹²

AMMONIUM PERCHLORATE (NH₄ClO₄)

The newest oxidizer to appear in significant use in pyrotechnics, ammonium perchlorate (AP), has found considerable use in modern solid-fuel rocket propellants and in the fireworks industry. The Space Shuttle alone uses approximately 2 million pounds of solid fuel per launch; the mixture is 70% ammonium perchlorate, 16% aluminum metal, and 14% organic polymer/epoxy, with a trace of iron oxide catalyst that can be varied to modify the burn rate.¹³ The aluminum powder is a surprising ingredient to find in a propellant, since it generates solid rather than gaseous reaction products, but its substantial heat output as a fuel and its excellent thermal conductivity both contribute to an enhancement of the burn rate of this propellant formulation.

Ammonium perchlorate undergoes a complex chemical reaction on heating, with decomposition occurring over a wide range, beginning near 200°C. Decomposition occurs prior to melting, so a liquid state is not produced—the solid starting material goes directly to gaseous decomposition products. The decomposition position reaction is reported by Shimizu² to be

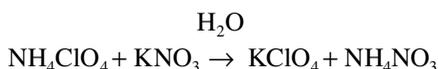


This equation corresponds to the evolution of 80 grams (2.5 moles) of oxygen gas per 2 moles (235 grams) of NH₄ClO₄, giving an active oxygen content of 34% (vs. 39.2% for KClO₃ and 46.2% for KClO₄). The fact that AP generates all gaseous products makes it a valuable material for propellant formulations. The decomposition reaction, above 350°C, is reported to be considerably more complex:¹⁴



Mixtures of ammonium perchlorate with fuels can produce high flame temperatures when ignited, and the hydrogen chloride (HCl) liberated during the reaction can aid in the production of colors. These two factors make ammonium perchlorate a good oxidizer for colored flame composition (see Chapter 8).

Ammonium perchlorate is more hygroscopic than potassium nitrate or potassium chlorate, and some precautions should be taken to keep mixtures dry. The hygroscopicity problem can be substantial if a given composition also contains potassium nitrate, or even comes in contact with a potassium nitrate-containing mixture. Here, the exchange reaction



can occur, especially in the presence of moisture. The exchange product, ammonium nitrate (NH₄NO₃), is very hygroscopic, and ignition problems may well develop over time.² Also, ammonium perchlorate should not be used in combination with a chlorate-containing compound, due to the possible formation of unstable (spontaneously explosive!) ammonium chlorate in the presence of moisture.

Magnesium metal should also be avoided in ammonium perchlorate compositions. Here the reaction



can occur in the presence of moisture due to the weakly acidic nature of ammonium perchlorate. Spontaneous ignition may occur if the heat buildup is substantial.

Under severe initiation conditions, ammonium perchlorate can be made to explode by itself.¹⁵ It appears to be difficult to get ammonium perchlorate to detonate, and shock appears to be needed to get the pure material to explode. Mixtures of ammonium perchlorate with sulfur and antimony sulfide are reported to be considerably more shock sensitive than comparable potassium chlorate compositions.² Fine ammonium perchlorate (largely 1 to 5 microns in number) mixed with fine aluminum powder (3 to 25 microns in size) can be detonated, while coarser ammonium perchlorate produces compositions that deflagrate under the same initiation conditions.¹⁶ Ammonium perchlorate compositions, ignited by flame, can be used to produce excellent flame colors, with little solid residue, but care must be exercised at all times with this oxidizer. The explosive properties of this material suggest that minimum amounts of bulk energetic composition should be prepared at one time, and large quantities should not be stored at manufacturing sites.

AMMONIUM PERCHLORATE IN THE NEWS

Prior to the perchlorate environmental concerns making the news,¹² ammonium perchlorate (AP) was involved in another newsworthy event. An explosion in 1988 arising from a fire at an ammonium perchlorate manufacturing facility near Henderson, Nevada, produced measurable property damage over a wide area, and reemphasized the energetic nature of ammonium perchlorate.^{17,18}

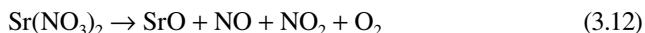
The fire began in the manufacturing area during routine maintenance operations, and quickly spread through the entire facility. Approximately 8 million pounds of AP was stored on site in 500- and 5,000-pound containers. At some point during the event, a natural gas line beneath the plant ruptured as well, adding “fuel to the fire” and making analysis of the event even more complex. Several smaller blasts were followed by a major explosion that registered on seismographs all over the western United States.

The investigation that followed after the event revealed the large quantity of ammonium perchlorate that was in storage at the facility, awaiting shipment to the solid propellant manufacturing industry. Fortunately, the emergency response system worked exceptionally well, and the event was limited to a single fatality. Further research confirmed that AP in fine particle size (15 microns and under) should be treated as a high explosive (A U. S. Department of Transportation Division 1.1 explosive, meaning a mass explosion hazard) for transportation, while it can be transported as a class 5 oxidizer in larger particle sizes.¹¹

STRONTIUM NITRATE [$\text{Sr}(\text{NO}_3)_2$]

This material is rarely used as the sole oxidizer in a pyrotechnic composition, but it is commonly combined with potassium perchlorate in red flame mixtures. It is a

white crystalline solid with a melting point of approximately 570°C. It is somewhat hygroscopic, so moisture should be avoided when using this material. Near its melting point, strontium nitrate decomposes according to



Strontium nitrite— $\text{Sr}(\text{NO}_2)_2$ —is formed as an intermediate in this decomposition reaction, and a substantial quantity of the nitrite can be found in the ash of low flame temperature mixtures.² At higher reaction temperatures, the decomposition is

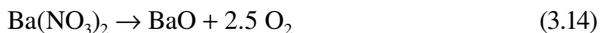


This is a strongly endothermic reaction, with a heat of reaction of +92 kcal, and corresponds to an active oxygen content of 37.7%. Little ash is produced by this high-temperature process, which occurs in mixtures containing magnesium or other “hot” fuels.

The highway flare, or fusee, typically uses a significant amount of strontium nitrate in its formulations, together with slow-burning fuels such as sulfur and sawdust, in order to obtain the long burning times (up to thirty minutes) required for these devices. The challenge in producing this device is to obtain good candlepower and a deep red flame color along with the slow burning times. Either can be accomplished by itself with little problem, but achieving both with the same composition takes just the right chemistry.

BARIUM NITRATE [Ba(NO₃)₂]

Barium nitrate is a white, crystalline, nonhygroscopic material with a melting point of approximately 592°C. It is commonly used as the principal oxidizer in green flame compositions, gold sparklers, and in photoflash mixtures in combination with potassium perchlorate. At high reaction temperatures, barium nitrate decomposes according to



This reaction corresponds to 30.6% available oxygen. At lower reaction temperatures, barium nitrate produces nitrogen oxides (NO and NO₂) instead of nitrogen gas, as does strontium nitrate.²

Mixtures containing barium nitrate as the sole oxidizer are typically characterized by higher ignition temperatures relative to potassium nitrate and potassium chlorate compositions. The higher melting point and decomposition temperature of barium nitrate are primarily responsible for these higher ignition values.

OTHER OXIDIZERS

A variety of other oxidizers are occasionally used in high-energy mixtures, generally with a specific purpose in mind. Barium chlorate— $\text{Ba}(\text{ClO}_3)_2$ —for example, has

been used in some green flame compositions. These mixtures can be very sensitive, however, and great care must be used during mixing, loading, and storing.

Barium chlorate is interesting because it exists as a *hydrate* when crystallized from a water solution. It has the formula $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. Water molecules are found in the crystalline lattice in a one-to-one ratio with barium ions. The molecular weight of the hydrate is 322.3 ($\text{Ba} + 2 \text{ClO}_3 + \text{H}_2\text{O}$), so the water must be included in stoichiometry calculations. On heating, the water is driven off at 120°C , producing anhydrous $\text{Ba}(\text{ClO}_3)_2$, which later melts at 414°C . The thermal decomposition of barium chlorate is strongly exothermic (-28 kcal/mole). This value, greater than that of 1 mole of potassium chlorate, causes barium chlorate mixtures to be very sensitive to various ignition stimuli.

Iron oxide (hematite, Fe_2O_3) is used in certain mixtures where a high ignition temperature and a substantial quantity of molten slag (and lack of gaseous product) are desired. The thermite reaction,

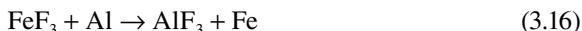


is an example of this type of reaction, and can be used to do pyrotechnic welding and assorted other applications where a hot molten slag is desired. The melting point of Fe_2O_3 is $1,565^\circ\text{C}$, and the ignition temperature of a thermite mix is above 800°C . A reaction temperature of approximately $2,400^\circ\text{C}$ is reached, and 950 calories of heat is evolved per gram of composition.^{2,6} Because of its significant heat of decomposition (199 kcal/mole), iron oxide will only react with active, energetic fuels such as Al, Si, B, or Zr. A mixture of iron oxide with sugar—a moderate fuel—will only produce rusty caramel if ignition of the mixture is attempted. There is not enough energy generated by the oxygen-sugar reaction to sustain the decomposition of the iron oxide.

Other oxidizers, including barium chromate (BaCrO_4), lead chromate (PbCrO_4), sodium nitrate (NaNO_3), lead dioxide (PbO_2), bismuth oxide (Bi_2O_3), and barium peroxide (BaO_2), will also be encountered in subsequent chapters. Bear in mind that reactivity and ease of ignition are often related to the melting point of the oxidizer, and the volatility of the reaction products determines the amount of gas that will be formed from a given oxidizer-fuel combination. Table 3.2 contains the physical and chemical properties of the common oxidizers, and Table 5.12 lists the melting and boiling points of some of the common reaction products.

Any oxygen-containing compound has the potential to serve as an oxidizer in an energetic mixture, provided that it is blended with a fuel that can provide sufficient energy upon oxidation to decompose the oxidizer and sustain the reaction.

Shidlovskiy has pointed out that metal-fluorine compounds should also have good oxidizer capability. For example, the reaction



is quite exothermic ($\Delta H = -70$ kcal/mole). However, the lack of stable, economical metal fluorides of the proper reactivity has limited research in this direction.¹

In summary, an oxidizer has two primary properties that determine its reactivity. One is its heat of decomposition, which indicates the amount of energy that must be

supplied by the oxidation of a fuel in order to liberate oxygen for subsequent reaction with more fuel and achieve propagation of the reaction. The second property of interest is the melting point of the oxidizer, which is a good indication of the temperature that must be reached in order for oxygen to be readily liberated from the oxidizer.

An oxidizer with a low melting point and a weakly endothermic—or even better, an exothermic—heat of decomposition should be capable of reacting with a fuel under extremely poor conditions, such as in very cold environments and with low heat output fuels. The classic example of this type of oxidizer is potassium chlorate, which can sustain combustion with poor fuels (such as sulfur or sucrose) under the most adverse conditions. On the other end of the reactivity scale, a combination of an active oxidizer with an energetic fuel, such as one of the active metal powders, will produce a highly reactive mixture and require great care in its preparation, handling, and use.

The other extreme for oxidizers will be those materials with highly endothermic heats of decomposition and high melting points, such as iron (III) oxide, Fe_2O_3 . Such materials will require a highly exothermic fuel (such as magnesium, aluminum, or zirconium) in order for a reaction to occur.

A comparison of two oxidizers, potassium chlorate (KClO_3) and iron(III) oxide (Fe_2O_3 —red iron oxide), shows the wide range of properties available for selection by a pyrotechnic formulator. Potassium chlorate will ignite and react with a wide range of fuels, while iron oxide requires a very energetic fuel in order for ignition and reaction to occur.

OXIDIZER SELECTION: A COMPARISON

	Potassium Chlorate, KClO_3	vs.	Iron(III) Oxide, Fe_2O_3
Melting point	336°C		1,565°C
Heat of decomposition	-10.6 kcal/mole		+197 kcal/mol

FUELS

REQUIREMENTS

In addition to an oxidizer, pyrotechnic mixtures will also contain one or more fuels—or electron donors—that react with the liberated oxygen from the oxidizer to produce an oxidized product plus heat. This heat will enable the high-energy chemist to produce a variety of possible effects: color, motion, light, smoke, or noise.

The desired pyrotechnic effect must be carefully considered when a fuel is selected to pair with an oxidizer for a high-energy mixture. Both the flame temperature that will be produced and the nature of the reaction products are important factors. The requirements for some of the major pyrotechnic categories are:

1. *Propellants*: A combination producing high reaction temperature, a large volume of low molecular weight gas, and a rapid burning rate is needed. Charcoal and organic compounds, such as polybutadiene, are often found

in these compositions because of the gaseous products formed upon their combustion. An energetic metal fuel such as aluminum can be added to speed up the burning rate by a combination of enhanced heat output and enhanced thermal conductivity for the burning material. Metal fuels will not enhance gas production in propellants, however, since their combustion products are largely solid metal oxides.

2. *Illuminating compositions*: A high reaction temperature is mandatory to achieve intense light emission, along with the presence in the flame of strong light-emitting species. Magnesium is commonly found in such mixtures due to its good heat output and high flame temperatures. The production of incandescent magnesium oxide particles in the flame aids in achieving good light intensity. Atomic sodium, present in vapor form in a flame, is a very strong light emitter, and sodium emission dominates the light output from the widely used sodium nitrate–magnesium compositions.
3. *Colored flame compositions*: A high reaction temperature produces maximum light intensity, but color quality depends upon having the proper emitters present in the flame, with a minimum of solid and liquid particles present that are emitting a broad spectrum of white light. Magnesium is sometimes added to colored flame mixtures to obtain higher intensity, but the color quality may suffer due to broad emission from MgO particles. Organic fuels (such as red gum and dextrine) are found in most color mixtures used in the fireworks industry, with magnalium (magnesium-aluminum alloy) now widely added to color compositions to raise flame temperature, color brightness, and heat output.
4. *Colored smoke compositions*: Gas evolution is needed to help disperse the smoke particles. High temperatures are not desirable here because decomposition of the complex organic dye molecules will occur. Metals are not found in these mixtures. Low-energy fuels such as sulfur and sugars are commonly employed.
5. *Ignition compositions*: Hot solid or liquid particles are desirable in igniter and first-fire compositions to ensure the transfer of sufficient heat to ignite the main composition. Fuels producing mainly gaseous products are not commonly used. Fuels such as boron and zirconium that produce good heat output and lots of hot particulate reaction products are often used.

A good fuel will react with oxygen (or a halogen like fluorine or chlorine) to form a stable compound, and substantial heat will be evolved. The considerable strength, and energetic formation, of the metal-oxygen and metal-halogen bonds in the reaction products accounts for the excellent fuel properties of many of the metallic elements.

A variety of materials can be used as fuels in energetic mixtures, and the choice of material will depend on a variety of factors—the amount of heat output required, ignitability, rate of heat release needed, cost of the materials, stability of the fuel and fuel-oxidizer pair, and amount of gaseous product desired. Fuels can be divided into three main categories: metals, nonmetallic elements, and organic compounds.

METALS

A good metallic fuel resists air oxidation and moisture, has a high heat output per gram, and is obtainable at moderate cost in a range of particle sizes, including very fine materials. Aluminum and magnesium, and alloys (magnalium) of these two metals, are the most widely used materials. Titanium, zirconium, manganese, zinc, tungsten, and other metals are also used in various applications.

The alkali and alkaline earth metals, such as sodium, potassium, barium, and calcium, would make excellent high-energy fuels, but except for magnesium, they are too reactive with moisture and atmospheric oxygen. Sodium metal, for example, reacts violently with water and must be stored in an inert organic liquid, such as xylene, to minimize its oxidation.

A metal can initially be screened for pyrotechnic possibilities by an examination of its standard reduction potential (Table 2.8). A readily oxidizable material will have a large, negative value, meaning it possesses little tendency to *gain* electrons and a significant tendency to *lose* them. Good metallic fuels will also be reasonably lightweight, producing high calories/gram values when oxidized. Table 3.4 lists some of the common metallic fuels and their properties.

Recent developments in the area of metallic fuels, such as aluminum, have largely focused on interest in nanopowders. While particles in the 1-micrometer range (1 micron, 1×10^{-6} m) have traditionally been considered fine, these new powders have particle sizes in the 10^{-8} to 10^{-9} meter range. These ultrafine powders exhibit the expected enhanced reactivity, and also pose some stability concerns—such as the possibility of being pyrophoric—with respect to oxidation due to their large surface area per gram.^{19,20}

TABLE 3.4
Properties of Metallic Fuels

Element	Symbol	Atomic Weight	Melting Point, °C ^a	Boiling Point, °C ^a	Heat of Combustion, kcal/gram ^b	Combustion Product	Grams of Fuel Consumed per Gram of O
Aluminum	Al	27.0	660	2,467	7.4	Al ₂ O ₃	1.12
Iron	Fe	55.8	1,535	2,750	1.8	Fe ₂ O ₃	2.32
Magnesium	Mg	24.3	649	1,107	5.9	MgO	1.52
“Magnalium”	Mg/Al (~50/50 alloy)	—	460	—	—	MgO/Al ₂ O ₃	1.32
Titanium	Ti	47.9	1,660	3,287	4.7	TiO ₂	1.50
Tungsten	W	183.8	3,410	5,660	1.1	WO ₃	3.83
Zinc	Zn	65.4	420	907	1.3	ZnO	4.09
Zirconium	Zr	91.2	1,852	4,377	2.9	ZrO ₂	2.85

^a R. C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, 63rd ed., Boca Raton, FL: CRC Press, 1982.

^b A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, OH, 1974.)

ALUMINUM (Al)

The most widely used metallic fuel is probably aluminum, with magnesium running a close second. Aluminum is reasonable in cost, lightweight, stable in storage, available in a variety of particle shapes and sizes, and can be used to achieve a variety of effects.²¹

Aluminum has a melting point of 660°C and a boiling point of approximately 2,500°C. Its heat of combustion is 7.4 kcal/gram. Aluminum is available in either flake or atomized form. The atomized variety consists of spheroidal particles. Spheres yield the minimum surface area (and hence minimum reactivity) for a given particle size, but this form will be the most *reproducible* in performance from batch to batch. Atomized aluminum, rather than the more reactive flake material, is used by the military for heat- and light-producing compositions because the variation in performance from shipment to shipment is usually less.

Large flakes, called *flitter aluminum*, are widely used by the fireworks industry to produce bright white sparks. Aluminum in fine flake form can be quite reactive with a range of oxidizers. A special pyro grade of aluminum is also available from some suppliers. This is a dark gray powder consisting of small particle sizes (less than 50 microns) and high surface area, and it is extremely reactive. The smaller the particle size of the flake aluminum, the more sensitive and reactive it will be. Fine flake aluminum is used to produce explosive mixtures for fireworks, and combinations of oxidizers with this pyro aluminum should only be prepared by skilled personnel, and only made in small batches. Their explosive power can be substantial, and they can be quite sensitive to ignition by spark and flame.

Aluminum surfaces are readily oxidized by the oxygen in the air, and a tight surface coating of aluminum oxide (Al₂O₃) is formed that protects the inner metal from further oxidation. Hence, aluminum powder can be stored for extended periods with little loss of reactivity due to air oxidation. Metals that form a loose oxide coating on exposure to the air, such as magnesium or iron, are not provided this surface protection, and extensive decomposition can occur during storage unless appropriate precautions are taken.

Compositions made with aluminum tend to be quite stable. However, moisture must be excluded if the mixture also contains a nitrate oxidizer. Otherwise, a reaction of the type

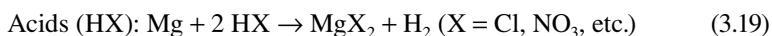


can occur, evolving heat and ammonia gas. This reaction is catalyzed and accelerated by the alkaline medium generated as the reaction proceeds, and autoignition is possible in a confined situation. A small quantity of a solid weak acid such as boric acid (H₃BO₃) can effectively retard this decomposition by neutralizing the alkaline products and maintaining a weakly acidic environment. The hygroscopicity of the oxidizer is also important in this decomposition process. Sodium nitrate and aluminum cannot be used together, due to the high moisture affinity of NaNO₃, unless the aluminum powder is coated with a protective layer of wax or similar material. Alternatively, the product can be sealed in moisture-proof packaging to exclude the presence of any water following the manufacturing process.¹

Potassium nitrate–aluminum compositions must be kept quite dry in storage to avoid decomposition problems, but mixtures of aluminum and nonhygroscopic barium nitrate can be stored with a minimum of precautions, as long as the composition does not actually get wet. Mixtures of magnesium metal with nitrate salts do not have this alkaline-catalyzed decomposition problem. A magnesium hydroxide, $\text{Mg}(\text{OH})_2$, coating on the metal surface apparently protects it from further reaction. This protection is not provided to aluminum metal by the alkaline-soluble aluminum hydroxide, $\text{Al}(\text{OH})_3$.

MAGNESIUM (MG)

Magnesium is a very reactive metal and makes an excellent fuel under the proper conditions. It is oxidized by moist air to form magnesium hydroxide, $\text{Mg}(\text{OH})_2$, and it readily reacts with all acids, including weak species such as vinegar (5% acetic acid) and boric acid. The reactions of magnesium with water and an acid (HX) are shown below:



Even the ammonium ion, NH_4^+ , is acidic enough to react with magnesium metal. Therefore, ammonium perchlorate and other ammonium salts should not be used with magnesium unless the metal surface is coated with linseed oil, paraffin oil, or a similar material.

Chlorate and perchlorate salts, in the presence of moisture, will oxidize magnesium metal, destroying the pyrotechnic effect during storage. Nitrate salts appear to be considerably more stable with magnesium.² Again, coating the metal with an organic material, such as paraffin, will increase the storage lifetime of the composition. A coating of potassium dichromate on the surface of the magnesium has also been recommended to aid in stability,² but the toxicity of this material makes it of questionable value for industrial applications.

Magnesium has a heat of combustion of 5.9 kcal/gram, a melting point of 649°C, and a low boiling point of 1,107°C. This low boiling point allows excess magnesium in a mixture to vaporize and burn with oxygen in the air in the pyrotechnic flame, providing additional heat (and light) in flare compositions. No heat absorption is required to decompose an oxidizer when excess magnesium reacts with atmospheric oxygen; hence, the extra heat gained by incorporating the excess magnesium into the mixture is substantial.

Magnesium metal is also capable of reacting with other metal ions in an electron-transfer reaction, such as



This process becomes much more probable if a composition is moistened, again pointing out the variety of problems that can be created if water is added to a magnesium-containing mixture. The standard potential for the Cu^{2+}/Mg system is +2.72 volts, indicating a very spontaneous process. Therefore, Cu^{2+} , Pb^{2+} , and other readily reducible metal ions must not be used in magnesium-containing compositions.

MAGNALIUM (MAGNESIUM-ALUMINUM ALLOY)

A material that has found significant popularity in pyrotechnics over the past thirty-five years is the 50/50 alloy of magnesium and aluminum, termed magnalium, with a formula of Al_2Mg_3 and a melting point of 460°C .² The alloy is considerably more stable than aluminum metal when combined with nitrate salts, and reacts much more slowly than magnesium metal with weak acids. It therefore offers stability advantages over both of its component materials.

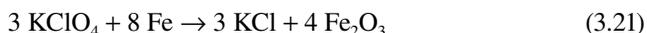
The Chinese pioneered wide use of magnalium in firework items to produce attractive white sparks, crackling effects, and bright color compositions. Shimizu also reports that a branching spark effect can be produced using magnalium with a black-powder-type composition.² Magnalium is now used widely around the world in the manufacturing of entertainment pyrotechnics.

IRON

Iron, in the form of fine filings, will burn and incandesce and can be used to produce attractive gold sparks, such as in the traditional wire fireworks sparkler. The small percentage (less than 1%) of carbon in steel can cause an attractive branching of the sparks due to carbon dioxide gas formation as the metal particles burn in air.

Iron filings are quite unstable on storage, however. They readily convert to iron(III) oxide (rust— Fe_2O_3) in moist air, and filings are usually coated with a paraffin-type material prior to use in a pyrotechnic mixture.

Iron is capable of producing a decent heat output when combined with a strong oxidizer such as potassium perchlorate. A composition consisting of iron and KClO_4 has been used in a variety of devices, including thermal batteries, when a mild heat source is required. The primary reaction that occurs should be



which is stoichiometric at 48 parts KClO_4 and 52 parts iron by weight.

OTHER METALS

Titanium metal (Ti) offers some attractive properties to the high-energy chemist. It is quite stable in the presence of moisture and most chemicals, and produces a brilliant silver-white spark and light effects with oxidizers. It is also possible to add titanium particles to color compositions and achieve an attractive effect of both color flame and white sparks. Lancaster feels that titanium is a safer material to use than either magnesium or aluminum, and recommends that it be used in place of iron filings in fireworks “fountain” items, due to its greater stability.²² Cost seems to be the major factor keeping titanium from being a much more widely used fuel.

Zirconium (Zr) is another reactive metal, but its extreme spark sensitivity is a major problem restricting its wider use in high-energy compositions. Zirconium in combination with potassium perchlorate (ZPP composition) is being used as an igniter material in electrically fired systems, and zirconium with iron(III) oxide is used in the military

A1A ignition composition. Flame temperatures of oxidizer-zirconium compositions typically exceed 4,000°C. If you want a really hot pyrotechnic composition—to light another energetic material very quickly—zirconium is the fuel of choice.

The spark sensitivity of fine zirconium by itself—without any oxidizer present—is usually less than 1 millijoule of spark energy, again putting zirconium compositions in a class by themselves. It makes no difference if the oxidizer is iron(III) oxide or potassium perchlorate, the resulting composition with zirconium will be very spark sensitive. Therefore, zirconium is usually shipped wet, blended wet with oxidizer, and is finally allowed to dry when the composition has been incorporated in small amounts on bridgewires for electrical ignition or in other similar systems.

In summary, zirconium-oxidizer mixtures will be very sensitive to spark, and they will react very quickly to produce high-temperature sparks ideal for ignition compositions. When you need to light something very quickly with high reliability, these might be materials you would choose. Otherwise, the sensitivity hazards of zirconium preclude wider use of the material.

NONMETALLIC ELEMENT FUELS

Several readily oxidized nonmetallic elements have found widespread use in the field of pyrotechnics. The requirements again are stability to air and moisture, good heat per gram output, and reasonable cost. Materials in common use include sulfur, boron, silicon, and phosphorus. Their properties are summarized in Table 3.5.

TABLE 3.5
Properties of the Nonmetallic Elements Used as Fuels in High-Energy Mixtures

Element	Symbol	Atomic Weight	Melting Point, °C ^a	Boiling Point, °C ^a	Heat of Combustion, kcal/gram ^{b,c}	Combustion Product	Grams of Fuel Consumed per Gram of O
Boron	B	10.8	2,300	2,550	14.0	B ₂ O ₃	0.45
Carbon (charcoal)	C	~12	Decomp.	—	7.8	CO ₂	0.38
Phosphorous (red)	P	31.0	590	Sublimes	5.9	P ₂ O ₅	0.78
Phosphorous (yellow)	P ₄	124.0 (as P ₄)	44	—	5.9	P ₂ O ₅	0.78
Silicon	Si	28.1	1,410	2,355	7.4	SiO ₂	0.88
Sulfur	S	32.1	119	445	2.2	SO ₂	1.00

^a R. C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, 63rd ed., Boca Raton, FL: CRC Press, 1982.

^b A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, OH, 1974.)

^c T. Shimizu, in K. Kosanke et al., *Pyrotechnic Chemistry, Journal of Pyrotechnics*, Whitewater, CO, 2004, chap. 2.

SULFUR

The use of sulfur as a fuel in pyrotechnic compositions dates back over one thousand years, and the material remains a widely used component today in black powder, colored smoke mixtures, and firework compositions. For pyrotechnic purposes, the material termed flour of sulfur that has been crystallized from molten sulfur is preferred. Sulfur purified by sublimation—termed *flowers of sulfur*—often contains significant amounts of oxidized, acidic impurities and can be quite hazardous in high-energy mixtures, especially those containing a chlorate oxidizer.²³

Sulfur has a particularly low (119°C) melting point. It is a rather poor fuel in terms of heat output, but it frequently plays another very important role in pyrotechnic compositions. It can function as a tinder, or a fire starter. Sulfur undergoes exothermic reactions at low temperature with a variety of oxidizers, and this heat output can be used to trigger other, higher-energy reactions with better fuels. Sulfur's low melting point provides a liquid phase, at low temperature, to assist the ignition process. The presence of sulfur, even in a small percentage, can dramatically affect the ignitability and ignition temperature of high-energy mixtures. Sulfur, upon combustion, is converted to sulfur dioxide gas and sulfate salts (such as potassium sulfate, K_2SO_4). Sulfur is also found to act as an oxidizer in some mixtures, winding up as the sulfide ion (S^{2-}) in species such as potassium sulfide (K_2S), a detectable component of black powder combustion residue.

When present in large excess, sulfur may volatilize out of the burning mixture as a yellowish white smoke. A 1:1 ratio of potassium nitrate and sulfur makes a respectable smoke composition employing this behavior.

BORON

Boron is a reasonably stable element, produces no gas upon oxidation, and can be oxidized to yield good heat output. The low atomic weight of boron (10.8) makes it an excellent fuel on a calories/gram basis. Boron has a high melting point (2,300°C), and it can prove hard to ignite when combined with a high-melting oxidizer. With low-melting oxidizers, such as with potassium nitrate (a mixture referred to in the pyrotechnics industry as $BKNO_3$), boron ignites more readily, yielding good heat production. The low melting point of the oxide product (B_2O_3) can interfere with the attainment of high reaction temperatures, however.¹

Boron is a relatively expensive fuel, but it frequently proves acceptable for use on a cost basis because only a small percentage is required (remember, it has a low atomic weight). For example, the reaction



burns well with only 5% by weight boron in the composition.⁶ Boron is virtually unknown in the fireworks industry, but it is a widely used fuel in igniter and delay composition for military and aerospace applications.

If there is a negative associated with boron, it is its tendency to readily undergo air oxidation, especially in the presence of moisture. This problem is aggravated

by the significant weight gain that occurs when boron undergoes oxidation. In the reaction



it can be calculated that 21.6 grams (2 moles) of boron will convert to 69.6 grams of boron oxide—a tripling of the weight. Hence, the oxidation of a small percentage of the boron in a container awaiting measurement for addition to a mixer will cause the actual weight of boron being added to the mixture to be significantly less than the intended value. In a boron sample that has undergone 5% oxidation, the actual weight of elemental boron remaining in 10 grams of the material has been reduced to 8.55 grams—the remainder is boron oxide. This will cause a significant change in the performance of a pyrotechnic composition prepared from the oxidized boron. The solution is to wash boron with water (boron oxide is water soluble) prior to use, dry it in a low-humidity environment, and store it in a tightly sealed container until it is weighed out.

SILICON

In many ways similar to boron, silicon is a safe, relatively inexpensive fuel used in igniter and delay compositions. It has a high melting point (1,410°C), and combinations of this material with a high-melting oxidizer may be difficult to ignite. The oxidation product, silicon dioxide (SiO_2), is high melting and, importantly, is environmentally acceptable. Silicon has been used for a number of years, with red lead oxide (Pb_3O_4) as the oxidizer, to produce fast-burning delay mixtures for use in blasting caps. The delay columns are manufactured with a range of delay times, and each provides a brief time lag (measured in milliseconds) between the firing signal and detonation of the cap. This allows the explosives engineer to design a blasting pattern whereby all of the explosive charges that have been carefully and systematically placed in a quarry or mine do not detonate simultaneously. The resulting brief delays produce a blast pattern that can aid greatly in reducing fly rock and ground vibrations compared to a blast where all charges are detonated simultaneously.

The reaction of silicon with iron oxide is an example of a moderate-reactivity, low-gas formulation seeking an application. The reaction zone moves through the composition as an incandescent zone, with minimum flaming. The reaction products (iron and silicon dioxide) are environmentally acceptable by most current criteria. The reaction is



which is stoichiometric at 83% iron(III) oxide and 17% silicon.

PHOSPHORUS

Phosphorus is an example of a material that is too reactive to be of any general use as a pyrotechnic fuel, although it is employed in military white smoke compositions,

and it has traditionally been used in toy pistol caps and trick noisemakers (party poppers) to produce an audible report.^{22, 23}

Phosphorus is available in two forms, white (or yellow) and red. White phosphorus appears to be molecular, with a formula of P_4 . It is a waxy solid with a melting point of 44°C , and ignites spontaneously on exposure to air. It must be kept cool and is usually stored under water. It is highly toxic in both the solid and the vapor form and causes burns on contact with the skin. Its use in pyrotechnics is limited to incendiary and white smoke compositions. The white smoke consists of the combustion product combined with atmospheric moisture, and is primarily phosphoric acid (H_3PO_4).

Red phosphorus is somewhat more stable, and is a reddish brown powder with a melting point of approximately 590°C (in the absence of air). In the presence of air, red phosphorus ignites near 260°C .² Red phosphorus is insoluble in water. It is easily ignited by spark or friction, and is quite hazardous any time it is mixed with oxidizers or flammable materials. Its fumes are highly toxic.³

Red phosphorus is mixed as a water slurry with potassium chlorate for use in toy caps and novelty noisemakers such as party poppers. These mixtures are quite sensitive to friction, impact, and heat, and a large amount of such mixtures must never be allowed to dry out in bulk form. Red phosphorus is also used in white smoke mixtures, and several examples can be found in Chapter 9.

SULFIDE COMPOUNDS

Several metallic sulfide compounds have been used as fuels in pyrotechnic compositions. Antimony trisulfide, Sb_2S_3 , is a reasonably low-melting material (m.p. 548°C) with a heat combustion of approximately 1 kcal/gram. It is easily ignited and can be used to aid in the ignition of more difficult fuels, serving as a tinder in the same way that elemental sulfur does. It has been used in the fireworks industry for white fire compositions and has been used in place of sulfur in flash and sound mixtures with potassium perchlorate and aluminum.

Realgar (arsenic disulfide, As_2S_2) is an orange powder with a melting point of 308°C and a boiling point of 565°C .² Due to its low boiling point, it has been used in yellow smoke compositions (in spite of its toxicity), and has also been used to aid in the ignition of difficult mixtures.

The use of all arsenic compounds, including realgar, is prohibited in common fireworks (the type purchased by individuals) by regulations of the U.S. Consumer Product Safety Commission.²⁴

ORGANIC FUELS

A variety of organic (carbon-containing) fuels are commonly employed in high-energy compositions. In addition to providing heat, these materials also generate significant gas pressure through the production of carbon dioxide (CO_2) and water vapor in the reaction zone.

The carbon atoms in these molecules are oxidized to carbon dioxide if sufficient oxygen is present. Carbon monoxide (CO) or elemental carbon is produced in an oxygen-deficient atmosphere, and a sooty flame is observed if a substantial amount

of carbon is generated. The hydrogen present in organic compounds winds up usually as water molecules. For a fuel of formula $C_xH_yO_z$, x moles of CO_2 and $y/2$ moles of H_2O will be produced per mole of fuel that is burned. To completely combust this fuel, $x + y/2$ moles of oxygen gas ($2x + y$ moles of oxygen atoms) will be required. The amount of oxygen that must be provided by the oxidizer in a high-energy mixture is reduced by the presence of oxygen atoms in the fuel molecule. The balanced equation for the combustion of glucose is shown below:



Only six oxygen molecules are required to oxidize one glucose molecule, due to the presence of six “internal” oxygen atoms in glucose. There are eighteen oxygen atoms on both sides of the balanced equation.

A fuel that contains only carbon and hydrogen—termed a *hydrocarbon*—will require more moles of oxygen per gram for complete combustion than will an equal weight of glucose or other oxygen-containing compound. A greater weight of oxidizer is therefore required per gram of fuel when a hydrocarbon-type material is used.

The grams of oxygen needed to completely combust a given fuel can be calculated from the balanced chemical equation. Use the Pyro Valence method discussed in Chapter 3 to determine the proper ratio of oxidizer to fuel for the stoichiometric composition. A sample calculation is shown below:

Potassium chlorate with glucose

Valence of $KClO_3 = -6$

Valence of glucose = +24

Mole ratio = 1:4

Balanced equation	$C_6H_{12}O_6 + 4 KClO_3 \rightarrow 6 CO_2 + 6 H_2O + 4 KCl$	
Moles	1	4
Grams	180	490
Weight %	26.9	73.1

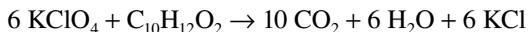
For polymers, the repeat unit in the polymer chain is used for Pyro Valence calculations, using the formula weight of the repeat unit for mass calculations. For example, starch can be represented by $(C_6H_{10}O_5)_n$, with a formula mass per repeat unit of 162 and a Pyro Valence of +24 ($+24 + 10 - 10 = +24$). The Pyro Valence procedure discussed in Chapter 2 provides the easiest way to balance oxidizer-organic fuel systems, including those that contain polymers.

For example, assume that a fuel with molecular formula (or polymer repeat unit) of $C_{10}H_{12}O_2$ is to be used in a new pyrotechnic composition. First, we determine its Pyro Valence:

C H O

Pyro Valence = $10(+4) + 12(+1) + 2(-2) = +48$ (very fuel rich)

To balance this material with an oxidizer, such as KClO_4 , with a valence of -8 , you will need six KClO_4 's ($6 \times 8 = 48$) per mole of organic compound, or



Balanced! It couldn't be any easier.

The more highly oxidized—or oxygen rich—a fuel is, the smaller its heat output per gram will be when it undergoes combustion. The flame temperature will also be lower for compositions using the highly oxidized fuel. Also, fuels that exist as hydrates (containing water of crystallization) will evolve less heat than similar, non-hydrated species due to the absorption of heat required to vaporize the water present in the hydrates. It is also important to include the molecular weight of the water molecule (18 grams/mole) in the calculation of the molecular weight of the hydrated fuel. A number of gums, resins, waxes, and similar natural products are available for use in energetic mixtures, and data on the base compositions and heats of formation for many of them have been published.^{25,26}

SPECIFIC ORGANIC FUELS

Two hot organic fuels are shellac and red gum. Shellac, secreted by an Asian insect, contains a high percentage of trihydroxypalmitic acid, $\text{CH}_3(\text{CH}_2)_{11}(\text{CHOH})_3\text{COOH}$. This molecule contains a low percentage of oxygen and produces a high heat/gram value.² Red gum is a complex mixture obtained from an Australian tree exudate that is harvested on Kangaroo Island. Its approximate base formula is $\text{C}_6\text{H}_7\text{O}_2$, with a Pyro Valence of $+27$ per 111 grams of material.²⁵ It has excellent fuel characteristics and a low melting point/decomposition temperature to aid in ignition, and tends to give a very white flame when combined with an oxidizer—there is a minimum of orange color in the flame, and a minimum of smoke is produced. Thus, it can be used in high-quality color compositions with minimal interfering effects.

Charcoal is another organic fuel, and it has been employed in high-energy mixtures for over a thousand years. It is prepared by heating wood in an oxygen-depleted environment. Volatile decomposition products and moisture are driven off and a residue that is primarily carbon remains. There can be significant batch-to-batch variation between charcoals from the same wood source. Shimizu reports that a highly carbonized sample of charcoal showed a 91:3:6 ratio of C, H, and O atoms.² A representative formula of $\text{C}_{16}\text{H}_{10}\text{O}_2$ has been published for charcoal, with a formula weight of 235 g/mole and a Pyro Valence of $+72$.²⁶

The pyrotechnic behavior of charcoal may also vary greatly, depending upon the type of wood used to prepare the material. The surface area and extent of conversion to carbon may vary widely from wood to wood and batch to batch, and each preparation must be checked for proper performance.²⁷ Historically, willow and alder have been the woods preferred for the preparation of charcoal by U.S. black powder manufacturers. Grape vines, eucalyptus, and numerous other carbon-containing materials have also been used elsewhere around the world.

Charcoal is frequently the fuel of choice when high heat and gas output as well as a rapid burning rate are desired. The addition of a small amount of charcoal to a sluggish composition will usually accelerate the burning rate and facilitate ignition. Being largely carbon in composition, charcoal will have a high fuel/gram content, and a Pyro Valence value of +4/atomic weight of 12 can be used as an approximation in calculations if the actual carbon content of the charcoal is unknown.

Larger particles of charcoal in a pyrotechnic mixture will produce attractive orange sparks in the flame, a property that is often used to advantage by the fireworks industry. In this case, they are considered to be an added component that does not participate in the primary pyrotechnic reaction, and are not included in oxygen balance calculations.

CARBOHYDRATES

The carbohydrate family consists of a large number of naturally occurring oxygen-rich organic compounds. The simplest hydrates—or sugars—have molecular formulas fitting the pattern $(C \cdot H_2O)_n$, and appeared to early chemists to be hydrated carbon. The more complex members of the family deviate from this pattern slightly.²⁵

Examples of common sugars include glucose ($C_6H_{12}O_6$), lactose ($C_{12}H_{22}O_{11}$), and sucrose ($C_{12}H_{22}O_{11}$). Starch is a complex polymer composed of glucose units linked together. The molecular formula of starch is similar to $(C_6H_{10}O_5)_n$, and the molecular weight of starch is typically greater than 1 million. Reaction with acid breaks starch down into smaller units. Dextrine, a widely used pyrotechnic fuel and binder, is partially hydrolyzed corn starch. Its molecular weight, solubility, and chemical behavior may vary considerably from supplier to supplier and from batch to batch. The testing of all new shipments of dextrine, as with most chemicals, is required for reproducibility and performance in pyrotechnic production.

The sugars also represent another example of the use of electronegativity and partial charges to explain reactivity. In the various sugar molecules, there are usually oxygen atoms bonded to a series of consecutive carbon atoms. This creates a chain of carbon atoms with adjacent partial positive charges, and tends to result in low decomposition temperatures for compounds in the sugar family. Cooks are familiar with the tendency of sugars to caramelize at low temperature in a cooking pan. This caramelization is the result of bond breaking and subsequent polymerization of the sugar to form tasty treats for the dessert table. In pyrotechnics, this bond breaking and the creation of reactive free radicals are responsible for the low ignition temperatures observed with many oxidizer-sugar compositions.

This is particularly true when potassium chlorate is the oxidizer. We have discussed previously the fact that potassium chlorate begins decomposing and evolving reactive oxygen at temperatures under 200°C. When combined with a sugar that is also decomposing at low temperatures, we see ignition temperatures that are under 200°C for potassium chlorate–glucose and potassium chlorate–sucrose compositions (see Chapter 5). When a differential thermal analysis is run on such mixtures, an ignition exotherm is observed right as you approach the melting point

and caramelization temperature of the specific sugar. Studies with other organic fuels have confirmed that it is the decomposition of the sugar molecules, rather than merely the solid-liquid phase change, that is responsible for the onset of ignition.

The simpler sugars are used as fuels in various pyrotechnic mixtures. They tend to burn with colorless flame and give off less heat per gram than less oxidized organic fuels. Lactose is used with potassium chlorate in some colored smoke mixtures to produce a low-temperature reaction capable of volatilizing an organic dye with minimum decomposition of the complex dye molecules. The simpler sugars can be obtained in high purity at a moderate cost, making them attractive fuel choices. Also, toxicity problems tend to be minimal with these fuels. Concerns with sugars include their hygroscopicity, as well as the fact that some sugars occur as hydrates, with water as a component in the solid material.

OTHER ORGANIC FUELS

The number of possible organic fuels is enormous. Considerations in selecting a candidate include:

1. *Extent of oxidation*: This will be a primary factor in the heat output per gram of the fuel.
2. *Melting point*: A low melting point, particularly when accompanied by a low decomposition temperature, can aid in ignitability and reactivity. A melting point that is too low can cause production and storage problems. One hundred degrees Celsius might be a good minimum value for a melting point.
3. *Boiling point/volatility*: If the fuel readily vaporizes or sublimates, the storage life of the mixture will be brief unless precautions are taken in packaging to prevent loss of the material.
4. *Chemical stability*: An ideal fuel should be available commercially in a high state of purity, and should maintain that high purity during storage. Materials that are easily air oxidized, such as aldehydes, are usually poor fuel choices.
5. *Solubility*: Organic fuels frequently double as binders, and some solubility in water, acetone, or alcohol is required to obtain good binding behavior.

Materials that have been used in pyrotechnic mixtures include nitrocellulose, polyvinyl alcohol, stearic acid, hexamethylenetetramine, kerosene, epoxy resins, and unsaturated polyester resins such as Laminac[®]. Salts of benzoic acid and its derivatives, such as potassium benzoate and sodium salicylate, also can serve as energetic fuels that are high melting and quite stable. The properties of most of these fuels can be found in a handbook prepared by the U.S. Army.³ Table 3.6 contains information on a variety of organic compounds that are of interest to the high-energy chemist.

TABLE 3.6
Properties of Some Common Organic Fuels

Compound	Formula	Molecular Weight	Melting Point, °C ^a	Grams of Fuel Consumed per Gram of O	Heat of Combustion, kcal/mol ^a
Monomers					
Glucose	C ₆ H ₁₂ O ₆	180.2	146 (anhydrous)	0.94	670
Naphthalene	C ₁₀ H ₈	128.2	80.5	0.33	1232 ^b
Shellac	Primarily C ₁₆ H ₃₂ O ₅	ca. 304	ca. 120	ca. 0.44	—
Stearic acid	C ₁₈ H ₃₈ O ₂	284.5	69.5	0.34	2,712
Sucrose	C ₁₂ H ₂₂ O ₁₁	342.3	188 (decomposes)	0.89	1,351
Polymers					
Dextrine	(-C ₆ H ₁₀ O ₅ -) _n • H ₂ O	—	Decomposes	ca. 0.94	ca. 4,179
Laminac	Polyester-styrene copolymer	—	ca. 200 (decomposes)	—	—
Nitrocellulose	(C ₆ H _{10-x} O _{5-x} (ONO ₂) _x) _n	—	ca. 200 (decomposes)	—	2,409
Polyvinyl chloride	(-CH ₂ CHCl-) _n	ca. 250,000	ca. 80 (softens)	ca. 0.78	4,375
Starch	(C ₆ H ₁₀ O ₅) _n	—	Decomposes	ca. 0.84	4,179

^a U.S. Army Material Command, *Engineering Design Handbook: Properties of Materials Used in Pyrotechnic Compositions*, Military Pyrotechnic Series, Part Three, Washington, DC, 1963 (AMC Pamphlet 706-187).

^b R. C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, 63rd ed., Boca Raton, FL: CRC Press, 1982.

BINDERS

A pyrotechnic composition will usually contain a small percentage (typically 2 to 6% by weight) of an organic polymer that functions as a binder, holding all of the components together in a homogeneous blend and providing mechanical strength to pressed and consolidated grains of composition. These binders, being organic compounds, will also serve as fuels in the mixture and generate gaseous reaction products. Each binder will have a unique heat of combustion, melting/decomposition temperature, and gas volume/gram, and therefore binders cannot be merely replaced on a pound-for-pound basis in a pyrotechnic formulation without the expectation that doing so might produce significant differences in exothermicity, burn rate, sensitivity to ignition stimuli, and gas output.²⁸⁻³⁰ Table 3.7 lists the fuel capacity of some common binders, and Table 3.8 lists the heats of combustion of some common binders.

TABLE 3.7
Fuel Capacity of Some Common Binders

Binder	Monomer Unit	Grams/Unit	Pyro Valence/Unit	Pyro Valence/ Gram
Paraffin	C ₂ H ₄	28	+12	+0.429
Polybutadiene	C ₄ H ₆	54	+22	+0.407
Waxes	~C ₃₆ H ₇₂ O ₂	536	+212	+0.396
Linseed oil	~C ₁₇ H ₃₆ O ₂	272	+100	+0.368
Polyvinyl alcohol (PVA)	C ₂ H ₄ O	44	+10	+0.227
VAAR (vinyl alcohol–acetate resin)	C ₆ H ₁₀ O ₃	130	+28	+0.215
Polyvinyl acetate	C ₄ H ₆ O ₂	86	+18	+0.209
Laminac	~C ₂₀ H ₁₆ O ₉	400	+78	+0.195
Polyvinyl chloride (PVC)	C ₂ H ₃ Cl	62.5	+10	+0.160
Dextrine, starch, and gums	C ₆ H ₁₀ O ₅	162	+24	+0.148
Viton®	C ₂ H ₂ F ₂	64	+8	+0.125
Alloprene (Parlon®)	C ₁₀ H ₁₁ Cl ₇	380	+44	+0.116
Nitrocellulose	C ₁₂ H ₁₅ N ₅ O ₁₀	389	+43	+0.111 (12.5% N)
Teflon	C ₂ F ₄	100	−4 (→ C)	−0.040

Without the binder, component materials might well segregate during manufacture and storage due to variations in density and particle size. The granulation process, in which the oxidizer, fuel, and other components are blended with the binder (and usually a suitable solvent) to produce grains of homogeneous composition, is often a critical step in the manufacturing process. Solvent, if used, is evaporated following granulation, leaving a dry, homogeneous material. Some liquid binders “cure” on exposure to air or by catalytic action, and a solvent might not be required in these systems. It is important to note that a solvent for a binder should not be capable of either reacting with or dissolving the oxidizer or the fuel. If one of the reactive components (oxidizer, primary fuel) dissolves to a significant extent in the solvent, its particle size will likely change when the solvent evaporates and the material is regenerated as a solid. This could cause variations in pyrotechnic performance.

In addition to aiding in achieving and maintaining homogeneity in the composition, binders reduce dusting in manufacturing operations, permit control of bulk density through granulation, and—again, in an extremely important role—provide mechanical strength to compositions when they are pressed or formed into specific configurations by acting like a glue to hold the composition together.

Dextrine (produced from corn starch), for example, has been widely used as a binder in the fireworks industry. Water is used as the wetting/activating agent for dextrine, avoiding the cost, environmental issues, and hazards associated with the

TABLE 3.8
Heats of Combustion and Oxidizer Consumption of Various Binders

Binder	Heat of Combustion (kcal/gram) ^a	Weight of KClO ₄ Consumed by 1 Gram of Binder	Weight of PbCrO ₄ Consumed by 1 Gram of Binder
Paraffin	10.8	7.42	27.7
Polybutadiene	—	7.04	26.3
Waxes	10	6.85	25.5
Linseed oil	8.3	6.37	23.7
PVA	ca. 5	3.93	14.6
VAAR	ca. 5–6	3.72	13.9
Polyvinyl acetate	5.5	3.62	13.5
Laminac	—	3.37	12.6
Polyvinyl chloride (PVC)	4.8	2.77	10.3
Dextrine/starch/gums	4.2	2.56	9.55
Viton [®]	—	2.16	8.06
Alloprene (Parlon [®])	3.3	2.01	7.48
Nitrocellulose	2.6	1.92	7.16 (12.5% N)
Teflon	—	0.692 (→ CO ₂)	2.58

^a R. C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, 63rd ed., Boca Raton, FL: CRC Press, 1982; T. J. Barton et al., The Influence of Binders in Pyrotechnic Reactions—Magnesium-Oxidant Systems, presented at 9th International Pyrotechnic Seminar, Colorado Springs, CO, August 1984.

use of organic solvents. Water-activated binders can only be used when the water does not react with one or more of the components of the mixture, or produce a particle size change in a component. Thorough drying will be required later in the manufacturing process to fully remove the water from the composition.

The U.S. military has used a material called *vinyl alcohol–acetate resin* (VAAR) as one of its primary binders for pyrotechnic compositions. VAAR is able to produce a good binding effect at low percentage by weight in many compositions compared to many of the other common binders. It is soluble in a methyl alcohol–methyl acetate solvent blend, and displays excellent long-term stability with a variety of compositions.

Other common binders include nitrocellulose (of lower than 12.6% nitrogen content, with acetone as the solvent), polyvinyl alcohol (used with water), and Laminac (an unsaturated polyester crosslinked with styrene—the material is a liquid until cured by catalyst, heat, or both, and no solvent is required). Epoxy binders can also be used in liquid form during the mixing process, and then allowed to cure to leave a final, rigid product; the caution here is the fact that many epoxy curing agents are amine compounds, which are basic. Be sure the epoxy system is compatible with all other components in the composition.

In selecting a binder, the chemist seeks a material that will provide good homogeneity with the use of a minimum of binder. Organic materials will reduce the

flame temperatures of compositions containing metallic fuels, and they can impart an orange color to flames if incomplete combustion of the binder occurs and carbon forms in the flame. A binder should be neutral and nonhygroscopic to avoid the problems that water and an acidic or a basic environment can introduce. For example, magnesium-containing mixtures require the use of a nonaqueous binder/solvent system, because of the reactivity of magnesium metal toward water. When iron is used in a composition, pretreatment of the metal with a wax or other protective coating is advisable, especially if an aqueous binding process is used.

MOST BINDERS ARE ALSO FUELS

Binders are critical components for energetic mixtures. In addition to their binding role, however, it is important to remember that most binders have fuel capability as well. At the 2 to 5% level by weight, they can affect ignition temperature, burn rate, ignition sensitivity, gas output, water resistance, and hygroscopicity of a composition. Any change in binder—either the use of a new material or the use of a different percentage in a composition—requires a careful reevaluation of the properties of an energetic mixture, including sensitivity to ignition. Table 3.9, showing the effect of binder percentage in a sodium nitrate–magnesium system, illustrates this point. The initial composition is 60 grams NaNO_3 and 40 grams Mg, and the table shows the grams of NaNO_3 consumable by the binder. A sample calculation is below:

$$\text{NaNO}_3 \text{ Pyro Valence/gram} = -5 \text{ P.V./mole} / 85 \text{ grams/mole} = -0.0588$$

$$\text{Polybutadiene (PB) Pyro Valence/gram} = +22 \text{ P.V./unit} / 54 \text{ grams/unit} = +0.407 \text{ for PB}$$

TABLE 3.9
Effect of Binder Percentage on the 60/40 Sodium Nitrate/Magnesium System

Additional Grams of Binder	Grams of Sodium Nitrate Consumable by Binder				
	PB	PVA	VAAR	Gum	NC
1	6.9	3.9	3.7	2.5	1.9
2	13.8	7.7	7.3	5.0	3.8
3	20.1	11.6	11.0	7.6	5.7
4	27.7	15.4	14.6	10.1	7.6
5	34.6	19.3	18.3	12.6	9.5
6	41.5	23.2	22.0	15.2	11.3
8	55.4	30.9	29.3	20.2	15.1
10	69.2	38.6	36.6	25.2	18.9

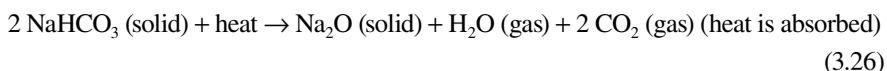
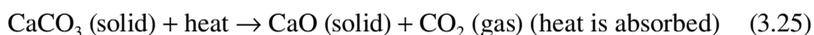
Note: PB = polybutadiene, PVA = polyvinyl alcohol, VAAR = vinyl alcohol–acetate copolymer, Gum = starch or gum, NC = 12.5% nitrocellulose.

Therefore, the weight ratio for NaNO_3/PB will be $0.407/0.0588 = 6.9$, to make the sum of the Pyro Valences = 0 (or produce a balanced or stoichiometric mixture of oxidizer and fuel binder). One gram of polybutadiene (PB) will consume 6.9 grams of sodium nitrate when the mixture is ignited. The conclusion drawn here is that the binder (or most organic compounds) present at a relatively low level can be a significant consumer of the available oxygen in a pyrotechnic mixture.

RETARDANTS

Occasionally, a pyrotechnic mixture will function quite well and produce the desired effect, except for the fact that the burning rate is a bit too fast. A material is needed that will slow down that reaction without otherwise affecting performance. This can be accomplished by altering the ratio of ingredients (e.g., typically by reducing the amount of fuel) or by adding an inert component to the composition. Excess metallic fuel is less effective as a coolant because of the ability of many fuels, such as magnesium, to react with the oxygen in the air and liberate heat. Also, metals tend to be excellent heat conductors, and an increase in the metal percentage can speed up a reaction by facilitating heat transfer through the composition during the burning process.

Materials that decompose at elevated temperatures with the absorption of heat (endothermic decomposition) can work well in some systems as rate retardants. Calcium and magnesium carbonate, and sodium bicarbonate are sometimes added to a mixture for this purpose.



However, gas generation occurs that may or may not affect the performance of the mixture.

Although endothermic, these reactions are thermodynamically spontaneous at high temperature due to the favorable entropy change associated with the formation of random gaseous products from solid starting materials.

Inert diluents such as clay and diatomaceous earth can also be used to retard burning rates. These materials absorb heat and separate the reactive components, thereby slowing the pyrotechnic reaction.

CATALYSTS

Catalysts have been rarely used in pyrotechnic compositions over the years, although there has been considerable interest in the use of catalysts to accelerate the decomposition of oxidizers in propellant formulations. Catalysts work by providing an alternate reaction pathway of lower activation energy than the primary (uncatalyzed) pathway. In energetic mixtures, the role of the catalyst is frequently to accelerate the

decomposition of the oxidizer, often by providing a reactive surface site where the breakdown can occur.

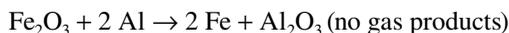
It is usually possible to obtain the desired burn rate with a pyrotechnic mixture by the appropriate selection of components as well as by varying particle sizes of the components and adjusting the fuel-to-oxidizer ratio. Interest in propellants has continued to focus on faster and faster burning materials, however, and hence the interest in catalysts has become significant.

Ammonium perchlorate is the primary oxidizer used for solid rocket propellant formulations, in large part because of its gas-generating capabilities. Ammonium perchlorate has been shown to be capable of catalytic decomposition, with metal oxides such as iron(III) oxide the most commonly used materials. A low percentage of catalyst added to a propellant formulation can produce a significant increase in propellant burn rate.

GAS VOLUME

The selection of an oxidizer and a fuel (and binder) for a pyrotechnic or propellant composition, together with the weight ratio to be used, determines the heat output as well as the gas output for the mixture under consideration. It is possible to select components so that no significant gas is evolved, or to select components to produce all gaseous products.

Some examples include:



Iron(III) oxide and aluminum—a thermite reaction



Ammonium nitrate and carbon—a gas generator

In a similar manner, oxidizer and fuel can be selected to yield high or low heat output per gram of composition, depending on what type of output is desired to accomplish the intended purpose of a given composition.

CONCLUSION

How many components should you use to produce an energetic mixture? The ideal energetic material is a one-component system. The high explosive trinitrotoluene (TNT) is an example of an ideal material—the pure compound is manufactured, melted at its low melting point of 81°C, and poured into containers to create explosive devices. Life could not be easier.

However, with pyrotechnics and propellants, it is far more common to have to combine a group of chemicals to produce the effect, sensitivity, and burn rate you are seeking. These will include an oxidizer, a fuel, probably a binder, and additional

components to fine-tune the composition. Do everything you can to keep the number of components to a minimum. The probability of manufacturing problems arising over time (that is, manufacturing the same composition and the same device every day and every month) goes up in what seems an exponential fashion as the number of components increases. Once you reach eight or more components in a composition, reproducibility problems are almost certain to arise from time to time in production.

REFERENCES

1. A. A. Shidlovskiy, *Principles of pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, OH, 1974.)
2. T. Shimizu, *Fireworks—The art, science, and technique*, Tokyo: T. Shimizu, 1981.
3. U.S. Army Material Command, *Engineering design handbook: Properties of materials used in pyrotechnic compositions*, Military Pyrotechnic Series, Part Three, Washington, DC, 1963 (AMC Pamphlet 706–187).
4. T. Shimizu, in K. Kosanke et al., *Pyrotechnic chemistry*, *Journal of Pyrotechnics*, Whitewater, CO, 2004, chap. 2.
5. R. C. Weast (Ed.), *CRC handbook of chemistry and physics*, 63rd ed., Boca Raton, FL: CRC Press, 1982.
6. H. Ellern, *Military and civilian pyrotechnics*, New York: Chemical Publishing Company, 1968.
7. M. Stanbridge, Reactions, in *Pyrotechnica XII*, Austin, TX: Pyrotechnica Publications, June 1988.
8. T. J. Barton et al., Factors affecting the ignition temperature of pyrotechnics, in *Proceedings, Eighth International Pyrotechnics Seminar*, ITT Research Institute, Steamboat Springs, CO, July 1982, 99.
9. J. H. McLain, *Pyrotechnics from the viewpoint of solid state chemistry*, Philadelphia: Franklin Institute Press, 1980.
10. J. Conkling and S. Halla, The reaction of potassium chlorate with organic fuels, presented at Annual Meeting of Explosives and Pyrotechnics Applications Section, ADPA, Los Alamos, NM, October 1984.
11. U.S. Department of Transportation, *Hazardous materials regulations*, Code of Federal Regulations, Title 49, Parts 172–173.
12. K. Sellers et al., *Perchlorate environmental problems and solutions*, Boca Raton, FL: CRC Press–Taylor & Francis Group, 2007.
13. www.nasa.gov/returntoflight/system/system_SRB.html.
14. U.S. Army Material Command, *Engineering design handbook: Theory and application*, Military Pyrotechnic Series, Part One, Washington DC, 1967 (AMC Pamphlet 706-185).
15. D. Price, A. R. Clairmont, and I. Jaffee, The explosive behavior of ammonium perchlorate, *Combustion and Flame*, 11, 415 (1967).
16. A. Tulis et al., Investigation of physical and chemical effects in energetic fuel-oxidizer powder compositions—Stoichiometry vs. particle size relationship, presented at Proceedings of the 11th International Pyrotechnics Seminar, Vail, CO, 1986.
17. J. W. Reed, Analysis of the accidental explosion at PEPCON, Henderson, Nevada, on May 4, 1998, *Propellants, Explosives, Pyrotechnics*, 17, 88 (1992).
18. R. Seltzer, Impact widening from explosion of Nevada rocket oxidizer plant, *Chemical and Engineering News*, August 8, 1998.
19. P. Brousseau and C. J. Anderson, Nanometric aluminum in explosives, *Propellants, Explosives, Pyrotechnics*, 27, 300, 2002.

20. D. E. G. Jones et al., Hazard characterization of aluminum nanopowder compositions, *Propellants, Explosives, Pyrotechnics*, 28, 120 (2003).
21. K. L. Kosanke and B. J. Kosanke, Aluminum metal powders in pyrotechnics, *Pyrotechnics Guild Bulletin* 85 (1993).
22. E.-C. Koch, Special materials in pyrotechnics: The chemistry of phosphorus and its compounds, *Journal of Pyrotechnics*, Issue 21, 2005.
23. R. Lancaster, *Fireworks principles and practice*, New York: Chemical Publishing Company, 1972.
24. U.S. Consumer Products Safety Commission, *Fireworks devices*, Code of Federal Regulations, Title 16, Part 1507.
25. W. Meyerriecks, Organic fuels: Composition and formation enthalpy. Part I. Wood derivatives, related carbohydrates, exudates, and resin, *Journal of Pyrotechnics*, Issue 8, 1998.
26. W. Meyerriecks, Organic fuels: Composition and formation enthalpy. Part II. Resins, charcoal, pitch, gilsonite, and waxes, *Journal of Pyrotechnics*, Issue 9, 1999.
27. J. E. Rose, The role of charcoal in the combustion of black powder, in *Proceedings, Seventh International Pyrotechnics Seminar*, ITT Research Institute, Vail, CO, July 1980, p. 543.
28. D. Barisin and I. Batinic-Haberle, The influence of the various types of binder on the burning characteristics of the magnesium-, boron-, and aluminum-based igniters, *Propellants, Explosives, Pyrotechnics*, 19, 127 (1994).
29. F. R. Taylor and D. E. Jackson, Development of a polymer binder for pyrotechnic compositions, presented at Proceedings, 11th International Pyrotechnics Seminar, Vail, CO, 1986.
30. T. J. Barton et al., The influence of binders in pyrotechnic reactions—Magnesium-oxidant systems, presented at 9th International Pyrotechnic Seminar, Colorado Springs, CO, August 1984.

4 Pyrotechnic Principles



A FUSEE: (Please see color insert following page 112). The highway flare, or fusee, is an intriguing pyrotechnic article, requiring a long burn time and good candlepower from the red flame. An item with long burn time is relatively easy to make. An item with high candlepower is relatively easy to make. An item with both long burn time and high candlepower is indeed a challenge, requiring just the right chemistry and technology in the manufacturing process. (Photo by Tim Wade and Dennis King, courtesy of MP Associates.)

A major key to pyrotechnic reactivity is homogeneity; anything you do to make a composition more homogeneous should enhance its reactivity—but be careful, you may also be enhancing its sensitivity. If you attempt to manufacture pyrotechnic articles, strange things will occur involving reactivity that seem to defy all logic. However, there *has* to be an explanation for a change in burn rate, sensitivity, candlepower, or other reactivity value. The challenge is to identify the source of the variability. When things seem to be at their worst, return to the basics of pyrotechnics in the search for an explanation and, more importantly, a solution to the problem.

INTRODUCTION

The secret to maximizing the rate of reaction for a given pyrotechnic, propellant, or explosive composition can be revealed in a single word: homogeneity. Any operation that increases the thoroughness of the blending of a high-energy mixture should lead

to an enhancement of reactivity. Reactivity, in general, refers to the rate—in grams or centimeters per second—at which starting materials are converted into products, but other performance factors, such as heat output, light output, or gas output, may be of equal or greater interest for a given situation.

The importance of intimate mixing was recognized as early as 1831 by Samuel Guthrie Jr., a manufacturer of fulminating powder used to prime firearms. Guthrie's mixture was a blend of potassium nitrate, potassium carbonate, and sulfur, and he discovered that the performance could be dramatically improved if he first melted together the nitrate and carbonate salts, and then blended in the sulfur. He wrote, "By the previously melting together of the nitro and carbonate of potash, a more intimate union of these substances was effected than could possibly be made by mechanical means."¹

However, he also experienced the hazards associated with maximizing reactivity, reporting, "I doubt whether, in the whole circle of experimental philosophy, many cases can be found involving dangers more appalling, or more difficult to be overcome, than melting fulminating powder and saving the product, and reducing the process to a business operation. I have had with it some eight or ten tremendous explosions, and in one of them I received, full in my face and eyes, the flame of a quarter of a pound of the composition, just as it had become thoroughly melted."¹ An enormous debt is owed to these pioneers in high-energy chemistry who were willing to experiment in spite of the obvious hazards and lack of personal protective equipment, and reported their results so others could build on their knowledge.

Varying degrees of homogeneity can be achieved by altering either the extent of mixing or the particle size of the various components (or both, for maximum effect). Striking differences in reactivity can result from changes in either of these, as Mr. Guthrie observed with his fulminating powder.

A number of parameters related to burning behavior can be experimentally measured and used to report the reactivity or performance of a particular high-energy mixture:^{2,3}

1. *Heat of reaction*: This value is expressed in units of calories (or joules) per mole or calories (or joules) per gram, and is determined using an instrument called a *calorimeter*. One calorie of heat is required to raise the temperature of 1 gram of water by 1°C, so the temperature rise of a measured quantity of water, brought about by the release of heat from a measured amount of high-energy composition, can be converted into calories of heat. Depending upon the intended application, a mixture liberating a high, medium, or low value may be desired. Some representative heats of reaction are given in Table 4.1. The experimentally measured heat of reaction can be compared to theoretical heats of reaction obtained from calculations using heat of formation values, as discussed in Chapter 2. It is always reassuring when experimental heats agree with the calculated values; this suggests that the expected reaction products are, in fact, forming in the course of the high-temperature reactions following ignition of the energetic material.

The actual atmosphere used for a heat of reaction experiment can play a critical role in determining the amount of heat that is produced and measured. If the ambient gas contains oxygen or nitrogen, reaction of fuels in the mixture may occur with the atmospheric gases present in the

TABLE 4.1
Representative Heats of Reaction for Pyrotechnic Systems

Composition	% by Weight	ΔH Reaction, kcal/g	Application
Magnesium	50	2.0	Illuminating flare
Sodium nitrate	44		
Laminac binder	6		
Potassium perchlorate	60	1.8	Photoflash
Aluminum	40		
Boron	25	1.6	Igniter
Potassium nitrate	75		
VAAR binder	+1%		
Potassium nitrate	71	1.0	Starter
Charcoal	29		
Black powder	91	0.85	Flash and report Military simulator
Aluminum	9		
Barium chromate	85	0.5	Delay
Boron	15		
Silicon	25	0.28	First fire
Red lead oxide	50		
Titanium	25		
Tungsten	50	0.23	Delay
Barium chromate	40		
Potassium perchlorate	10		

Source: F. L. McIntyre, *A Compilation of Hazard and Test Data for Pyrotechnic Compositions*, Report AD-E400-496, U.S. Army Armament Research and Development Command, Dover, NJ, October 1980.

combustion chamber, as well as with the oxidizers present in the pyrotechnic composition. The use of inert atmospheres, such as argon or helium, can prevent these fuel-atmosphere reactions from occurring. Experimenters must always be sure to report the atmosphere used in determining any heat output/calorimetric values.

As a general rule of thumb, a reaction that generates a heat of reaction of 1 kcal/gram or greater is significantly exothermic, while a value exceeding 2 kcal/gram is a very hot reaction. When a composition with a heat of reaction well below 1 kcal/gram is encountered, concerns should begin to rise regarding the ability of the reaction to propagate under adverse conditions, such as low ambient temperatures or the use of a small-diameter column of minimally confined energetic material.

TABLE 4.2
Burning Rates of Binary Mixtures of Nitrate Oxidizers
with Magnesium Metal

% Oxidizer (by weight)	% Magnesium	Burning Rate (inches/minute) ^a	
		Barium Nitrate Oxidizer	Potassium Nitrate Oxidizer
80	20	2.9	2.3
70	30	—	4.7
68	32	5.1	—
60	40	10.7	—
58	42	—	8.5
50	50	16.8	13.3
40	60	38.1	21.8
30	70	40.3	29.3
20	80	Erratic	26.4

Source: U.S. Army Material Command, *Engineering Design Handbook: Theory and Application*, Military Pyrotechnic Series, Part One, Washington, DC, 1967 (AMC Pamphlet 706–185).

^a Loading pressure was 10,000 psi into 1.4 in.² cases.

2. *Burning rate*: This is typically measured in units of inches, centimeters, or grams per second for slow mixtures, such as delay compositions, and in meters per second for fast materials. One way to alter burning rates is by varying the oxidizer or fuel that is used, as well as the ratios of ingredients, as shown in Table 4.2. Burning rates are also sometimes reported as burn times, in units of seconds per centimeter or seconds per gram—the *inverse* of the previously stated units. Always carefully read the units when examining burning rate data. When units of distance or mass per second are used, a larger value means a faster rate. When burn times (seconds to burn 1 centimeter or 1 gram of material) are used, the smaller number is the faster burning material!

The experimental burning rate depends on a large number of variables that will be discussed in Chapter 5. It is important to specify experimental conditions (such as ambient temperature, burn chamber pressure, loading or consolidation pressure, etc.) when reporting burn rates for energetic materials.

3. *Light intensity*: This is measured in units of candela or candlepower. The intensity is determined to a large extent by the temperature reached by the burning composition. Intensity from incandescent particles will increase exponentially (a fourth power relationship) as the flame temperature rises.
4. *Color quality*: This will be determined by the relative intensities of the various wavelengths of visible light emitted by vapor phase species present in the pyrotechnic flame. Only those wavelengths falling in the visible region of the electromagnetic spectrum will contribute to the color. An

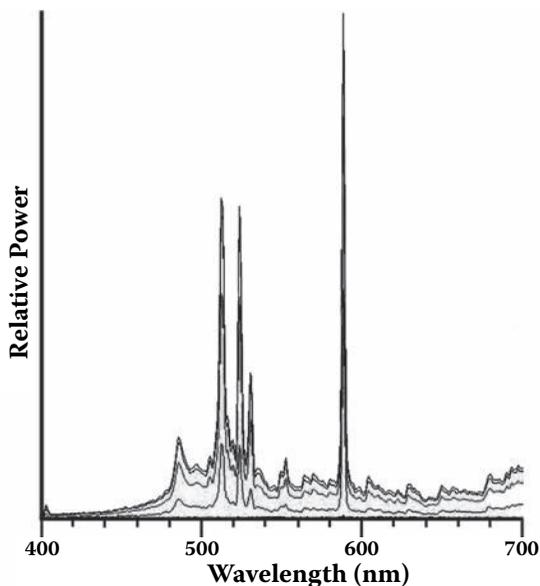


FIGURE 4.1 Light output from a green flare. The radiant output from a burning pyrotechnic composition can be analyzed using an instrument known as a spectrophotometer. Energy output can be monitored as a function of wavelength. A good white light mixture will emit reasonably intense light over the entire visible region. Color will be produced when the emission is concentrated in a narrow portion of the visible range. The output from this flare falls largely between 500 and 540 nm—the green portion of the visible spectrum (the strong peak at approximately 589 nm is most likely from sodium impurities in the pyrotechnic mixture, further discussed in Chapter 8). Green light emission is usually associated with the presence of a barium compound in the mixture (which leads to the production of molecular BaCl in the vapor state upon ignition), typically the primary emitter of green light.

emission spectrum, showing the intensity of light emitted at each wavelength over the wavelength range that is examined, can be obtained if the proper instrumentation—an emission spectrophotometer—is available. An example of this is shown in Figure 4.1.

5. *Volume of a gas produced:* Gaseous products are frequently desired as output when a high-energy mixture is ignited. Gas can be used to eject sparks, disperse smoke particles, inflate a life-saving protective “bag,” and provide propellant behavior. When severely confined, gas output can be used to create an explosion. The presence of organic compounds—containing carbon, hydrogen, and perhaps nitrogen—in an energetic material can generally be counted upon to produce significant amounts of gas products. Organic binders and sulfur should be avoided if a gasless, or very low gas-producing, composition is desired. In addition, for a particular composition to be of practical interest as a gas generator, it must produce a

significant amount of pyrotechnic effect *per gram* of mixture. Efficiency *per unit volume* is also an important consideration when available space is limited. Of course, gas volume is a function of temperature and pressure, as well as the number of moles of gas present (see the ideal gas law in Chapter 2). When water is a significant product from an energetic material, the measured gas pressure (at a constant volume) will decrease significantly from the initial pressure value as the products cool below 100°C, the condensation point of water.

6. *Pressure rate of rise*: Of the various measures of performance or reactivity, it is quite possible that the best method for comparing two batches or preparations of energetic material for reproducibility is the measurement of pressure generation vs. time, following ignition of the material (the United Nations time/pressure test).⁴ This type of study provides the experimenter with both a time component and an output component. Both the peak pressure and the time to reach peak pressure relate to the performance of the energetic material. If a batch of composition prepared on Monday and a batch prepared on Thursday give overlapping pressure rate-of-rise curves, the two batches should be expected to behave in a similar manner when they are loaded into end items in the manufacturing process.

VARIABILITY

To reproducibly create the desired pyrotechnic effect from a given mixture, the chemist must be aware of the large number of variables that can affect performance. These factors must be held constant from batch to batch and day to day to achieve reproducible behavior. Substantial deviations can result from variations in any of the following:^{2,3}

1. *Moisture*: The best rule is to avoid the use of water in processing pyrotechnic compositions, and to avoid the use of all hygroscopic (water-attracting) ingredients. If water is used to aid in binding and granulating, an efficient drying procedure *must* be included in the manufacturing process. The final product should be analyzed for moisture content, if reproducible burning behavior is critical. Why is water so bad? The answer lies in several of the important physical and chemical properties of H₂O. Water is an excellent solvent for many polar and ionic compounds. If a component to be used in a given composition is water soluble, and water is used to aid in activating a binder and blending the composition, the water will dissolve some of the water-soluble material. Upon subsequent drying, the dissolved component will resolidify, but it will most likely now be a *different* particle size than the starting material that was first placed in the mixer. This can change both the performance and sensitivity of the composition. Water is also difficult to evaporate—it has a high heat of vaporization compared to other solvents, such as acetone, that are used to dissolve binders. A longer and perhaps

warmer drying operation will be required to remove water (compared to a solvent such as acetone or ethyl alcohol, for example) following mixing and granulating. If significant water remains in an energetic material in an end item, the water will absorb a significant amount of heat as it vaporizes during the burning of the composition. This may hinder ignition and slow up the burn rate of the composition. Finally, water is a reactive oxidizing chemical with fuels like magnesium, boron, and zinc. Residual water in a composition may slowly react with these fuels during storage—slowing up the burn rate of the composition, by a reaction such as



and thereby create ignition problems as well as generate hydrogen gas that can cause a sealed device to bulge in storage.

- Particle size of ingredients:* Homogeneity, and pyrotechnic performance, will increase as the particle size of the various components is decreased. The finer the particle sizes, the more reactive a particular composition should be, with all other factors held constant. Table 4.4 illustrates this principle for a sodium nitrate–magnesium flare composition. Note the similarity in performance for the two smallest particle sizes, suggesting that an upper performance limit may exist with respect to the metal fuel particle size. It is critical that a manufacturer have the in-house ability to measure and confirm the particle size of each new arrival of chemical material. Modern instrumental methods of analysis allow for the rapid and accurate determination of the distribution of particles in a chemical sample. The science and technology of particle size and particle shape analysis are topics worthy of their own books. For decades, particle size distributions were primarily measured using a nest of standard sieves, with the holes in the screens decreasing in diameter as you moved down the nest (see Table 4.3). A weighed sample of the chemical of interest was placed on the top sieve in the nest, a cover was put in place, and the nest was mechanically shaken for a specified period. The weights of the material that was held on each successively finer sieve in the nest were then measured, giving a distribution by weight percent of the particle sizes in the sample. Newer instrumental methods of size analysis use a physical property of the particles in a sample, such as light scattering or sedimentation rate, to obtain a pattern of behavior for the sample. A programmed computer then takes the physical data and converts the observed behavior of the sample into a distribution of spherical particles, again by diameter, that would produce the observed pattern. This type of method can be quite good at comparing two samples (such as last month's shipment of metal powder and this month's shipment). If the two samples produce similar results in the analyzer, the two materials are likely to be similar in particle size and particle size distribution, and they should show similar pyrotechnic behavior. If the two results are quite different,

TABLE 4.3
Openings in U.S. Standard Sieves

Normal Sieve Mesh Designation	Opening Size, in Microns
#20 mesh	841
#40 mesh	450
#100 mesh	150
#200 mesh	75
#270 mesh	53
#325 mesh	44
#400 mesh	37

Source: Aldrich Chemical Company, *Handbook of Fine Chemicals*, 2003–2004 ed., T848. Also available at www.sigmaaldrich.com/chemistry.

Note: The mesh designation is the number of openings per linear inch in the sieve. Material that passes through a #400 mesh sieve is very fine, but it still can be material that is up to 37 microns in size. Material in the 5-micron range cannot be analyzed with any accuracy using sieves; an instrumental method is needed.

TABLE 4.4
Effect of Particle Size on Performance of a Flare Composition

Composition	Component	% by Weight	Average Particle Size
	Magnesium metal	48	See Table below
	Sodium nitrate	42	34 micrometers (10^{-6} meters)
	Laminac binder	8	—
	PVC	2	27 micrometers
Magnesium			
Average Particle Size, micrometers	Flare Candlepower (1,000 candles)		Flare Burning Rate, inches/minute
437	130		2.62
322	154		3.01
168	293		5.66
110	285		5.84

Source: U.S. Army Material Command, *Engineering Design Handbook: Theory and Application*, Military Pyrotechnic Series, Part One, Washington, DC, 1967 (AMC Pamphlet 706–185).

differences in reactivity and sensitivity may be observed in energetic material made using the two materials. Also, it never hurts to have a microscope available to view the particles for shape—spheres, flakes, irregular granules, etc. Again, the important thing is similarity in appearance from drum to drum and shipment to shipment.

3. *Surface area of the reactants*: For a high-energy reaction to rapidly proceed, the oxidizer must be in intimate contact with the fuel. Decreasing the particle size of the components will increase this contact, as will increasing the available surface area of the particles. A smooth sphere will possess the minimum surface area for a given mass of material. An uneven, porous particle (a Thomas' English Muffin, so to speak—full of “nooks and crannies”) will exhibit much more free surface per gram, and consequently should be much more reactive material than a smooth sphere of the same nominal particle size. Particle size is important, but it is surface area that is truly critical in determining reactivity. Several examples of this phenomenon are presented in Tables 4.5 and 4.6.
4. *Thermal conductivity*: For a column of pyrotechnic composition to burn smoothly and rapidly, the reaction zone must readily travel down the length of the composition. Heat is transferred from layer to layer, raising the adjacent material to the ignition temperature of the particular composition. Good thermal conductivity can be essential for smooth propagation of burning, and this is an important role played by metal fuels in many mixtures. Metals are the best thermal conductors, with organic compounds

TABLE 4.5
Effect of Particle Size on the Burning Rate of Tungsten
Delay Mixtures

	Mix A (M 10)	Mix B (ND 3499)
% tungsten	40	38
% barium chromate	51.8	52
% potassium perchlorate	4.8	4.8
% diatomaceous earth	3.4	5.2
Tungsten surface area, square centimeters/gram	1,377	709
Tungsten average diameter, 10 ⁻⁶ meters	2.3	4.9
Burning rate of mixture, inches/second	0.24 (faster)	0.046 (slower)

Source: U.S. Army Material Command, *Engineering design handbook: Theory and application*, Military Pyrotechnic Series, Part One, Washington, D.C, 1967 (AMC Pamphlet 706–185).

TABLE 4.6
Effect of Particle Size on Burning Rate

Composition	Titanium metal	48% by weight
	Strontium nitrate	45
	Linseed oil	4
	Chlorinated rubber	3
Titanium Size Range, micrometers		Relative Burning Rate
Less than 6		1.00 (fastest)
6–10		0.68
10–14		0.63
14–18		0.50
Greater than 18		0.37 (slowest)

Source: B. J. Thomson and A. M. Wild, Factors Affecting the Rate of Burning of a Titanium–Strontium Nitrate Based Composition, presented at Proceedings of Pyrochem International 1975, Pyrotechnics Branch, Royal Armament Research and Development Establishment, UK, July 1975.⁶

Note: Curiously, the system showed the *opposite* effect for strontium nitrate. Decreasing the particle size of the oxidizer from 10.5 to 5.6 micrometers produced a 25% decrease in burning rate.

ranking among the worst. Table 2.13 lists the thermal conductivity values of some common materials. Increase the thermal conductivity of a given composition, holding all other factors constant, and the burn rate of the material should increase.

- Outside container material:* Performance of a pyrotechnic mixture can be affected to a substantial extent by the type of material used to contain the mixed composition. If a good thermal conductor such as metal is used, heat may be carried away laterally from the composition through the wall of the container to the surroundings. The thickness of such a metal wall will also be an important consideration. If sufficient heat does not pass down the length of the pyrotechnic mixture, burning may not propagate and the device will not burn completely. The worst-case scenario would be a thin column of a low heat output composition in a thick metal tube. Organic materials, such as cardboard, are widely used to contain low-energy pyrotechnic compositions, such as highway flares (fusees) and fireworks, to minimize this problem (cardboard is a poor thermal conductor).
- Loading pressure:* There are two general rules to describe the effect of loading pressure—or consolidation—on the burning behavior of a pyrotechnic composition, and the correct rule to use depends on the importance of the role played by hot gases in propagation of the reaction. If the pyrotechnic reaction, in the postignition phase, is largely propagated via hot gases penetrating forward into the unreacted material, then a high loading

TABLE 4.7
Effect of Loading Pressure on the Burning Rate of a Delay Mixture

Composition	Barium chromate	90
	Boron	10
Loading Pressure (1,000 psi)	Burning Rate (seconds/gram) ^a	
36	0.272 (fastest)	
18	0.276	
9	0.280	
3.6	0.287	
1.3	0.297	
0.5	0.309 (slowest)	

Note: This is a gasless delay mixture—the burning rate *increases* as loading pressure increases. Gassy mixtures will show the opposite behavior.

^a A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)

pressure will reduce the porosity of the composition and retard the passage of these hot gases down the column of composition. A lower rate, in units of grams of composition reacting per second, will be observed at high loading pressures. (*Note:* One must be cautious in interpreting burn rate data vs. loading pressure, because an increase in loading pressure should lead to an increase in the density of the composition. What may appear to be a *slower* rate, expressed in units of millimeters per second, may actually be a *faster* rate in terms of grams per second). Low-gas or gasless compositions use particle-to-particle contact for heat transfer, and will show the opposite effect upon consolidation—the burn rate should increase, in units of grams per second—as the loading pressure increases. Table 4.7 illustrates the effect of loading pressure on the burn rate of a low-gas boron–barium chromate composition; note that the rate is listed in units of seconds per gram, and the *smaller* number means the fastest rate.

7. *Degree of confinement:* In Chapter 1, the variation in the burning behavior of black powder was discussed as a function of the degree of confinement. Increased confinement leads to accelerated burning. Shimizu reports a burning rate in air of .03 to .05 meters/second for black powder paste impregnated in twine. The same material, enclosed in a paper tube of 1 centimeter inside diameter, had a burning rate of 4.6 to 16.7 meters/second—over a hundred times faster!⁵ This behavior is typical of confined loose powders, and points out the potential danger of confining mixtures that burn somewhat sluggishly in the open air.

This effect is particularly important when consideration is given to storage, as well as the selection of manufacturing equipment for pyrotechnic compositions. Equipment for the processing of energetic material—such as

mixers, granulators, and dryers—should be vented to ambient pressure. The equipment will often not come from the manufacture with pre-installed pressure-relief vents or valves as a standard feature, if the equipment is not normally sold to manufacturers of energetic material. For processing foodstuffs, medicines, and other non-energetic material, purity and hygiene are the foremost considerations, and the equipment is often designed to be tightly sealed during operation to keep out contaminants (mice, roaches or flies, for example). Storage containers, workrooms, and storage facilities for energetic materials must be designed to rapidly vent in case of an ignition that leads to pressure buildup. Such venting is designed and intended to prevent a fire from progressing to an explosion. Several factors contribute to the effect of confinement on burning rate. First, as was discussed in Chapter 2, an increase in temperature produces an exponential increase in rate of a chemical reaction. In a confined high-energy system, the temperature of unreacted material can rise dramatically should an ignition occur, as heat is not effectively lost to the surroundings. A sharp rise in reaction rate occurs, liberating more heat, raising the temperature further, accelerating the reaction until an explosion occurs or the reactants are consumed. The minimum quantity of material needed to produce an explosion, under a specified set of conditions, is referred to as the *critical mass*. Also, in a confined system, the hot gases that are produced cannot escape and thereby can build up substantial pressure, holding heat at the burning surface and driving the hot gases into the high-energy mixture, thereby causing a rate acceleration.

Burning behavior can therefore be summarized in two words: homogeneity and confinement. An increase in either should lead to an increase in burning rate for most high-energy mixtures. Note, however, that “gasless” compositions do not show the dramatic confinement effects found for “gasier” compositions. Burn rate will be discussed further in Chapter 5.

REQUIREMENTS FOR A GOOD HIGH-ENERGY MIXTURE

The requirements for a commercially feasible high-energy mixture can be summarized as follows, keeping in mind the preceding discussion of factors that affect performance:

1. The composition produces the desired effect and is efficient in terms of both effect/gram and effect/dollar.
2. The composition can easily and safely be manufactured, handled, transported, stored, and used, assuming normal treatment and the expected variations in temperature.
3. Ignition is reliable in the end item and sensitivity meets acceptable criteria.
4. Storage lifetime is acceptable, even in humid conditions.
5. There is reasonably low toxicity and adverse environmental impact associated with both the starting materials and reaction products.

These requirements seem rather simple, but they do restrict or eliminate a number of potential starting materials. Either these compounds must be deleted from our acceptable list or special precautions must be taken in order to use them. Examples include:

Potassium dichromate ($K_2Cr_2O_7$): This is a strong oxidizer, but it only contains 16% oxygen by weight. It has a corrosive effect on the mucous membranes, and its toxicity and suspected carcinogenicity suggest the use of alternate oxidizers. It is one of the family of hexavalent chromium compounds that have received considerable adverse publicity.

Ammonium perchlorate (NH_4ClO_4): This is a good oxidizer, and can be used to make excellent propellants and colored flames. However, it is a self-contained oxidizer-fuel system (much like ammonium nitrate), poses potential explosive behavior in large quantities, and is a member of the perchlorate family.

Perchlorates in general ($X^+ClO_4^-$): The various perchlorates, such as potassium perchlorate ($KClO_4$) and ammonium perchlorate (NH_4ClO_4) used in solid propellants and pyrotechnics, have been under great scrutiny as a possible source of ground water contamination, as discussed in Chapter 3. Once rated among the ideal oxidizers, the perchlorates are now being avoided in the development of new energetic materials.

Magnesium metal (Mg): This is an excellent fuel and produces brilliant illuminating mixtures. The metal is water reactive, however, suggesting short shelf-life and possible spontaneous ignition if magnesium-containing mixtures become wet. *Conclusion:* Replace magnesium with the more stable aluminum (or a magnalium alloy of aluminum with magnesium). If magnesium gives the best effect and must be used, coat the metal with an organic, water-repelling material.

Zirconium metal powder (Zr): This material is associated with world record spark sensitivity and explosive behavior when mixed with an oxidizer. Use it only when you need flame temperatures and reaction products in the 4,000°C and above range.

PREPARATION OF HIGH-ENERGY MIXTURES

The most hazardous operations in the high-energy chemistry field involve the mixing of oxidizer and fuel in large quantities, and the subsequent drying of the composition (if water or other liquid is used in the mixing and granulating processes). In these operations, large quantities of bulk powder are present in one location, and if accidental ignition should occur, there is a good chance that an explosive reaction rate may be reached.

For this reason, mixing and drying operations should be isolated from all other plant processes, and remote-controlled equipment should be used wherever and whenever possible, using video technology for surveillance of the operation. All high-energy manufacturing facilities should be designed with the idea in mind that an accident will occur at some time during the life of the facility. The plant should

be designed to minimize any damage to the facility, to the neighborhood, and most importantly, to the operating personnel, should an incident occur.⁷ The manufacturing operation can be divided into several stages:

1. *Preparation of the individual components:* Materials to be used in the manufacturing process may have to be initially dried, as well as ground or crushed to achieve the proper particle size, and screened to separate out large particles or foreign objects. Oxidizers should never be processed with the same equipment used for fuels, nor should oxidizers and fuels be stored in the same area prior to use. All materials must be clearly labeled at all times.
2. *Preparation of compositions:* This step is a major key to proper performance. The more homogeneous a mixture is, the greater its reactivity will be. The high-energy chemist is always walking a narrow line in this area, however. By maximizing reactivity—with small particle sizes and intimate mixing—you are also affecting sensitivity, and increasing the chance of accidental ignition during manufacturing and storage. A compromise is usually reached involving careful specification of particle size, purity of starting materials, and safe operating procedures. Follow all standard operating procedures.
3. *Mixing:* A variety of methods can be used for mixing. Materials can be blended through wire screens, using brushes. Hand screening has been used in the fireworks industry, but should never be used with explosive or unstable mixtures. Brushes provide a safer method of screening the oxidizer and fuel together. Materials can also be tumbled together to achieve homogeneity, and this can (and should) be done remotely. Remote mixing, and barricading, is strongly recommended for sensitive explosive compositions such as the flash and sound powder used in firecrackers and salutes, and the photoflash powders used by the military. For some of these compositions and devices, it is possible to add the oxidizer and fuel(s) in separate increments, and then tumble the end items (remotely) to achieve blended composition in the end items. This procedure enables the manufacturer, when possible, to avoid having to mix larger bulk quantities of a sensitive, explosive powder.
4. *Granulation:* Following mixing, the powders are often granulated, generally using a small percentage of binder to aid in the process. The composition is treated with water or an organic liquid (such as alcohol or acetone) to activate the binder, and then worked through a large-mesh screen. (*Note:* Composition that is blended with the aid of a binder-solvent solution can proceed directly to the granulation stage after mixing.) Grains of well-mixed composition are produced that will retain the homogeneity of the composition better than loose powder. Without the granulation step, light and dense materials might segregate during transportation and storage, and dust generation is likely. The granulated material is dried in a remote, isolated area, and is then ready to be loaded into finished items. *Remember:* Sizable quantities of bulk powder are present at this stage, and the material

must be protected from heat, friction, shock, impact, and an electrostatic spark. As an alternative to granulation, extrusion of paste-like composition can be done with many compositions, using equipment specifically designed with energetic materials in mind. This process permits the formation of specific geometric shapes for the finished grains of composition. Venting is of particular importance with this type of equipment.

5. *Pressing/loading*: An operator, working with the minimum quantity of bulk powder, loads the composition into tubes or other containers, or produces pellets for later use in finished items. The making of stars—small pieces of color-producing composition used in aerial fireworks, distress flares, and illuminant signals—is an example of this pelleting operation. Loading pressure, dwell time, barricading, and equipment maintenance are all critical factors in pressing operations.⁷
6. *Testing*: An important final step in the manufacturing process is the continual testing of each lot of finished items to ensure proper performance. Significant differences in performance can be obtained by slight variation in the particle size or purity of any of the starting materials, and a regular testing program as part of the manufacturing process is the only way to be certain that proper performance is being achieved.

PROCESS HAZARD ANALYSIS

An important feature of the manufacturing of all energetic materials today is the use of hazard analysis methodology for all operations involving the presence of exposed energetic materials. A team, including personnel working in the area of the process under review, technically trained individuals, and persons familiar with hazard analysis methodology, reviews each operation. First, the current standard operating procedures are examined, along with information such as Material Safety Data Sheets, equipment specifications, sensitivity data, and past incidents involving the process. Then the team reviews the process, looking for possible things that might go wrong and lead to an incident. Corrective actions, if required, are recommended and implemented as necessary. If any change occurs in a given process, a new hazard analysis is conducted to determine if the change requires any modifications to the hazard analysis plan for the operation, such as new or revised standard operating procedures.

VARIATION FROM DAY TO DAY

Pyrotechnic compositions in particular have acquired a reputation for variability in manufacturing—compositions made on Monday will occasionally not behave the same as compositions made on Thursday. “Why?” is always the question, and the source can be any one of a number of individual factors discussed previously in this chapter, or a combination of several factors. Troubleshooting is a part of the life of anyone who is involved in manufacturing pyrotechnics.

The list of likely suspects always includes particle size variation, moisture, and chemical purity, as well as each stage in the manufacturing process. Establishing and maintaining good quality control procedures on incoming shipments of chemical

components is critical. The following is a checklist developed a number of years ago, in a discussion at one of my Summer Pyrotechnic Seminars, in an effort to identify places in the manufacturing process where variation in end item performance might result if any deviation from the standard operating procedure occurs. Hopefully, this chart might possibly serve as a checklist for someone trying to identify a possible source of variation in pyrotechnic/propellant performance.

POSSIBLE AREAS WHERE VARIATION IN THE PERFORMANCE AND SENSITIVITY OF PYROTECHNIC MIXTURES CAN OCCUR DURING THE MANUFACTURING PROCESS

- Starting chemicals—purity and age
- Particle size/shape (surface area)
- Variation by particle size of chemicals within a drum (due to settling)
- Drying of individual materials (prior to weighing)
- Formula (percent change)—an intentional change to alter performance
- Evaporation of solvent in binder solution
- Weighing of chemicals (accuracy of scales)
- Percent actually delivered to the mixer (spills, residual in containers, etc.)
- Introduction of foreign material/moisture throughout the process
- Mixing—type of mixer used
- Mixing time, speed, energy (does mixing process affect particle size?)
- Sequence of chemical addition to the mixer
- Solvent evaporation rate in the mixer
- Humidity and temperature in mixer/mixing area
- Granulation—final grain size of blended mix
- Drying of blended mixture—percent residual solvent/moisture

(At this stage, initial performance tests are typically run on the mixture; if it meets specifications, it proceeds to the loading area. Otherwise, it is reworked, cross-blended, or destroyed.)

- Storage (prior to loading)—exposure to moisture
- Loading/pressing—loading pressure, dwell time
- Loading—number of increments
- Loading—amount of fill (volume vs. weight)
- Hardware variation—size of parts, seals in end items
- Wall thickness and venting pressure of a confinement tube
- End item storage/treatment/handling
- External temperature and pressure when the device is ignited

REFERENCES

1. T. L. Davis, *The chemistry of powder and explosives*, 3. New York: John Wiley & Sons, 1941.
2. U.S. Army Material Command, *Engineering design handbook: Theory and application*, Military Pyrotechnic Series, Part One, Washington, DC, 1967 (AMC Pamphlet 706–185).

3. A. A. Shidlovskiy, *Principles of pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)
4. *Recommendations on the transport of dangerous goods—Manual of tests and criteria*, 4th rev. ed., United Nations (www.unece.org), 2003.
5. T. Shimizu, *Fireworks from a physical standpoint*, Part One, trans. A. Schuman, Pyrotechnica Publications, Austin, TX, 1982.
6. B. J. Thomson and A. M. Wild, Factors affecting the rate of burning of a titanium–strontium nitrate based composition, presented at Proceedings of Pyrochem International 1975, Pyrotechnics Branch, Royal Armament Research and Development Establishment, UK, July 1975.
7. *DOD contractor's safety manual for ammunition and explosives*, Department of Defense Explosives Safety Board, DOD 4145.26-M, March 13, 2008 edition. Available at www.dtic.mil/whs/directives.

5 Ignition and Propagation



TITANIUM SPARKS: (See color insert following page 112) A titanium fountain uses relatively coarse titanium particles blended into a moderately fast-burning pyrotechnic composition to produce a beautiful spray of white sparks. This type of fountain effect is widely used in the fireworks industry as well as in theatrical pyrotechnical articles (special effects) for stage presentations. (Photo by Tim Wade and Dennis King, courtesy of MP Associates.)

For an energetic material to be of any practical use, you have to be able to prepare it safely *and* you have to be able to ignite it—safely and reliably—using something less dramatic than a blowtorch.

IGNITION PRINCIPLES

A pyrotechnic composition must be capable of undergoing reliable ignition when an ignition stimulus is provided, and yet be stable in transportation and storage. The ignition behavior of every mixture must be studied, and the proper ignition system can then be specified for use with each composition. For easily ignited materials, the “spit” from a burning black powder fuse is often sufficient. The ignition method for propellants is frequently an impact-sensitive energetic “primer” that produces a spray of hot particulates and flame to rapidly get the propellant burning. Another common igniter is an electric match, consisting of a wire circuit terminating in a small-diameter bridgewire that is coated with a small dab of heat-sensitive composition. An electric current is passed through the circuit, producing sufficient heat to ignite the bridgewire composition and produce a flame. The burst of flame then ignites the next composition in the ignition sequence. For pyrotechnic mixtures with high ignition temperatures, a priming composition or first fire is often used. This is an easily ignited composition that can be reliably activated by a fuse or other igniter. The flame and hot particulates that are produced are then used to ignite the main composition.

Successful performance of a high-energy mixture depends upon:

1. Ignition: The ability to *ignite* the material using an external stimulus, as well as the *stability* of the composition in the absence of the stimulus.
2. Propagation: The ability of the mixture, once ignited, to sustain or *propagate* burning through the remainder of the composition.

These two processes (ignition and propagation) share a number of common factors, but there are also some differences related to the involvement of *external* vs. *internal* energy. A composition is required that will readily ignite and burn, and produce the desired effect ordered by the customer, at an acceptable cost, while remaining quite stable during manufacture and storage. This is not an easy set of requirements to meet, and is one of the main reasons why a relatively small number of materials are used in preparing high-energy mixtures.

For ignition to occur, a portion of the mixture must be heated to its *ignition temperature*, which is defined as the minimum temperature required for the initiation of a rapid, self-propagating exothermic reaction. Upon ignition, the reaction then proceeds on its own—or *propagates*—through the remainder of the energetic mixture, in the absence of any additional external energy input.

Ignition of an energetic material can be achieved using a variety of types of energy input. Traditional methods, such as flame, spark, impact, and friction, continue to be used to initiate devices. Ignition using an electric current has been the state of the art for ignition of many types of energetic materials for decades. New methods to create a hot spot are being developed, such as the use of high intensity light (employing fiber optics and laser technology) and are intended for use where there are specific

concerns with electrical ignition that involve possible unintended ignition due to electrostatic discharge and stray radio frequency (RF) signals.¹

Application of the ignition stimulus (such as a spark or flame) initiates a complex sequence of events in the chemical composition, if the externally applied energy is effectively absorbed by the energetic material. The solid components may undergo crystalline phase transitions, melting, boiling, and decomposition. Liquid and vapor phases may be formed, and a chemical reaction will eventually occur at the surface where the energy input is applied, if the necessary *activation energy* has been provided via a temperature rise in a portion of the material receiving the external energy.

The heat released by the occurrence of the high-energy reaction raises the temperature of the next layer or grain of composition. If the heat evolution and thermal conductivity are sufficient to supply the required activation energy (via a temperature increase) to the next layer, further reaction will occur, liberating additional heat, and propagation of the reaction through the mixture takes place. The rates and quantity of heat transfer *to*, heat production *in*, and heat loss *from* the high-energy composition are all critical factors in achieving propagation of burning via a self-sustaining chemical reaction.

The combustion process itself is quite complex, involving high temperatures and a variety of short-lived, high-energy chemical species. The solid, liquid, and vapor states may all be present in the actual flame, as well as in the region immediately adjacent to it. *Products* will be formed as the reaction proceeds, and they will either escape as gaseous species or accumulate as solids in the reaction zone, as shown in Figure 5.1.

A moving, high-temperature reaction zone, progressing through the composition, is characteristic of a combustion (or burning) reaction. This zone separates unreacted starting material from the reaction products. A high-temperature zone of this type is *not* found in normal chemical reactions, such as those carried out in a flask or beaker,

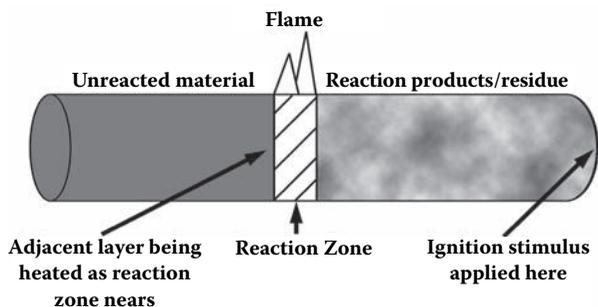


FIGURE 5.1 Burning pyrotechnic composition. Several major regions are present in a reacting pyrotechnic composition. The actual self-propagating exothermic process is occurring in the reaction zone. High temperature, flame and smoke production, and the likely presence of gaseous and liquid materials characterize this region. Behind the advancing reaction zone are solid products formed during the reaction (unless all products were gaseous). Immediately ahead of the reaction zone is the next layer of composition that will undergo reaction. This layer is being heated by the approaching reaction, and melting, solid–solid phase transitions, and low-velocity preignition reactions may be occurring. The thermal conductivity of the composition is quite important in transferring heat from the reaction zone to the adjacent, unreacted material. Hot gases as well as hot solid and liquid particles aid in the propagation of burning.

where the entire system is at the same temperature and molecules react randomly throughout the container. Combustion and deflagration (which is a very rapid combustion) are distinguished from detonation by the absence of a significant pressure differential between the region undergoing reaction and the remainder of the unreacted composition.²

A variety of factors affect the ignition temperature and the burning rate of a high-energy mixture, and the chemist has the ability to alter most of these factors to achieve a desired change in performance.

One requirement for ignition appears to be the need for either the oxidizer or fuel to be in the liquid (or vapor) state, and reactivity becomes even more certain when *both* are liquids or gases. The presence of a low-melting fuel can substantially lower the ignition temperature of many compositions.³ This is particularly true when the melting of a fuel is accompanied by thermal decomposition of the material, generating readily oxidizable fragments. Sulfur and organic compounds have been employed numerous times as tinders in high-energy mixtures to facilitate ignition. Several examples of this phenomena are shown in Table 5.1. Sulfur melts at 119°C, while most sugars, gums, starches, and other organic polymers have melting points or decomposition temperatures of 300°C or less. The presence of a fluid state provides the first requirement for ignition—intimate mixing of oxidizer and fuel. There is still an energy requirement—the activation energy—that must be overcome, however, in order to achieve ignition. This activation energy relates to the decomposition of the oxidizer resulting in the release of oxygen, as well as the activation or decomposition of the fuel to accept the oxygen and form reaction products.

Many of the oxidizers used in high-energy mixtures, such as potassium nitrate, are ionic solids, and the looseness of the ionic lattice is quite important in determining their reactivity.⁴ A crystalline lattice has some vibrational motion at normal room temperature, and the amplitude of this vibration increases as the temperature of the solid is raised. At the melting point, the forces holding the crystalline solid together collapse, producing the randomly oriented liquid state. For reaction to occur in a high-energy system, the fuel- and oxygen-rich oxidizer anion must become intimately mixed, on the ionic or molecular level. Liquid fuel or fuel fragments can diffuse into the solid oxidizer lattice *if* the vibrational amplitude in the crystal is sufficient. Once sufficient heat is generated to begin decomposing the oxidizer, the higher-temperature combustion reaction begins, involving free oxygen gas and fuel atoms or radicals, and very rapid reaction rates can result. We are concerned here with the processes that *initiate* the ignition process.

Professor G. Tammann, one of the pioneers of solid-state chemistry, considered the importance of the lattice motion to reactivity, and used the ratio of the actual temperature of a solid divided by the melting point of the solid (with all temperatures expressed in the Kelvin or absolute scale) to quantify this concept.

$$\alpha = \text{Temperature (solid)}/\text{Temperature (melting point)} \text{ (in K)} \quad (5.1)$$

Tammann proposed that diffusion of a mobile species into a crystalline lattice should be “significant” at an α -value of 0.5 (or halfway to the melting point, on the Kelvin scale). At this temperature, later termed the *Tammann temperature*, a solid has approximately 70% of the vibrational freedom present at the melting point, and diffusion into the lattice becomes probable.⁴ If this represents the approximate temperature where diffusion becomes probable, it is, therefore, also a temperature where

TABLE 5.1
Effect of Sulfur and Organic Fuels on Ignition Temperature

Composition	% by Weight	Ignition Temperature, °C
IA. KClO ₄	66.7	446 ^a
Al	33.3	
IB. KClO ₄	64	360
Al	22.5	
S	10	
Sb ₂ S ₃	3.5	
IIA. BaCrO ₄	90	615 ^a (3.1 milliliter per gram of evolved gas)
B	10	
IIB. BaCrO ₄	90	560 (29.5 milliliter per gram of evolved gas)
B	10	
Vinyl alcohol–acetate resin	+1%	
IIIA. NaNO ₃	50	772 ^b (50-milligram sample, heated at 50°C/minute)
Ti	50	
IIIB. NaNO ₃	50	357
Ti	50	
Boiled linseed oil	+6%	

^a F. L. McIntyre, *A compilation of hazard and test data for pyrotechnic compositions*, Report ARLCD-CR-80047. Dover NJ: U.S. Army Armament Research and Development Command, 1980.

^b T. J. Barton et al., Factors affecting the ignition temperature of pyrotechnics, in *Proceedings, Eighth International Pyrotechnics Seminar*, Steamboat Springs, CO: IIT Research Institute, July 1982, 99.

a chemical reaction between a good oxidizer and a mobile, reactive fuel becomes possible. Oxidizers begin to release oxygen at slow rates at temperatures below their melting points, and the rate of oxygen loss tends to become quite significant for many oxidizers as the melting point is reached. This is very important point from a safety standpoint—the potential for a reaction may exist at surprisingly low temperatures, especially with sulfur or organic fuels present.

For example, the melting point of potassium nitrate is 334°C, or $334 + 273 = 607$ Kelvin. Take half of this value (303.5 K), and then subtract 273 to convert back to the Celsius scale, giving a value of 30.5°C (or 93°Fahrenheit)—a temperature likely to be found in a warm storage area. Table 5.2 lists the Tammann temperatures of some of the common oxidizers. The *low* temperatures shown for potassium chlorate and potassium nitrate may well account for the large number of mysterious, accidental ignitions that have occurred with fuel/oxidizer compositions containing these materials. Potassium chlorate is particularly vulnerable to this phenomenon, because the decomposition of the oxidizer

TABLE 5.2
Tammann Temperatures of the Common Oxidizers (and Magnesium)

Oxidizer	Formula	Melting Point, °C	Melting Point, K	Tammann Temperature, °C
Sodium nitrate	NaNO ₃	307	580	17
Potassium nitrate	KNO ₃	334	607	31
Potassium chlorate	KClO ₃	356	629	42
Strontium nitrate	Sr(NO ₃) ₂	570	843	149
Barium nitrate	Ba(NO ₃) ₂	592	865	160
Potassium perchlorate	KClO ₄	610	883	168
Lead chromate	PbCrO ₄	844	1,117	286
Iron oxide	Fe ₂ O ₃	1,565	1,838	646
Magnesium metal	Mg	651	924	189

is an *exothermic* process (see Table 3.2) that actually contributes energy to help get the ignition process under way. The significantly *endothermic* decomposition of potassium nitrate requires that a higher temperature be reached before decomposition commences and oxygen is released at a significant rate for reaction with a waiting fuel species.

Tammann Temperature indicates the temperature where mobility is possible in a solid oxidizer material. The other requirement for reaction is the presence of a reactive fuel or fuel fragment to accept oxygen from the oxidizer, thereby generating additional energy to lead to ignition. Adequate mobility and adequate energetics are both required for ignition to occur. The same logic applies to oxygen atoms from an oxidizer diffusing into a high-melting solid fuel and reacting with surface fuel atoms to generate heat.

Ease of ignition also depends on the particle size and surface area of the ingredients. This factor is especially important for metallic fuels with melting points higher than or comparable to that of the oxidizer. Some metals, including aluminum, magnesium, titanium, and zirconium, can be quite hazardous when present in fine particle size (in the 1 to 5 micrometer range), not to mention particles in the nanometer range. Particles this fine may spontaneously ignite in the air, and are often quite sensitive to static discharge.⁵ For safety reasons, reactivity is usually sacrificed to some extent when metal powders are part of a mixture, and ultrafine particle sizes are avoided to minimize accidental ignition.

A final requirement for ignition appears to be for the fuel to have reached a temperature where it has been activated toward oxidation. For metallic fuels, this usually involves the shedding of a surface oxide coating, exposing fresh metal atoms to the oxygen that is released from the oxidizer. This process tends to become significant when the temperature of the metal is well above its Tammann temperature and is approaching its melting point, and numerous oxidizer–metal fuel systems show ignition temperatures that coincide with the onset of melting of the fuel. For magnesium-oxidizer systems, as an example, ignition temperatures in the 600 to 650°C range are commonly observed (see Table 5.4).

For organic fuels, the activation process appears to involve the fuel reaching a temperature where decomposition of the carbon chain commences, generating free radical

fragments that are susceptible to oxidation. Organic compounds typically reach their decomposition temperatures from 200°C–350°C, depending on the particular molecular structure of the fuel. Many sugars, such as glucose and sucrose, have low decomposition temperatures (the familiar caramelization reaction that causes sugars to turn brown on heating), while hydrocarbon chains without electronegative substituents tend to be more thermally stable. The presence of oxygen atoms on each carbon atom in a sugar molecule leads to considerable internal bond strain, as each carbon in the chain is rendered partially positive due to the presence of the attached, electronegative oxygen atom. The adjacent, partially positive carbon atoms tend to repel each other, leading to molecular instability at relatively low temperature. This same phenomenon is also responsible for the sensitivity of some molecular explosives, such as nitroglycerine, where the presence of electronegative atoms on adjacent carbon atoms destabilizes the molecule and renders the material shock and impact sensitive. Sulfur's tendency to act as a tinder, or ignition aid, when present in pyrotechnic compositions can be traced to a low melting point that leads to activation toward oxidation.

Several examples will be given to illustrate these principles. In the potassium nitrate–sulfur system, the liquid state initially appears during heating with the melting of sulfur at 119°C, as illustrated in the thermogram for sulfur, Figure 5.3. Sulfur occurs in nature as an eight-member ring—the S_8 molecule. This ring begins to fragment into species such as S_3 at temperatures above 140°C. However, even with these fragments present, reaction between sulfur and the solid does not occur at a rate sufficient to produce ignition until the KNO_3 melts at 334°C (Figure 5.2) and oxygen evolution increases. Intimate mixing can occur when both species are in the liquid state, and ignition is observed just above the KNO_3 melting point. Although some reaction (a preignition reaction (PIR)) presumably occurs between sulfur and solid KNO_3 below the melting point, the low heat output obtained from the oxidation of sulfur, combined with the *endothermic* decomposition of KNO_3 , prevents ignition from taking place until the entire system is liquid. Only then is the reaction rate great enough to produce a self-propagating reaction. Figures 5.2–5.4 show the thermograms of the components and the mixture. Note the strong exotherm (release of heat) corresponding to ignition

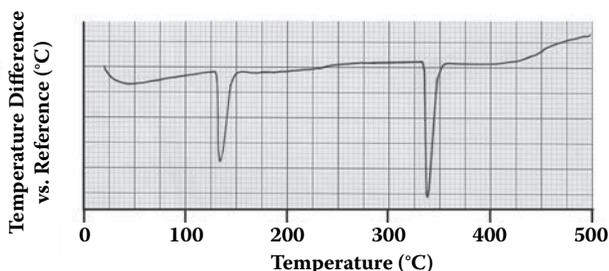


FIGURE 5.2 Thermogram of pure potassium nitrate. Endotherms are observed near 130 and 334°C. These peaks correspond to a rhombic-to-trigonal crystalline transition and melting, respectively. Note the sharpness of the melting point endotherm near 334°C. Pure compounds will normally melt over a very narrow range. Impure compounds will have a broad melting point endotherm.

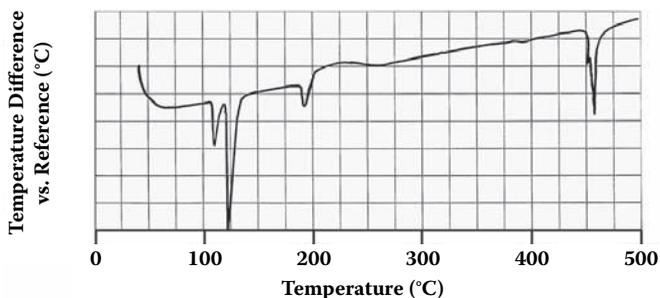


FIGURE 5.3 A sulfur thermogram. Endotherms for a rhombic-to-monoclinic crystalline phase transition and melting are seen at 105°C and 119°C, respectively. An additional endotherm is observed near 180°C. This peak corresponds to the fragmentation of liquid S_8 molecules into smaller units. Finally, vaporization is observed near 450°C.

for the $KNO_3/S/Al$ mixture just above 330°C, as illustrated in Figure 5.4, the thermograms for this system.

In the potassium chlorate–sulfur system, a different result is observed. Sulfur again melts at 119°C and begins to fragment above 140°C, but a strong exotherm corresponding to ignition of the composition is found well below 200°C! Potassium chlorate has a melting point of 356°C, so ignition is taking place well below the melting point of the oxidizer. We recall, though, that $KClO_3$ has a Tamman temperature of 42°C. A mobile species, such as liquid, fragmented sulfur, can penetrate the lattice well below the melting point and be in position to react. We also recall that the thermal decomposition of $KClO_3$ is *exothermic* (10.6 kcal of heat is evolved per mole of oxidizer that decomposes). A compounding of heat evolution is obtained; heat is released by the $KClO_3/S$ reaction and by decomposition of additional $KClO_3$,

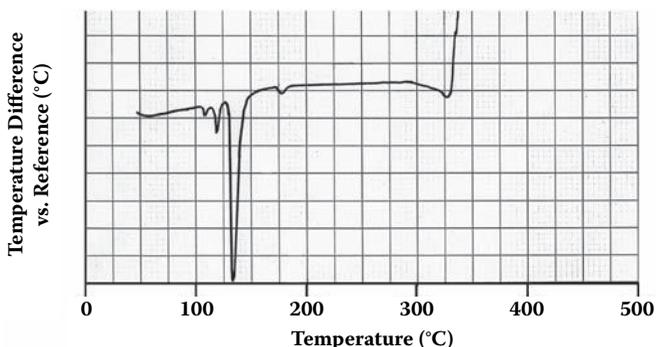


FIGURE 5.4 The potassium nitrate–sulfur–aluminum system. Endotherms for sulfur can be seen near 105 and 119°C, followed by the potassium nitrate phase transition near 130°C. As the melting point of potassium nitrate is approached (334°C), an exotherm is observed. A reaction has occurred between the oxidizer and fuel, and ignition of the mixture evolves a substantial amount of heat.

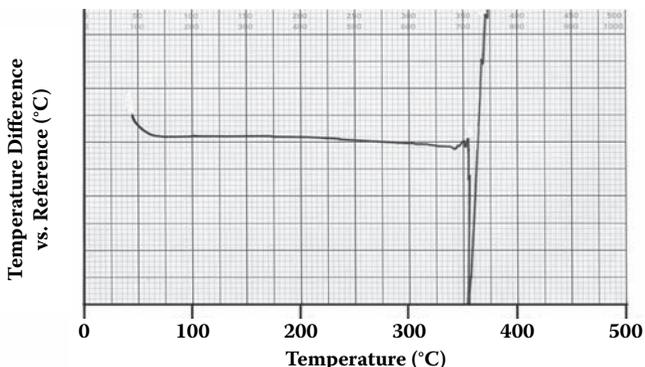


FIGURE 5.5 Thermogram of pure potassium chlorate, KClO_3 . No thermal events are observed prior to the melting point (356°C). Exothermic decomposition occurs above the melting point as oxygen gas is liberated along with heat.

generating oxygen to react with additional sulfur. More heat is generated and an Arrhenius-type rate acceleration occurs, leading to ignition well below the melting point of the oxidizer. This combination of low Tammann temperature and exothermic decomposition helps account for the dangerous and unpredictable nature of potassium chlorate. Figures 5.5 and 5.6 show the thermal behavior of the KClO_3/S system. Similarly, ignition of the potassium chlorate–sucrose system is observed near 190°C , the melting and decomposition temperature of sucrose.

As we proceed to higher-melting fuels and oxidizers, we see a corresponding increase in the ignition temperatures of two-component mixtures containing these materials. The lowest ignition temperatures are associated with combinations of low-melting fuels and low-melting oxidizers, while high-melting combinations generally display higher ignition temperatures. Table 5.3 gives some examples of this principle.

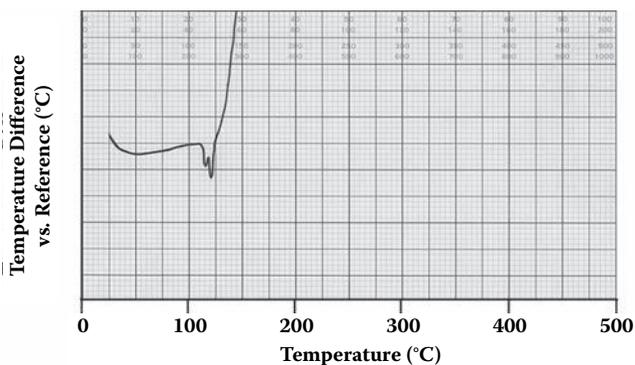


FIGURE 5.6 The potassium chlorate–sulfur system. Sulfur endotherms are seen near 105°C and 119°C , as expected. A violent exothermic reaction is observed below 150°C . The ignition temperature is approximately 200° below the melting point of the oxidizer (KClO_3 m.p. = 356°C). Ignition occurs near the temperature at which S_8 molecules fragment into smaller parts.

TABLE 5.3
Ignition Temperature of Pyrotechnic Mixtures

Component	Melting Point, °C	Ignition Temperature, °C
I. KClO ₃	356	150
S	119	
II. KClO ₃	256	195 ^a
Lactose	202	
III. KClO ₃	356	540
Mg	649	
IV. KNO ₃	334	390 ^a
Lactose	202	
V. KNO ₃	334	340
S	119	
VI. KNO ₃	334	565 ^a
Mg	649	
VII. BaCrO ₄ (90)	Decomposes at high temperature	685 ^b
B (10)	2,300	
VIII. Chinese firecracker (KClO ₃ , S, Al)		150
IX. KClO ₃		200
Sugar		
X. Black powder (KNO ₃ , S, charcoal)		340
XI. Flash powder (KClO ₄ , S, Al)		450
XII. Gold sparkler (Ba(NO ₃) ₂ , Al, dextrine, iron filings)		>500

^a A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)

^b H. Ellern, *Military and Civilian Pyrotechnics*, New York: Chemical Publishing Company, 1968.

Note: Ignition temperatures for VIII–XII determined by differential thermal analysis. These values represent the temperature at which a strong exothermic reaction appears in the thermogram of the mixture. An audible effect can be heard during many of these trials, indicating a violent reaction. Mixtures were in stoichiometric proportions unless otherwise indicated.

TABLE 5.4
Ignition Temperatures of Magnesium-Containing Mixtures

Oxidizer	Ignition Temperature, °C ^a
NaNO ₃	635
Ba(NO ₃) ₂	615
Sr(NO ₃) ₂	610
KNO ₃	650
KClO ₄	715

Source: U.S. Army Material Command, *Engineering Design Handbook: Theory and Application*, Military Pyrotechnics Series, Part One, Washington, DC, 1967 (AMC Pamphlet 706-185)

Note: All mixtures contain 50% magnesium by weight.

^a Loading pressure was 10,000 psi.

Table 5.3 shows that several potassium nitrate mixtures with low-melting, readily decomposed fuels have ignition temperatures near the 334°C melting point of the oxidizer. Mixtures of KNO₃ with higher-melting metal fuels show substantially higher ignition temperatures. Table 5.4 shows that a variety of magnesium-containing compositions have ignition temperatures close to the 649°C melting point of the metal, where the magnesium oxide coating is lost and fresh fuel atoms are exposed for oxidation. Since the system at this point is well above the Tammann temperature of magnesium, diffusion of oxygen (from the oxidizer) can occur into the metal lattice and ignition results.

A review of ignition temperatures found in the pyrotechnic literature may well reveal a substantial variation in reported values for the same composition. This is often due to differences in the experimental conditions employed to measure the temperature corresponding to ignition. The weight ratio of components, degree of mixing, loading pressure (if any), heating rate, and quantity of sample can all influence the observed ignition temperature. It is important to note that the ignition temperature of a particular energetic mixture is *not* a fundamental constant; ignition temperatures reported by different groups using different experimental methods may vary by as much as ±25°C or more for the same composition. Which number is correct? They all probably are, and each is a function of the specific experimental procedure that was employed. As differential scanning calorimetry (DSC) has evolved into the primary method used to determine ignition temperatures for energetic materials, however, the range of values reported for pyrotechnic mixtures has narrowed.

The traditional method for measuring ignition temperatures, used extensively by Henkin and McGill in their classic studies of the ignition of explosives,⁷ consisted of placing small quantities (3 or 25 milligrams, depending on whether the material was expected to denotate or deflagrate) of composition in a constant-temperature bath and measuring the time required for ignition to occur. The bath temperature was

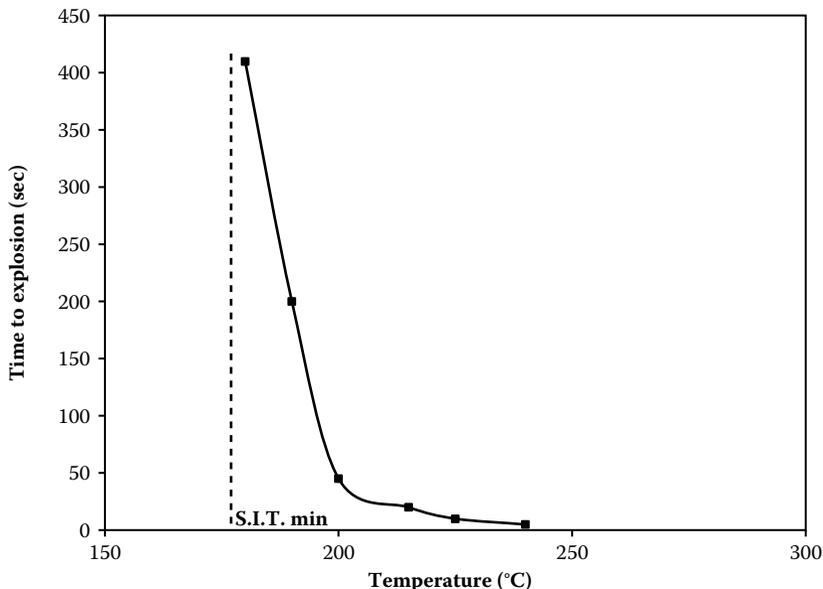


FIGURE 5.7 Time to explosion vs. temperature for nitrocellulose. As the temperature of the heating bath is raised, the time to explosion decreases exponentially, approaching an instantaneous value. The extrapolated temperature value corresponding to infinite time to explosion is called the spontaneous ignition temperature, minimum (S.I.T. min). (From H. Henkin and R. McGill, *Ind. and Eng. Chem*, 44, 1391 [1952]).

then raised a few degrees, and the experiment was repeated. Ignition temperature was defined, using this technique, as the bath temperature at which ignition occurs in 5 seconds. Data obtained in this kind of study can be plotted to yield interesting information, as shown in Figure 5.7.

Data from time vs. temperature studies can also be plotted as log time vs. $1/T$, yielding straight lines as predicted by the Arrhenius equation (see Chapter 2). Figure 5.8 illustrates this concept, using the same data plotted in Figure 5.7. Activation energies can be obtained from the slope of such plots. Deviations from linear behavior and abrupt changes in slope are sometimes observed in Arrhenius plots due to changes in the reaction mechanism or other complex factors.

Henkin-McGill plots can be quite useful in the study of ignition, providing us with important data on temperatures at which spontaneous ignition might occur. These data can be especially useful in establishing maximum storage temperatures for high-energy compositions—the temperature should be one corresponding to *infinite* time to ignition (and well below the spontaneous ignition temperature, minimum—S.I.T. (min)—shown in Figure 5.7). At any temperature above this point, ignition during storage is likely to occur. Ignition might also occur at temperatures below the S.I.T. (min) point, however, as the mass of the sample increases and self-heating occurs within the material. S.I.T. studies on small samples should never serve as the sole basis of a thermal stability hazard analysis.

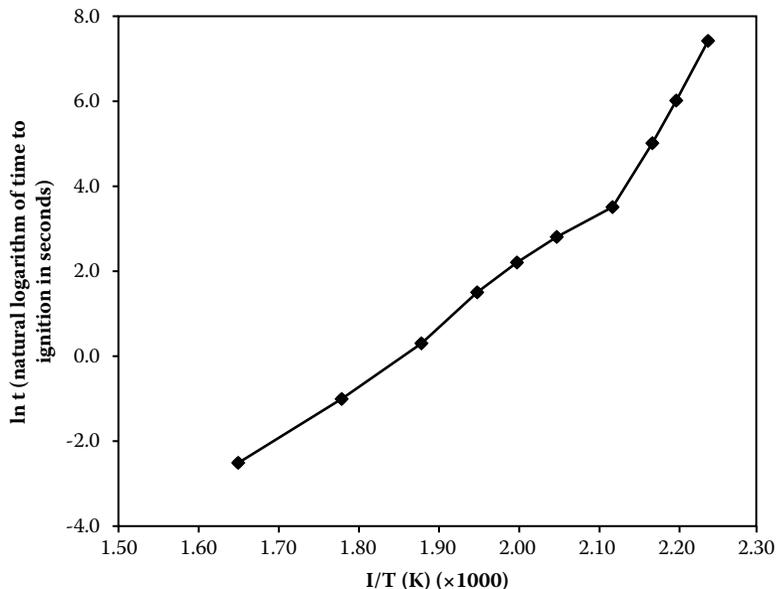


FIGURE 5.8 Henkin-McGill Plot for nitrocellulose. The natural logarithm of the time to ignition is plotted vs. the reciprocal of the absolute temperature (K). An essentially straight line is produced, and activation energies can be calculated from the slope of the line. The break in the plot near 2.1 may result from a change in the reaction mechanism at that temperature. (From H. Henkin and R. McGill, *Ind. and Eng. Chem.* 44, 1391 [1952].)

Ignition temperatures determined by differential scanning calorimetry (DSC) usually correspond reasonably well to those obtained by a Henkin-McGill study. DSC values tend to be more reproducible from laboratory to laboratory, and from sample to sample. Differences in heating rate, sample size, homogeneity, etc., can cause some variation in values obtained with thermal analysis technique. For any direct comparison of ignition temperatures, it is best to run all of the mixtures of interest under identical experimental conditions, thereby minimizing the number of variables.

One must also keep in mind that these experiments are measuring the *temperature sensitivity* of a particular composition, in which the entire sample is heated to the experimental temperature. Ignition sensitivity can, and must, also be discussed in terms of the relative ease of ignition of a small portion of a pyrotechnic material due to other types of potential stimuli, including static spark, impact, friction, and flame. Sensitivity is discussed further in Chapter 6.

SUMMARY OF IGNITION

For ignition to occur with an energetic mixture, a temperature must be reached (in at least a portion of the sample) where the oxidizer has been raised to a temperature where the evolution of oxygen is occurring at a significant rate, and a fuel must be in

a state where it can readily react with the released oxygen. In practice, the activation temperature for an oxidizer is usually observed to be a temperature approaching the melting point of the oxidizer. For metallic and elemental fuels, the activation temperature is usually found to be near the melting point of the fuel—this is the temperature where any oxide coating will melt away, exposing fresh, reactive fuel atoms, as well as a temperature where diffusion of a mobile species is possible within the solid material. For organic fuels, the activation temperature should correspond to the decomposition temperature of the organic molecule, with the formation of readily oxidizable free radicals that will react with oxygen from the oxidizer to produce heat and propagate the reaction.

In summary, ignition factors include (but are not limited to):

- Selection of oxidizer, fuel, and other components
- Particle sizes of oxidizer and fuel
- Grain size of the homogeneous composition (if present as granular material)
- Type and amount of energy input
- The presence of any sensitizers, intentional or unintentional

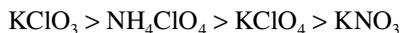
PROPAGATION OF BURNING

FACTORS

The ignition process initiates a self-propagating, high-temperature chemical reaction at the surface of the energetic mixture. The rate at which the reaction then proceeds through the remainder of the composition will depend on the nature of the oxidizer and fuel, as well as on a variety of other factors. Rate can be expressed in two ways: mass reacting per unit time or length burned per unit time, or as the reciprocal of these units—the time required to burn a given distance or mass of material. The loading pressure used, and the resulting density of the composition, will determine the relationship between rates involving length and mass.

Reaction velocity is primarily determined by the selection of the oxidizer and fuel (but there are a large number of other factors, as we shall see). The rate-determining step in many high-energy reactions appears to be an endothermic process, with decomposition of the oxidizer frequently the key step. The higher the decomposition temperature of the oxidizer, and the more endothermic its decomposition, the slower the burning rate will be (with all other factors held constant).

Shimizu reports the following reactivity sequence for the most common fire-works oxidizers:¹¹



Shimizu notes that potassium nitrate is not slow when used in black powder (in which the homogeneity is maximized by extended energetic mixing) and metal-containing compositions in which a “hot” fuel is present. Sodium nitrate is quite similar to potassium nitrate in reactivity (but is considerably more hygroscopic).

TABLE 5.5
Burning Rates of Stoichiometric Binary Mixtures

Fuel	Linear Burning Rate, mm/s ^a			
	Oxidizer			
	KClO ₃	KNO ₃	NaNO ₃	Ba(NO ₃) ₂
Sulfur	2	X ^b	X	—
Charcoal	6	2	1	0.3
Sugar	2.5	1	0.5	0.1
Shellac	1	1	1	0.8

Source: A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)

^a Compositions were pressed in cardboard tubes of 16 mm diameter.

^b X indicates that the mixture did not burn.

Shidlovskiy has gathered data on burning rates for some of the common oxidizers.² Table 5.5 contains data for oxidizers with a variety of fuels. Again, note the high reactivity of potassium chlorate.

The fuel also plays an important role in determining the rate of combustion. Metal fuels, with their highly exothermic heats of combustion and excellent thermal conductivity values, tend to increase the rate of burning. The presence of low-melting, volatile fuels (sulfur, for example) tends to retard the burning rate, although they *enhance* ignitability. Heat is used up in melting and vaporizing these materials rather than going into raising the temperature of the adjacent layers of the unreacted mixture and thereby accelerating the reaction rate. The presence of moisture can greatly retard the burning rate by absorbing substantial quantities of heat through vaporization. The old saying “Keep your powder dry” has a scientific basis—the heat of vaporization of water (540 calories/gram at 100°C) is one of the largest values found for liquid materials. A composition cannot get hotter than 100°C until all water has been removed, and considerable heat is required to remove each gram of water. Benzene, C₆H₆, as a contrasting example of a liquid with substantially weaker intermolecular attractive forces, has a heat of vaporization of only 94 calories/gram at its boiling point, 80°C.

The higher the activation temperature of a fuel (generally its melting point or decomposition temperature), the slower is the burning rate of compositions containing the material, again with all other factors equal. Shidlovskiy notes that aluminum compositions are slower burning than corresponding magnesium mixtures due in part to this phenomenon.²

The transfer of heat from the burning zone to the adjacent layers of unreacted composition is also critical to the combustion process. Metal fuels aid greatly here, due to their high thermal conductivity. For binary mixtures of oxidizer and fuel, combustion rate increases as the metal percentage increases, well past the stoichiometric point. For magnesium mixtures, this effect is observed up to 60%–70% magnesium

by weight, and similar effects have been observed with other metal fuels, including tungsten, molybdenum, and zirconium. This behavior results from the increasing thermal conductivity of the composition with increasing metal percentage. With magnesium, a metal with a low boiling point around 1,100°C, excess magnesium that is vaporized by the heat evolved from the pyrotechnic reaction between oxidizer and fuel can react with oxygen from the atmosphere,¹ and thereby can provide additional enhancement of the reaction rate as well as light output.

Stoichiometric mixtures should be expected—initially and logically—to be the fastest burners, and this is observed when the oxidizer and fuel have similar thermal conductivities (such as an oxidizer–organic fuel mixture). Sometimes it is difficult to predict exactly what the actual preferred reaction(s) will be at the high reaction temperatures encountered with these systems, so a trial-and-error approach is often advisable. A series of mixtures should be prepared—varying the fuel/oxidizer ratio above and below the stoichiometric point while keeping everything else constant. The formulation yielding the maximum burning rate is then experimentally determined. When a *metal* fuel is present, expect the system to show increasing burn rates as the metal percentage is increased beyond the stoichiometric point, due to the increased thermal conductivity of the system as the metal percentage increases. The extra metal helps to capture more of the heat produced by the reaction, and effectively transfers this heat into the next layer of composition, raising the temperature closer to the ignition point. Table 5.6 shows how stoichiometry affects the burn rate of a binary strontium nitrate–magnesium red flare composition. The fuel-rich composition has the fastest burn rate and the highest candlepower, while the oxidizer-rich composition, as expected, burns the slowest and the dimmest. Table 5.7 shows the effect of varying the metal fuel, organic fuel/binder ratio while keeping the oxidizer percentage constant. Reducing the metal percentage in the mixture and increasing the binder percentage slows up the burn rate and reduces the candlepower of the sodium nitrate–magnesium illuminant mixture.

Variation in loading density, achieved by varying the pressure used to consolidate the composition in a tube, can also affect the burning rate. A typical high-energy reaction evolves a substantial quantity of gaseous products, and a significant portion

TABLE 5.6
Stoichiometry Effect on Burn Rate

	Stoichiometric	Oxidizer Rich	Fuel Rich
% magnesium (fuel)	36.3	28.8	42.8
% strontium nitrate	63.7	71.2	57.2
Burn rate, inches/second	0.12	0.059	0.16
Candlepower (max.)	1,400	180	5,100

Source: W. Pulchalski, The Effect of Angular Velocity on Pyrotechnic Performance, presented at Proceedings, 4th International Pyrotechnics Seminar, Steamboat Springs, CO. 1974.

Note: Composition was pressed at 70 K psi.

TABLE 5.7
Burn Rate of an Illuminant Composition vs. Binder Percentage

% Magnesium ^a	% Sodium Nitrate ^b	% Binder ^c	Burn Rate (in./s) ^d	Candlepower
55	39	6	0.139	291,800
55	37	8	0.106	240,700
55	35	10	0.094	195,000
55	33	12	0.088	180,600

Source: B. V. Diercks, D. R. Dillehay, and J. G. Day, The Use of Encapsulated Binders in Illuminant Manufacture, 8th International Pyrotechnics Seminar, Steamboat Springs, CO, 1982.

^a Magnesium was type 1, ellipsoidal, -30/+50 mesh.

^b Sodium nitrate was 55 microns by sieve, 20 microns by Fisher subsieve sizer.

^c Binder was an epoxy resin-polysulfide mix.

^d Flares were pressed at 14,000 psi in two increments.

of the actual combustion reaction occurs in the vapor phase. For these reactions, the combustion rate (measured in grams consumed/second) will increase as the loading density *decreases*. A lightly consolidated, porous powder should burn the fastest, perhaps reaching an explosive velocity, while a highly consolidated mixture, loaded under considerable pressure, will burn slower. The combustion front in such mixtures is carried along by hot gaseous products. The more *porous* the composition is, the faster the reaction should be. The ideal fast composition is one that has been granulated to achieve a high degree of homogeneity *within* each particle, but yet consists of small grains of powder with high surface area. Burning will accelerate rapidly through a loose collection of such particles.

The exception to this loading pressure rule is the category of gasless compositions, such as the barium chromate–boron or iron oxide–silicon systems. Here, burning is believed to propagate through the mixture without the significant involvement of the vapor phase, and an increase in loading pressure should lead to an increase in burning rate, due to more efficient heat transfer via tightly compacted solid and liquid particles. Thermal conductivity is quite important in the burning rates of these compositions. Table 4.7 illustrates the effect of loading pressure for the gasless barium chromate–boron system.

EFFECT OF EXTERNAL PRESSURE

The gas pressure (if any) generated by the combustion products, combined with the prevailing atmospheric pressure, will also affect the burning rate. The general rule here predicts that an increase in burning rate will occur as the external pressure increases. The ambient external pressure will act as confinement to gas products and heat attempting to escape from the reaction zone. This causes more of the heat to be retained by the burning composition, thereby accelerating the burn rate of the composition. This factor can be especially important when oxygen is a significant component of the gaseous

phase, and the oxygen remains in the reaction zone for a longer time, thereby increasing the probability it will react with fuel. The magnitude of the external pressure effect indicates the extent to which the vapor phase is involved in the combustion reaction.

The effect of external pressure on the burning rate of black powder and numerous other propellants has been quantitatively studied. The general equation for the burn rate of a propellant is

$$\text{Burn rate (m/s)} = aP^n \quad (5.2)$$

where a represents the chemistry and engineering of the system, P represents the pressure in the burn chamber, and n is the exponential coefficient that is a constant for the given propellant material. The gassier the propellant is in terms of reaction products, the higher the exponential value should be. Propellants are discussed further, and some typical a (preexponential) and n (exponential) values for several propellants are given in Chapter 7. As seen in Chapter 7, a nitroglycerine/nitrocellulose “smokeless powder” has a slower burn rate at 1 atmosphere than black powder. However, at high pressures such as those typically found in the firing chambers of guns, the smokeless powders will significantly surpass black powder in burn rate.

Shidlovskiy reports the experimental empirical equation for the combustion of Russian black powder to be

$$\text{Burn rate} = 1.21 P^{0.24} \text{ (cm/s)} \quad (5.3)$$

where P is pressure, in atmospheres. Predicted burning rates for black powder, calculated using this equation, are given in Table 5.8.

This increase in burn rate with confining pressure is a phenomenon that is well known and widely used in designing propellant devices. A restrictor, or choke, is often used in such devices to build up a higher internal pressure, and thereby speed up the propellant burn rate, and create more thrust.

TABLE 5.8
Predicted Burning Rates for Black Powder at Various External Pressures

External Pressure, atm	External Pressure, psi	Linear Burning Rate, cm/s
1	14.7	1.21
2	29.4	1.43
5	73.5	1.78
10	147	2.10
15	221	2.32
20	294	2.48
30	441	2.71

Source: A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Moscow, 1964.
(Translated by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)

Note: The Shidlovskiy equation is valid for the pressure range 2 to 30 atmospheres.

For gasless heat and delay compositions, little external pressure effect is expected. This result, plus the increase in burning rate observed with an increase in loading pressure, can be considered good evidence for the absence of any significant gas phase involvement in a particular combustion mechanism. For the ferric oxide–aluminum ($\text{Fe}_2\text{O}_3/\text{Al}$), manganese dioxide–aluminum (MnO_2/Al), and chromic oxide–magnesium ($\text{Cr}_2\text{O}_3/\text{Mg}$) systems, some slight gas phase involvement is indicated by the three- to fourfold rate increase observed as the external pressure is raised from 1 to 150 atm. The chromic oxide–aluminum system, however, reportedly burns at exactly the same rate (2.4 mm/s) at 1 and 100 atm, suggesting that it is a true gasless system.²

Data for the burning rate of a delay system as a function of increasing external pressure (a nitrogen atmosphere was used) are given in Table 5.9.

Another matter to consider is whether or not pyrotechnic compositions will burn, and at what rate, at very low pressure. For reactions that use oxygen from the air as an important part of their functioning, a substantial drop in performance is expected at low pressure. Mixtures high in fuel (such as the magnesium-rich illuminating compositions) will not burn well at low pressures. Stoichiometric mixtures, in which all oxygen needed to burn is provided by the oxidizer, should be the least affected by pressure variations. Data for burn rate of a delay mixture as the ambient pressure is reduced below 1 atmosphere are given in Table 5.10, and the burn rate is observed to slow up, as predicted, at lower pressures.

An interesting study by Schneitter of the ignition and performance of flash powder and black powder at low ambient pressures showed that attempts to ignite either

TABLE 5.9
Burning Rate of a Delay Mixture as a Function of External Pressure

Composition	Potassium permanganate, KMnO_4	64%
	Antimony	36%
External Pressure, psi	Burning Rate, ^a cm/s	
14.7	.202	
30	.242	
50	.267	
80	.296	
100	.310	
150	.343	
200	.372	
300	.430	
500	.501	
800	.529	
1,100	.537	
1,400	.543	

Source: J. S. Glasby, *The Effect of Ambient Pressure on the Velocity of Propagation of Half-Second and Short Delay Compositions*, Report D.4152, Imperial Chemical Industries, Nobel Division, Ardeer, Scotland.

^a Compositions were loaded into 105 mm brass tubes at a loading pressure of 20,000 psi.

TABLE 5.10
The Effect of Low Ambient Pressure on the
Burn Rate of a Delay Composition^a

External Pressure, P (in atm)	Burn Rate, mm/s ^b
1.0	16.9
0.74	16.0
0.50	15.9
0.26	15.5
0.11	14.9

Source: N. Davies, T. T. Griffiths, E. L. Charsley, and J. A. Ramsey, The Effect of Low Ambient Pressure on the Burn Rate of a Delay Composition, 10th International Pyrotechnics Seminar, Karlsruhe, Germany, 1985.

^a The delay composition is 30% boron and 70% bismuth oxide. This delay has been used in the UK for many years.

^b The delay system provided burn rates from 5 to 35 mm/s, as the %B was varied. The maximum rate occurred with 15% boron.

potassium perchlorate-aluminum flash powder composition or commercial black powder of fine grain size using electric matches in a vacuum were unsuccessful, whereas the material readily ignited at normal atmospheric pressure.⁸ The compositions *could* be ignited under the same vacuum conditions using an incandescent Nichrome wire filament, but ignition delays of up to 3.5 seconds were observed. Oxygen gas that is present in the air was shown not to be the critical factor, as the compositions ignited normally by means of an electric match in 1 atmosphere of either helium or nitrogen gas.

EFFECT OF EXTERNAL TEMPERATURE

As discussed in Chapter 2, rates of chemical reactions increase as ambient temperature increases. It can be anticipated that ease of ignition and burning rate will depend on the initial temperature of an energetic composition. Ignition of a cold composition will require more energy input for the initial layer or grain of composition to reach its ignition temperature. The effect should be most pronounced for compositions of low exothermicity and high ignition temperature.

Pyrotechnic and propellant devices that have been conditioned at a low temperature are also expected to burn slower than identical devices that have been conditioned at warmer temperatures. This is due primarily to the fact that the temperature rise that is required, via heat transfer from the reaction zone, for the succeeding layer of material to go from its initial temperature to the ignition temperature is a larger value for a cold device than a warm one.

Hence, the temperature at which devices are stored prior to use can be a factor in the performance of the items if no temperature equilibration to a standard value is

TABLE 5.11
Effect of Ambient Temperature on Burn
Time of a Delay Composition

Temperature, °C	Burning Time, in seconds
-40	3.43 ± 0.13
Ambient	3.30 ± 0.07
165	3.15 ± 0.14

Source: L. Lopez, F. Taylor, and R. Broad, The Replacement of Undesirable Barium Chromate by Iron (III) Oxide in the Tungsten/Potassium Perchlorate/Barium Chromate/Binder Delay System, 16th International Pyrotechnics Seminar, Jonkoping, Sweden, 1991.

Note: Composition: Potassium perchlorate (33%), red iron oxide (18%), and tungsten (49%). Loading pressure: 36,000 psi, column length approximately 0.64 inches.

provided prior to use. In research and development work, it is important to eliminate variation in the temperature of end items when burn rates or burn times are measured. The effect of ambient temperature on the burn time of a delay composition is shown in Table 5.11. It can be seen that the effect is relatively minor in this system, with a variation of approximately 10% over the wide temperature range that was studied, from very cold to very warm.

Considerably more thermal input is needed to provide the necessary activation energy at -30°C than is needed when the mixture is initially at +40°C (or higher). For black powder, a 15% slower rate is reported at 0 vs. 100°C, at an external pressure of 1 atmosphere.² Some high explosives show an even greater temperature sensitivity. The detonation velocity of nitroglycerine, for example, is 2.9 times faster at 100°C than it is at 0°C.²

In summary, cold energetic devices will require a stronger ignition stimulus, and burn slower, than warm devices with all other factors being equal.

BURNING SURFACE AREA

The burning rate—expressed in either grams/second or millimeters/second—should increase as the burning surface area increases. Small grains will burn faster than large grains due to their greater surface area per gram. Compositions loaded into a narrow tube should burn more slowly than the same material in a wide tube. The heat loss to the walls of the container is less significant for a wide-bore tube, relative to the heat retained by the composition. For each composition, and each loading pressure, there will be a minimum diameter capable of producing stable burning. This minimum diameter will decrease as the exothermicity of the composition increases.

A thick-walled metal tube is particularly effective at *removing* heat from a burning composition, and propagation of burning down a narrow column can be difficult for all but the hottest of mixtures if metal (particularly a thick metal tube) is used for the container material. On the other hand, the use of a metal wire for the *center* of the popular

wire sparkler retains the heat evolved by the barium nitrate-aluminum reaction and *aids* in propagating the burning down the length of the thin pyrotechnic coating.

A mixture that burns well in a narrow tube may possibly reach an explosive velocity in a thicker column, so careful experiments should be done any time a diameter change is made. For narrow tubes, one must watch out for the possible restriction of the tube by solid reaction products, thereby preventing the escape of gaseous products. An explosion may result if this occurs, especially for fast compositions.

SUMMARY OF BURN RATE

The burn rate of a pyrotechnic composition is determined by a large number of factors. All of these factors must be controlled in the manufacturing process to produce items that give reproducible performance from day to day and month to month. Burn rate factors include, but are not limited, to:

- Selection of oxidizer, fuel, and other components
- Weight ratio of the components
- Particle sizes of the components
- Homogeneity of the blended composition
- Presence of moisture
- Consolidation pressure (of pressed materials)
- External pressure and temperature when used

Therefore, to intentionally change a burn rate, without changing the hardware for a device, the following are some of the options:

1. Change the starting chemicals (new oxidizer, new fuel, or both).
2. Change the oxidizer-fuel ratio.
3. Change the particle size of one or more components.
4. Add a catalyst or a retardant to the composition.
5. Mix for a longer time to increase homogeneity of the composition.

Some of these options may be feasible for a given burn rate problem. Most will require a reevaluation of the new material for sensitivity, and will require a requalification of the material and the end item for most military applications if the tolerances in the specifications and technical drawings for a device are exceeded.

Given all the factors that affect the burn rate of an energetic material, it is easy to see why there is not yet a computer program one can use to predict a burn rate.

COMBUSTION TEMPERATURE

A pyrotechnic reaction generates a substantial quantity of heat, and the actual flame temperature reached by these mixtures is an area of study that has been attacked from both the experimental and theoretical directions.⁹

Flame temperatures can be measured directly, using special high-temperature optical methods. They can also be calculated (estimated) using heat of reaction

data and thermochemical values for heats of fusion and vaporization, heat capacity, and transition temperatures. Calculated values tend to be higher than the actual experimental results, due to heat loss to the surroundings as well as the endothermic decomposition of some of the reaction products. Details regarding these calculations, with several examples, have been published.⁶

Considerable heat will be used to melt and vaporize the reaction products. Vaporization of a reaction product is commonly the limiting factor in determining the maximum flame temperature. For example, consider a beaker of water at 25°C. As the water is heated, at 1 atmosphere pressure, the temperature of the liquid rises rather quickly to a value of 100°C. To heat the water over the temperature range of 25°C to 100°C, a heat input of approximately 1 calorie per gram of water per degree rise in temperature is required. To raise 500 grams of water from 25°C to 100°C will require:

$$\begin{aligned}\text{Heat required} &= (\text{grams of water})(\text{heat capacity})(\text{temperature change}) \\ &= (500 \text{ grams})(1 \text{ cal/}^\circ\text{C-gram})(75^\circ) \\ &= 37,500 \text{ calories}\end{aligned}$$

Once the water reaches 100°C, however, the temperature increase stops. A plateau is reached, and the water boils at 100°C. Liquid is converted to the vapor state, and 540 calories of heat (the heat of vaporization of water) is needed to convert 1 gram of water from liquid to vapor. To vaporize 500 grams of water, at 100°C,

$$(500 \text{ grams})(540 \text{ cal/gram}) = 270,000 \text{ calories}$$

we can calculate that 270 kcal of heat is required. Until this quantity of heat is put into the system, and all of the water is vaporized, no further temperature increase will occur in the system (now all vapor). Similar phenomena involving the vaporization of pyrotechnic reaction products such as magnesium oxide (MgO) and aluminum oxide (Al₂O₃) tend to limit the peak temperature attained in pyrotechnic flames. The boiling points of some common combustion products are given in Table 5.12.

The experimentally measured flame temperatures of many oxidizer-magnesium compositions show values near 3,600°C (the boiling point of magnesium oxide); oxidizer-aluminum compositions tend to produce flame temperatures near 3,000°C (the melting point of aluminum oxide). As a result, the intensity of the light emission from an oxidizer-magnesium flare will be considerably greater than that of a flare containing the same oxidizer mixed with aluminum. Remember, light emission from incandescing black bodies is proportional to temperature to the fourth power—that 600°C difference in flame temperature is very noticeable. If you want a really bright, intense flame, the fuel material of choice would be zirconium, since the boiling point of ZrO₂ approaches 5,000°C. The brightness of this composition may be harmful to your eyes.

Mixtures using organic (carbon-containing) fuels usually attain lower flame temperatures than those compositions consisting of an oxidizer and a metallic fuel. This reduction in flame temperature can be attributed to the lower heat output of the

TABLE 5.12
Melting and Boiling Points of Common Nongaseous Pyrotechnic Products

Compound	Formula	Melting Point, °C	Boiling Point, °C
Aluminum oxide	Al ₂ O ₃	2,072	2,980
Barium oxide	BaO	1,918	ca. 2,000
Boron oxide	B ₂ O ₃	450	ca. 1,860
Magnesium oxide	MgO	2,852	3,600
Potassium chloride	KCl	770	1,500 (sublimes)
Potassium oxide	K ₂ O	350 (decomposes)	—
Silicon dioxide	SiO ₂	1,610 (quartz)	2,230
Sodium chloride	NaCl	801	1,413
Sodium oxide	Na ₂ O	1,275 (sublimes)	—
Strontium oxide	SrO	2,430	ca. 3,000
Titanium dioxide	TiO ₂	1,830–1,850 (rutile)	2,500–3,000
Zirconium dioxide	ZrO ₂	ca. 2,700	ca. 5,000

Source: R. C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, 63rd ed., Boca Raton, FL: CRC Press, 1982.

organic fuels vs. metals, as well as to some of the lower heat output going toward the decomposition and vaporization of the organic fuel and its by-products. The presence of even small quantities of an organic component (possibly added as a binder) in an oxidizer–metal fuel mixture can markedly lower the flame temperature, as the available oxygen is consumed by the carbonaceous material in competition with the metallic fuel.¹⁰ Table 5.13 illustrates this behavior, with data reported by Shimizu.¹¹

This reduction of flame temperature can be minimized somewhat by using binders with a high oxygen content. In such binders, the carbon atoms are already partially oxidized, and they will therefore consume less oxygen per gram (and per mole) than pure hydrocarbons in going to carbon dioxide during the combustion process. The balanced chemical equations for the combustion of hexane (C₆H₁₄) and glucose (C₆H₁₂O₆) illustrate this (both are six-carbon molecules):



(The second reaction uses less oxygen per mole of fuel as well as per gram of fuel.)

Pyrotechnic flames typically fall in the 1,500 to 3,000°C range. Table 5.14 lists approximate values for some common classes of high-energy reactions.²

Binary mixtures of oxidizer with metallic fuel yield the highest flame temperatures, and the choice of oxidizer does not appear to make a substantial difference in the temperature attained. For compositions without metal fuels, this does not seem to be the case. Shimizu has collected data for a variety of compositions and has

TABLE 5.13
Effect of Organic Fuels on Flame Temperature of
Magnesium-Oxidizer Mixtures

Composition	Oxidizer	55% by weight
	Magnesium	45% by weight
	Shellac	Either 0 or 10% additional
Approximate Flame Temperature, °C^a		
Oxidizer		
	KClO₄	Ba(NO₃)₂
Without shellac	3,570	3,510
With 10% shellac	2,550	2,550

Source: T. Shimizu *Fireworks—The Art, Science and Technique*
 Tokyo: T. Shimzu, 1981.

^a Temperature was measured 10 millimeters from the burning surface
 in the center of the flame.

observed that potassium nitrate mixtures attain substantially lower flame temperatures than similar mixtures made with chlorate or perchlorate oxidizers. This result can be attributed to the substantially endothermic decomposition of KNO₃ relative to the other oxidizers combined with the lower heat output per gram of the nonmetal fuels. Table 5.15 presents some of the Shimizu data.¹¹

A final factor that can limit the temperature of pyrotechnic flames is unanticipated high-temperature chemistry. Certain reactions that do not occur to any measurable extent at room temperature become quite probable at higher temperatures.

TABLE 5.14
Maximum Flame Temperature of
Various Classes of Pyrotechnic Mixtures

Type of Composition	Maximum Flame Temperature, °C
Photoflash, illuminating	2,500–3,500
Solid rocket fuel	2,000–2,900
Colored flame mixtures	1,200–2,000
Smoke mixtures	400–1,200

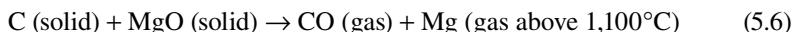
Source: A. A. Shidlovskiy, *Principles of Pyrotechnics*,
 3rd ed., Moscow, 1964. (Translated by Foreign
 Technology Division, Wright-Patterson Air Force
 Base, Ohio, 1974.)

TABLE 5.15
Flame Temperature for Oxidizer-Shellac Mixtures

Composition	Oxidizer	75%
	Shellac	15%
	Sodium oxalate	10%
Oxidizer		Approximate Flame Temperature, °C
Potassium chlorate, KClO ₃		2,160
Potassium perchlorate, KClO ₄		2,200
Ammonium perchlorate, NH ₄ ClO ₄		2,200
Potassium nitrate, KNO ₃		1,680

Source: T. Shimizu, *Fireworks — The Art Science and Technique*, Tokyo: T. Shimizu, 1981.

An example of this is the reaction between carbon (C) and magnesium oxide (MgO). Carbon can be produced from organic molecules in the flame.



This is a strongly endothermic process, but it becomes possible at high temperature due to a favorable entropy change—formation of the random vapor state from solid reactants. Such reactions provide another reason for the lower flame temperatures achieved when organic binders are added to oxidizer-metal mixtures.⁴

PROPAGATION INDEX

A simple method for assessing the ability of a particular composition to burn under adverse conditions is the propagation index, originally proposed by McLain⁴ and later modified by Rose.¹² The original McLain expression was

$$\text{PI} = \Delta H_{\text{reaction}} / T_{\text{ignition}} \quad (5.7)$$

where the propagation index (PI) is a measure of a mixture's tendency to sustain burning upon initial ignition by an external stimulus. The equation contains the two main factors that determine burning ability: the amount of heat released by the chemical reaction and the ignition temperature of the mixture. If a substantial quantity of heat is released and the ignition temperature is low, then reignition from layer to layer should occur readily and propagation is likely. Conversely, mixtures with low heat output and high ignition temperature should propagate poorly, if at all. Propagation index values for a variety of compositions are given in Table 5.16. The temperatures used in these calculations were Celsius rather than Kelvin values.

TABLE 5.16
Propagation Index Values for Pyrotechnic Mixtures^a

Composition	% by Weight	Heat of Reaction, cal/gram	Ignition Temperature, °C	Propagation Index (cal/g-°C)
I. Boron igniter		1,600	565	2.8
Boron	23.7			
Potassium nitrate	70.7			
Laminac resin	5.6			
II. Black powder		660 ^b	330	2.0
Potassium nitrate	75			
Charcoal	15			
Sulfur	10			
III. Titanium igniter		740	520	1.4
Titanium	26			
Barium chromate	64			
Potassium perchlorate	10			
IV. Manganese delay		254	421	0.60
Manganese	41			
Lead chromate	49			
Barium chromate	10			

^a J. E. Rose, *Flame Propagation Parameters of Pyrotechnic Delay and Ignition Compositions*, Report IHMR 71-168, Naval Ordnance Station, Indian Head, MD, 1971.

^b L. de Yong and F. Lu, *Propellants, Explosives, Pyrotechnics*, 23, 328, 1998.

Rose recommended modifying the original McLain expression by the addition of terms for the pressed density of the composition and for the burning rate of the mixture. He reasoned, especially for delay compositions compressed in a tube, that the ability to propagate should increase with increasing density, due to better heat transfer between grains of composition. Burning rate should also be a factor, he argued, because faster-burning mixtures should lose less heat to the surroundings than slower compositions.¹²

REFERENCES

1. L. de Yong and F. Lu, Radiative ignition of pyrotechnics: Effect of wavelength on ignition threshold, *Propellants, Explosives, Pyrotechnics*, 23, 328 (1998).
2. A. A. Shidlovskiy, *Principles of pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)
3. T. J. Barton et al., Factors affecting the ignition temperature of pyrotechnics, in *Proceedings, Eighth International Pyrotechnics Seminar*, Steamboat Springs, CO: IIT Research Institute, July 1982, 99.
4. J. H. McLain, *Pyrotechnics from the viewpoint of solid state chemistry*, Philadelphia: Franklin Institute Press, 1980.

5. H. Ellern, *Military and civilian pyrotechnics*, New York: Chemical Publishing Company, 1968.
6. U.S. Army Material Command, *Engineering design handbook: Theory and application*, Military Pyrotechnic Series, Part One, Washington, DC, 1967 (AMC Pamphlet 706-185).
7. H. Henkin and R. McGill, Rates of explosive, Decomposition of explosives, *Ind. and Eng. Chem*, 44, 1391, 1952.
8. R. L. Schneitter and S. C. Schneitter, Ignition of salute compositions and black powder under vacuum and inert gases, presented at Proceedings, 4th International Symposium on Fireworks, Halifax, Nova Scotia, Canada, October 1998.
9. L. V. De Yong and F. J. Valenta, *Evaluation of selected computer models for modeling pyrotechnic and propellant devices*, IHTR Technical Report 1279, September 1989.
10. J. E. Tanner, *Effect of binder oxygen content on adiabatic flame temperature of pyrotechnic flares*, RDTR 81, Crane, IN: Naval Ammunition Depot, August 1972.
11. T. Shimizu, *Fireworks—The art, science and technique*, Tokyo: T. Shimizu, 1981.
12. J. E. Rose, *Flame propagation parameters of pyrotechnic delay and ignition compositions*, Report IHMR 71-168, Indian Head, MD: Naval Ordnance Station, 1971.
13. F. L. McIntyre, *A compilation of hazard and test data for pyrotechnic compositions*, Report ARLCD-CR-80047, Dover NJ: U.S. Army Armament Research and Development Command, 1980.

6 Sensitivity



COMET IN THE AIR: (See color insert after page 112) A large pellet of light-producing pyrotechnic composition, fired into the air, is referred to as a *comet*. These can be used for entertainment as well as emergency signaling purposes. Duration of the burn and size of the effect are determined by both the chemistry that is used and the actual mass of the pellet. The compositions must possess a sensitivity characteristic such that they are safe to press into compacted pellets, yet light reliably when they are fired into the air. (Photo by Tim Wade and Dennis King, courtesy of MP Associates.)

An energetic material is of little value if you cannot safely mix it, load it into an end item, transport and store the manufactured device, and yet have the device function properly when a reasonably mild (or requisitely strong) ignition stimulus is applied. This chapter gives a new meaning to the term *sensitivity training*.

SENSITIVITY TESTING

In investigating the sensitivity of an energetic material, a specified, the test engineer applies a controlled level of energy (in one of a variety of forms) to a specified quantity of the material, and the system is observed for positive signs that a reaction has occurred—a flash of light, sparks, smoke, a characteristic odor, or an audible report. The sensitivity of an energetic mixture is a matter of significant research interest, but it is also a matter of vital interest to the manufacturer of the mixture. Each energetic material must be sensitive

to ignition, but yet only function when you want it to ignite in order to achieve reliable performance from a particular device. Some type of external energy input is used to ignite the first component in the device. The remaining components in the device are in turn ignited by the output from the preceding component as the device sequentially functions.

One of the first things to know about sensitivity is the fact that it is a very complex subject. The only correct answer to a question like “Is this mixture sensitive?” is another question: “Sensitive to what?” A particular composition may be extremely sensitive to electrostatic spark, but not have any heightened sensitivity to elevated temperature. Similarly, a friction-sensitive material may not be particularly sensitive to spark. Each mode of energy input interacts with the components of an energetic material in a different way. If the applied energy is effectively absorbed by the composition, a temperature rise may occur. If the rising temperature approaches the ignition temperature of the composition, ignition may result.

In some instances, the energy input is strongly absorbed by the mixture; in other systems, there is little transfer of energy to the composition. Hence, there is no alternative but to test each new composition for its sensitivity by running the whole scan of standard sensitivity tests: friction, impact, spark, and thermal, with shock sensitivity often measured as well.

Another key point is that sensitivity has a *probability* factor associated with it—you can run sensitivity tests on a given energetic material and perform ten tests at each energy level that is examined. At low levels of energy input, zero of ten trials produce a positive result. Raise the energy input level and you may observe that the material ignites in six of ten trials. As you raise the energy level of the ignition stimulus even higher—be it friction, impact, or spark—the number of positive tests observed in ten successive trials should continue to increase and reach ten out of ten positive results. Ignition is a statistical event—the energy that is introduced into the sample must be effectively absorbed by the sample and a temperature rise must occur in at least part of the sample, bringing that portion to its ignition temperature. A sufficient amount of the sample must then in turn ignite in order for a positive result to be detected and recorded. There is not an on/off switch with respect to sensitivity; each sample, as placed in the test fixture, will have minor differences in content and orientation in the sample holder, and the delivery of energy from the test apparatus will similarly vary slightly from test to test. The end result will be a probability curve. Low levels of energy input will result in close to zero ignitions of the sample. These values represent levels that will be associated with safety in manufacturing and subsequent handling of the energetic material. High levels of energy input should result in close to 100% ignition of test samples. These high levels represent the ability of the composition to produce reliable ignition of the material in an end item, if the proper ignition energy is provided by the engineer who designs the ignition mechanism for the item.

During the manufacturing process, chemicals are initially mixed to produce a reasonably homogeneous blend of oxidizer, fuel, binder, and other components. These mixtures are then pressed into tubes, extruded as thick pastes, or otherwise used in the manufacturing process. During these operations, it is possible that the chemical mixtures will experience impact, friction, spark, and heat. It is therefore extremely important that the manufacturer have knowledge of the sensitivity of all its energetic mixtures to each of these various types of energy input.

No energetic composition should be deemed truly safe, however, even if it appears to be insensitive to a range of ignition stimuli. All pyrotechnic and propellant compositions are designed to function by burning or deflagration (very rapid burning), and a mixture that does *not* release its energy rapidly when exposed to a moderately energetic ignition source will be of extremely limited value. Manufacturers must have technical data on the sensitivity of their mixtures to ignition from various stimuli, and they must then analyze their manufacturing processes to determine all of the possible sources of energy that compositions might experience during mixing, loading, and assembly into finished devices. In a study by the U.S. Army, a systematic evaluation of the properties of a range of pyrotechnic compositions was carried out, using the identical test equipment, technician, and test procedures for all of the tested materials. This study provided a wealth of information on the factors that affect the sensitivity of pyrotechnic compositions.¹

The sensitivity of a high-energy mixture to an ignition stimulus is influenced by a number of factors. A mixture of an energetic fuel (e.g., aluminum) with an easily decomposed oxidizer (e.g., potassium chlorate, KClO_3) is expected to be quite sensitive to a variety of ignition stimuli. A composition with a poor fuel and a stable oxidizer should be much less sensitive, if it can be ignited at all. Ignition temperature, as determined by thermal analysis or a Henkin-McGill time-to-ignition study,² is but one measure of sensitivity, and there is not any simple correlation between ignition temperature and static spark, impact, or friction sensitivity. Some mixtures with reasonably high ignition temperatures (potassium perchlorate, KClO_4 , mixed with fine particle size aluminum is a good example) can be quite spark sensitive, because aluminum metal is an effective absorber of the energy in a spark, and the reaction is highly exothermic and becomes self-propagating once a small portion is ignited. Sensitivity and output are not necessarily related and are determined by different combinations of factors. A given mixture can have high sensitivity and low output, low sensitivity and high output, or any other combination of these two properties. McLain has proposed categorizing the relative hazards of pyrotechnic compositions based on the combination of these two properties.³

Those mixtures that have both high sensitivity and substantial output are the ones that must be treated with the greatest care. A potassium chlorate–sulfur–aluminum flash and sound mixture is an example of this type of dangerous composition, having both a low ignition temperature ($<200^\circ\text{C}$) and significant spark sensitivity (depending heavily on the type of aluminum powder that is used). A potassium perchlorate–zirconium ignition composition (ZPP) is another that is extremely sensitive to spark, and it has seen increased use in recent years as an energetic ignition composition that very quickly produces very high flame temperatures when ignited.⁴

The ignition sensitivity of energetic compositions can vary considerably, depending on the type of energy interacting with the chemical mixture. It is necessary for a given energy input to be efficiently transferred to the composition for a temperature rise to occur and ignition to be achieved. Energy input may occur via impact or friction, and thereby involve mainly energy that is kinetic in nature. A spark is a combination of thermal, electrical, and shock input, while exposure of a composition to flame or heat involves the application of thermal energy.

To achieve ignition in systems that contain molecular fuels such as a sugar, oxygen-rich anions like chlorate or nitrate, or both, it is necessary for some chemical bonds in the mixture to absorb a sufficient quantity of the incident energy for bond

breaking to occur. This energy transfer frequently involves raising the vibrational energy of various chemical bonds in the starting materials to the point where the restoring force is overcome, and the bond breaks, creating so-called free radicals, or atoms/molecules with unpaired valence electrons. Reaction products then form from reaction between oxidizer and fuel, and a net release of energy occurs. If this released energy is sufficient in quantity, and is efficiently captured by adjacent layers or grains of blended chemical composition, the ignition process is repeated through the mixture, and propagation of the burning reaction is achieved with no additional input of external energy required. Sensitivity testing measures the minimum level of a specific type of energy input required to initiate the ignition process for a given energetic composition, under a specific set of test conditions.

A number of specific types of test equipment have been developed over the past seventy-five years for measuring sensitivity to elevated temperature, impact, friction, and electrical spark, and it is unfortunate that a universal test fixture for measuring each type of sensitivity has yet to be agreed upon by the international explosive and pyrotechnic community. Test apparatuses vary from country to country, and there are even multiple types of impact and friction test equipment used within a given country. The United Nations has produced a set of tests and criteria for studying both the sensitivity and output of energetic materials and devices containing energetic materials.⁵

It is therefore difficult, if not impossible, to directly compare impact or friction sensitivity results obtained on different types of test equipment. It can also be difficult to directly compare results obtained from the same type of test apparatus used by a different test engineer in a different facility. Each test apparatus has its own unique characteristics, and each tester has his or her own slight differences in test procedures. Both of these variables can produce different test results. Relative *rankings* of sensitivities, however, generally bear some semblance of order, but quantitative comparisons between test laboratories are not advisable. Sensitivity testing by its very nature yields abstract results. The specific geometry of the test fixture, sample size, grain size, rate of energy delivery, and a host of other factors all contribute to the resulting sensitivity value. A change in any of these can alter the observed results, so caution is always needed.

So, how do we use sensitivity data? We use it by comparing the sensitivity of a new composition to other compositions with a history of manufacturing and handling safety. If the sensitivity results for a new material are comparable to those for a material with a history of accidents, special caution is called for. This approach only works when the sensitivity data are obtained using the same type of test apparatus, preferably the identical device with the tests run by the same test operator. Even here, however, sensitivity of a particular composition to each type of energy input can vary from day to day and batch to batch should changes in particle size, moisture content, homogeneity, sample age, and chemical purities occur.

SPARK SENSITIVITY

Most spark sensitivity devices work on the general principle of using a variable voltage power supply to charge a capacitor, and then the resulting stored-up energy is discharged as an electrostatic spark through a needle-like tip (the cathode) into the

sample under investigation, which rests on a positively charged anode.⁷ The energy of the spark can be calculated by the equation E (in Joules) = $\frac{1}{2} CV^2$, where C is the capacitance in farads and V is the voltage (in volts) from the power supply.

Experience has shown that the presence of certain fuels in pyrotechnic mixtures, particularly when present in fine particle size, tends to cause the resulting mixtures to have significant sensitivity to spark. Zirconium, boron, and phosphorus are particularly noted for their spark sensitivity. Fine magnesium or aluminum powder can also enhance spark sensitivity, and fine grains of blended oxidizer-fuel mixture will have a significantly greater sensitivity to spark than coarser grains. This is of importance to manufacturers, because there is always the possibility of generating fine pyrotechnic dust during processing.

Spark sensitivity values for specific pyrotechnic compositions tend to correlate fairly well from laboratory to laboratory when a minimum ignition energy, in joules (J), is determined and starting chemicals similar in particle size and shape are used. In assessing a spark sensitivity hazard, a value of 0.10 J or less for spark ignition energy is often regarded as indicating a spark sensitivity concern requiring a full static protection program. A moving human being can develop and hold a spark energy of approximately 0.015 J (15 mJ), so compositions and fuels that have spark ignition energies near this value are of particular concern in manufacturing and handling.⁷ The previously stated alarm value of 0.10 J (100 mJ) adds a safety factor of 6 to 7 to the 15 mJ human spark energy value.

Vapors from organic solvents such as acetone and alcohol (often used to activate binders in the mixing process for energetic materials) can form mixtures with air that are both spark sensitive and explosive, showing spark sensitivity values below 1 mJ in many cases. A layer of volatile, ignitable solvent may form at the surface of a drying energetic mixture, blend with atmospheric oxygen, and thereby create a serious spark hazard that persists until all the solvent has been removed. Many of these solvent-air mixtures are readily ignited by the energy in a human-generated spark. One safe solvent to use to eliminate spark sensitivity as a solvent concern is water, but water creates its own set of performance and aging problems with many pyrotechnic compositions. (*Remember: Keep your powder dry!*).

Spark sensitivity values for a series of pyrotechnic compositions are given in Table 6.1. It can be seen that these values tend to be considerably greater than 0.10 J, unless a fine metal powder (such as aluminum) is used. Keep in mind that spark sensitivities can vary greatly for a given oxidizer-fuel mixture, with the particle size and surface oxidation state of the fuel often playing a very significant role. A manufacturer cannot rely on spark sensitivity results other than those obtained on compositions produced by his company.

Knowing whether a given composition has the potential to be ignited by a static spark is important, but keep in mind that spark sensitivity for a given material can also vary from batch to batch, based on a number of other factors, such as grain size, homogeneity, and humidity. A thorough hazard analysis—using the appropriate sensitivity data—must be done on each operation where there is exposed energetic material in order to determine the level of spark protection and worker protection that is required.

TABLE 6.1
Electrical Spark Sensitivities of Various Pyrotechnic Compositions

Composition	Components		Minimum Electrical Spark Ignition, in joules (J) ^a	
Black powder	Charcoal	15	3.125	
	Potassium nitrate	75		
	Sulfur	10		
Military ignition mixture	Iron(III) oxide	25	0.0004	
	Zirconium	65		
	Diatomaceous earth	10		
	VAAR binder	+1%		
Military first-fire mixture	Lead oxide, Pb ₃ O ₄	55	0.276	
	Silicon	33		
	Titanium	12		
	Nitrocellulose binder	+1.8%		
Red fireworks stars	Charcoal	4	0.685	
	Red gum	18		
	Potassium perchlorate	60		
	Strontium carbonate	18		
Military white flare mixture	Sodium nitrate	49	>50	
	Magnesium (20/50 mesh)	40		
	Laminac polyester binder	11		
Chinese firecracker powder	Aluminum		0.056	
	Sulfur			
	Potassium chlorate			
Flash powder (fine powder)	Dark pyro aluminum		Varies based on particle size of oxidizer (below):	
	Potassium perchlorate (fine)			0.032
	Potassium perchlorate (coarse)			0.980

^a These values were obtained using a device patterned after the U.S. Bureau of Mines electrical spark apparatus. The value reported is the minimum energy at which at least one sample in ten ignited. These values are from Aikman et al.¹ or were similarly determined by the late Fred McIntyre, formerly of Sverdrup Technology, Bay St. Louis, Mississippi, one of the authors of Aikman et al.¹

FRICION SENSITIVITY

Friction sensitivity studies have shown a relationship to ignition temperature and heat of reaction, but the critical factor in friction sensitivity appears to be the presence in a composition of a significant amount of a gritty or hard granular component. Such a material, when exposed to frictional action, will generate hot spots that can lead

TABLE 6.2
Effect of Titanium Powder^a on Sensitivity of
Black Powder^b

% Ti	Impact (figure of insensitiveness)	Friction (figure of friction)
0	149	7.1
5	127	5.3
10	136	3.6
20	115	3.5
40	69	4.5
60	61	5.1

Source: R. K. Wharton, R. J. Rapley, and J. A. Harding, The Mechanical/Sensitiveness of Titanium/Black Powder Pyrotechnics Composition, *Propellants, Explosives, Pyrotechnics*, 18, 25, 1993.

^a Low values indicate greater sensitivity to ignition in these tests.

^a Titanium particle size was 355 to 500 microns.

^b Black powder was fine “meal A” granulation.

to ignition. Metal particles are a particular concern in the generation of frictional hot spots. The addition of titanium to fine black powder has been shown to have a significant effect on the friction sensitivity as well as the impact sensitivity of the composition, as shown in Table 6.2.⁸ Impact sensitivity increased as the proportion of titanium increased, while friction sensitivity was the greatest for compositions containing 20%–30% titanium metal by weight.

Several types of friction sensitivity apparatuses are in current use in the energetic materials field, and they tend to differ significantly in the fundamental nature of their means of energy input into the test sample.⁵ The lack of a standard, quantitative method of evaluating friction sensitivity has limited the detailed evaluation of this type of energy input, but friction is always a concern when energetic compositions are pressed into tubes. The proper alignment of tools and equipment used in pressing operations is very important in minimizing the possibility of a friction-related incident.

The good news about friction sensitivity is that we know how to solve a friction problem—add a lubricant. The addition of a small amount of wax or oil to a friction-sensitive composition can dramatically reduce the friction sensitivity of the composition. The only question remaining is whether or not you have changed any other property of the composition by the addition of the lubricant. A small percentage of such an ingredient can alter the burn rate and ignition temperature, as well as other properties of the composition. A complete reevaluation of sensitivity and performance is always required when a new component is added to a composition, even in a low percentage. An example of the range of friction sensitivity that can be observed for pyrotechnic compositions, with and without the presence of lubricating

TABLE 6.3
Rotary Friction Sensitivities for Some Pyrotechnic Compositions

Composition	Components	Ignition Energy, ft-lb ² /s
IM 28 Incendiary	Barium nitrate (40) Potassium perchlorate (10) Magnalium alloy (50)	19
SW522 Smoke	Potassium perchlorate (20) Potassium nitrate (20) Aluminum (20) Zinc dust (40)	52
M22 Flash mixture	Magnesium (-200/+325 mesh) (75) Teflon (10) Viton (15)	>55,041

Source: L. M. Aikman et al., Improved Mixing, Granulation, and Drying of Highly Energetic Pyro-Mixtures *Propellants, Explosives, Pyrotechnics*, 12, 17, 1987.

components, is shown in Table 6.3, where the first two compositions contain significant metal powder and no lubricant, while the third composition contains significant lubricant and is quite insensitive to friction.

IMPACT SENSITIVITY

The generation of hot spots by the collision of a heavy, hard object with the surface of an explosive or pyrotechnic mixture appears to be the primary ignition trigger associated with impact sensitivity. Impact causes the compression of air pockets in the energetic material, leading to temperature rises due to adiabatic compression of the entrapped air. Another possible effect of impact is the ability of a given material to absorb the kinetic energy associated with impact and convert this energy into vibrational energy in a solid material sufficient to initiate a sequence of bond breaking that leads to ignition.

Some commercial explosives incorporate small glass microspheres that are specifically added to generate hot spots throughout the explosive and assist in achieving detonation of the material when a moderate detonation stimulus such as a blasting cap is inserted into the explosive material. Detonation of the blasting cap produces a number of sites of high temperature within the explosive near the detonator, through adiabatic compression of the microspheres, and the detonation then proceeds through the material, continuing to be assisted by the microspheres. The effectiveness of these spheres at sensitizing explosives provides substantial support for the hot spot theory of detonation initiation. In the case of pyrotechnic and propellant materials, hot spot generation by impact will lead to ignition if a sufficient number of hot spots are created that exceed the ignition temperature of the material, and the heat that is thereby produced is sufficient to propagate the reaction through the remaining material. Table 6.4 shows impact sensitivity data for various compositions, while Table 6.5 shows a comparison

TABLE 6.4
Impact Sensitivity Data for Three Pyrotechnic Compositions

Composition	Percent by Weight	Impact Sensitivity (in inches)	Comment
1. Magnesium (-200/+325 mesh)	75	3.75	Not friction sensitive
Polytetrafluoroethylene	10		
Fluorelastomer	15		
2. Zirconium	65	10	Spark sensitivity <1 mJ
Iron oxide	25		
Diatomaceous earth	10		
VAAR binder	+1%		
3. Magnesium (-30/+50 mesh)	51	>10	Spark sensitivity > 50 J (good), but friction sensitivity is 204 ft-lb ² /s (poor)
Sodium nitrate	42		
Epoxy/polysulfide binder	7		

Source: L. M. Aikman et al., Improved Mixing, Granulation, and Drying of Highly Energetic Pyromixtures. *Propellants, Explosives, Pyrotechnics*, 12, 17, 1987.

TABLE 6.5
Friction and Impact Sensitivity for the ZPP System

% Composition (Zr/KClO ₄)	Impact Sensitivity, height of 50% explosion (in cm)	Friction Sensitivity (pistol load up to which insensitive, in Kgf)
10/90	115	36.0
20/80	106.5	36.0
30/70	106.25	36.0
40/60	90.0	14.4
50/50	92.5	10.8
60/40	99.1	5.4
70/30	92.5	4.8
80/20	103.0	3.6
90/10	94.0	2.0

Source: U. C. Durgapal et al., Study of Zirconium-Potassium Perchlorate Pyrotechnic System, presented at Proceedings of the 13th International Pyrotechnics Seminar, Grand Junction, CO, 1988.

Note: Impact sensitivity varies little with change in % Zr, by weight, while friction sensitivity does change eighteen-fold, becoming more sensitive as the Zr percentage is increased.

of impact and friction data for a potassium perchlorate–zirconium (ZPP) composition. It can be seen in Table 6.5 that friction sensitivity for this system is significantly affected by changes in the fuel/oxidizer ratio, while impact sensitivity shows only minor changes as the oxidizer/fuel ratio is varied.

THERMAL SENSITIVITY

Thermal sensitivity data are now primarily obtained using the thermal analysis method of differential scanning calorimetry (DSC) (see Chapter 2). Thermal sensitivity is the most reproducible, and best understood, of the various types of sensitivity tests, owing to the relatively minor effect of the specific test conditions on the value that is obtained. Thermal sensitivity is the result of the chemistry that occurs in a given mixture upon heating, and it is relatively independent of factors such as homogeneity, particle size, and percent composition. It can be very dependent, however, on the addition or omission of a component in a particular composition, especially if that component plays a role in the initial exothermic reaction that occurs upon heating of the material.

Ignition temperature measurements determine the minimum temperature at which a composition begins to react in a rapid, exothermic, self-propagating manner as a sample is heated. Such measurements are based on the exposure of the sample material to a continually increasing temperature, and the experimental method is affected to only a minor degree by factors such as blended grain size, degree of confinement, and even the testing method and heating rate that is employed. Ignition temperature is therefore a fairly reproducible value for a given pyrotechnic composition from laboratory to laboratory as well as from country to country. The reproducibility of ignition temperatures, for a specific energetic mixture, is usually within $\pm 25^\circ\text{C}$ from one study to another, regardless of the variables from study to study.

Thermal sensitivity gives an indication of the potential hazard represented by exposure of a given composition to elevated temperature during mixing, drying, and storage. It also gives the manufacturer an idea of ignition transfer problems that a given formulation is likely to present. For example, compositions that are difficult to ignite typically have high ignition temperatures of 500°C or more, while easy-to-light mixtures usually have ignition temperatures substantially lower in value. Many chlorate-based stars, long valued by the fireworks industry for their ease of ignition and reliable propagation of burning, have ignition temperatures below 200°C . Their ease-of-ignition benefit during use in an end item is offset by their sensitivity to ignition during manufacturing, however. Some representative ignition temperatures are given in Table 6.6.

Many of the oxidizers used in pyrotechnic compositions melt at relatively low temperatures (Table 3.2), and melting of the oxidizer often precedes or coincides with ignition when the oxidizer is mixed with an elemental fuel such as magnesium or boron. The melting process of a pure material can be detected by thermal analysis and typically appears as a sharp endotherm on the temperature-heat differential plot, or thermogram. Significant release of oxygen by the oxidizer is frequently associated with the onset of melting of the solid oxidizer material. A thermal analysis technique known as thermal gravimetric (TG) analysis, which monitors any change in sample weight as a function of increasing temperature, can be used to study the release of

TABLE 6.6
Ignition Temperatures (by DSC) of Some Pyrotechnic Compositions

Composition	% by Weight	T_{ignition} in °C	Use
A. Potassium chlorate	42	193	Base mix for colored smokes (without dye)
Sugar	28		
Magnesium carbonate	30		
Nitrocellulose binder	+3.4%		
B. Red lead oxide	73.3	200	Delay mixture
Silicon	18.4		
Nitrocellulose	8.3		
C. Potassium nitrate	10	334	Ignition mixture
Barium chromate	65		
Boron	21		
VAAR binder	4		
D. Potassium nitrate	70.7	410	Ignition mixture
Boron	23.7		
Polyester binder	5.6		
E. Sodium nitrate	49	502	Illuminant
Magnesium (−20/+50 mesh)	40		
Polyester binder	11		
F. Potassium perchlorate	20	587	White smoke
Potassium nitrate	20		
Aluminum	20		
Zinc dust	40		
G. Red lead oxide	85	786	Delay mixture; compare to composition B above—the percent of nitrocellulose is the reason that the T_{ignition} is lowered
Silicon	15		
Nitrocellulose binder	+1.8%		

Source: L. M. Aikman et al., Improved Mixing, Granulation, and Drying of Highly Energetic Pyromixture. *Propellants, Explosives, Pyrotechnics*, 12, 17, 1987.

oxygen by a sample of pure oxidizer, since the sample will become lighter in weight as oxygen gas is released on heating.

Metal fuels, in general, have higher melting points than most oxidizers, and the metal is often protected by a surface oxide coating that retards further oxidation of the metal as oxygen is released by the oxidizer upon heating of an oxidizer-fuel mixture. The oxide coating is shed as the metal fuel approaches its melting point, and a fresh, active metal surface is exposed. Rapid oxidation usually follows. Hence,

oxidizer-metal compositions frequently display ignition temperatures approaching the melting point of the metal, as shown in Table 5.3.

Organic compounds consisting of carbon, hydrogen, oxygen, and sometimes nitrogen—often used as fuels and binders in energetic mixtures—are typically characterized by decomposition temperatures in the 200–350°C range, temperatures that are often *lower* than the melting point of the oxidizer that is mixed with the fuel. The weakest chemical bonds in the organic molecules break, forming very reactive fragments (free radicals) that are often quite susceptible to oxidation, and are converted to carbon dioxide, carbon monoxide, and water by reaction with atmospheric oxygen or with oxygen released by the thermal decomposition of the solid oxidizer. Once the oxidizer begins to release oxygen, exothermic reactions should begin to quickly occur. This oxidation of the organic fragments releases heat, raising the overall temperature of the system. This temperature elevation then accelerates all of the decomposition reactions that are occurring. More heat is liberated and the overall process is sent into an upward spiral, leading to ignition and propagation of burning.

Thermal sensitivity therefore requires that a sample be heated to a temperature where two conditions are met:

1. The oxidizer reaches a temperature where sufficient evolution of oxygen occurs.
2. The fuel reaches a temperature where it is in a chemical state capable of reacting with the oxygen released by the oxidizer. For a metal fuel, this will typically occur as the metal approaches its melting point. For a carbon-based fuel, this will occur when the compound reaches its decomposition temperature (typically between 200 and 350°C).

A mixture consisting of an oxidizer, metal fuel, and organic binder can therefore display interesting ignition temperature (and thermal sensitivity) behavior. At low percentages of binder, the heat released by the decomposition and oxidation of the binder is not sufficient to activate the metal fuel by raising the sample temperature to the metal's melting point. With higher binder percentages, the low-temperature reaction between oxidizer and binder may now be sufficient to activate the metal, leading to an ignition temperature several hundred degrees below the ignition temperature of a binary mixture of the same metal and oxidizer. The binder is not only providing mechanical strength and cohesion to the mixture, but it may also thermally sensitize the mixture by providing a low ignition temperature fuel to the system. Several examples of this phenomenon are given in Tables 5.1 and 6.6.

It is for this reason that any change in an energetic formula must be watched carefully for sensitivity changes. A mixture with 2% organic binder may have an ignition temperature considerably higher than the same mixture with 6% binder. Minor changes may also affect the spark and friction sensitivity of energetic mixtures. For example, the addition of 4% diatomaceous earth (which can be a gritty material) as a diluent to slow up a delay composition may significantly *enhance* the friction sensitivity of the mixture, and may simultaneously *decrease* the spark sensitivity of the material. It is therefore important to fully reassess the sensitivities of a composition anytime that a

change in formulation is made. It is especially important to reevaluate sensitivity if a chemical substitution or replacement is made, such as the replacement of aluminum by a magnesium-aluminum alloy. New sensitivity values should be determined, and the new or revised mixture must then be determined to be acceptable from a sensitivity point of view, before any large quantity of the new mixture is blended and processed.

It must also be realized that sensitivity measurements relate to the composition *as tested*. Grain size, extent of residual solvent, humidity, and time elapsed following mixing are among the factors that can affect sensitivity values. During the mixing process, it is possible that the protective oxide coating acquired by some fuels might be removed, exposing fresh fuel surface that might be more sensitive to a spark or other stimulus. Once mixing is finished, the fuel gradually reacquires a protective coating, and its sensitivity is likely to change, becoming less spark sensitive as this reoxidation process occurs.

Spark sensitivity data for a calcium chromate–boron composition, measured as a function of blending time in a rotating ball mill, are shown in Table 6.7.⁶ These figures clearly show that sensitivity can change during the manufacturing process and clearly indicate that the sensitivity of in-process mixtures can be significantly different than the measured sensitivity values on aged composition. In the Wang and Hall study,⁶ the composition is presumably undergoing a change in homogeneity, a reduction in component particle size, and a polishing of the boron particles as the boron oxide coating of the boron particles is removed during mixing—making the composition more sensitive to spark. It can be assumed that there will be a rise in the spark sensitivity value (decrease in spark sensitivity) for the mixture following the ball milling operation as it ages and the boron surface reoxidizes over time. The final spark sensitivity level observed when the composition stabilizes over time will be a reflection of the relative contributions of the various factors that are involved.

TABLE 6.7
Electrostatic Spark Sensitivity^a vs.
Mixing Time in a Ball Mill

Time of Ball Mill Treatment (hours)	Spark Sensitivity (mJ)
0	>750 ^b
0.5	529
1	270
5	77
50	27

^a The composition is calcium chromate (80) and boron (20).

^b These values were taken immediately upon removal from the ball mill with minimal exposure time to air.

REDESIGNING A COMPOSITION

If a composition is determined to be too sensitive for safe use, the only alternative is to redesign the composition in an effort to find a replacement material that works as well as the bad composition, but is one that can be produced and used safely in manufacturing. This can be an expensive proposition, since the new mix must go through a complete qualification and approval process, but there is little choice but to proceed with finding a replacement should sensitive values suggest a high probability of ignition incidents should the bad material be produced and used in manufacturing operations.

An example of such a situation involved an ignition mixture for a smoke device. The initial ignition composition consisted of the following:

Barium chromate, BaCrO ₄	65
Potassium nitrate, KNO ₃	10
Boron, B	21
VAAR binder	4

Sensitivity testing of this material yielded the following results:¹

Spark sensitivity	0.107 J
Impact sensitivity	3.75 in. (BoE apparatus)
Friction sensitivity	86 ft-lb ² /s (rotary friction)
Ignition temperature	334°C

While the ignition temperature was in the moderate range, impact, friction, and spark sensitivity values for this material were all of concern. Given that the mixture was being used to ignite colored smoke composition containing potassium chlorate and sugar (ignition temperature under 200°C), a milder ignition mixture with much better sensitivity properties could be used. The replacement material was as follows:

Potassium nitrate, KNO ₃	49
Silicon	36
Charcoal	6
Stearic acid (lubricant)	5
Nitrocellulose binder	4

In this material, the spark-sensitive fuel boron has been replaced by silicon, and the wax-like stearic acid has been added to reduce friction and impact sensitivity. This material showed the following sensitivity values:

Spark sensitivity	>50 J
Impact sensitivity	>10 in.
Friction sensitivity	47,114 ft-lb ² /s
Ignition temperature	>330°C

A much safer material to use in the manufacturing process was developed, with no loss of reliability or performance for the end item.

SUMMARY

Unfortunately, there is no such thing as a fixed or constant value for the ignition sensitivity of an energetic mixture, whether the stimulus is spark, impact, friction, or elevated temperature. Sensitivity can vary greatly due to factors such as particle size, grain size, homogeneity, aging, moisture content, and the type of energy impinging upon the material. The only safe thing to do is consider *all* energetic materials to be sensitive to *all* types of ignition stimuli, at least until a history of safety has been established for a given material. Change one variable in the whole equation, however, and it's back to square one—the material must be considered highly sensitive until it has been thoroughly retested for sensitivity to all modes of energy input.

A general rule of thumb when talking about sensitivity is illustrated in Table 6.8, showing where general terms of *high*, *moderate*, and *comparably insensitive* can be applied to specific data on ignition temperature, spark sensitivity, and impact sensitivity. However, no standard set of terms or sensitivity equivalents has yet been agreed upon in the pyrotechnics community, and this table should be used only as a general starting point, and not a scientific standard. A key distinction between this table and the one originally proposed by Bailey et al.⁹ is the raising of the spark sensitivity level for high classification from 1 mJ to 100 mJ. This has been done to include any composition that tests near human spark energy levels of 10 mJ–15 mJ into the high category, with a safety factor of approximately 6–7 added in.

Again, the best way to use sensitivity data is in a comparative manner. For example, we know that zirconium–potassium perchlorate (ZPP) is very spark sensitive and has been involved in manufacturing incidents that have been traced to spark initiation. If a new composition is developed that has the same spark sensitivity as ZPP (measured on the same test apparatus), we know that we are going to have to be very careful working with the new material, and we should make every effort to modify the composition and thereby make it less sensitive, in this case to spark, before using the composition in a manufacturing facility.

TABLE 6.8
A Proposal for Sensitivity Value Classification

Term	Ignition Temperature, °C	Spark, mJ	Impact Height, Inches (BoE apparatus)
High sensitivity	<200	<100 mJ	<3.75
Moderate sensitivity	200–400	100–450	3.75–10
Comparatively insensitive	>400	>450	>10

Note: Values have been modified from the proposal in Bailey et al.,⁹ which is an excellent paper for discussion/friendly debate purposes.

REFERENCES

1. L. M. Aikman et al., Improved mixing, granulation, and drying of highly energetic pyromixtures, *Propellants, Explosives, Pyrotechnics*, 12, 17 (1987).
2. H. Henkin and R. McGill, Rates of explosive decomposition of explosives, *Ind. and Eng. Chem.*, 44, 1391 (1952).
3. J. H. McLain, *Pyrotechnics from the viewpoint of solid state chemistry*, Philadelphia: Franklin Institute Press, 1980.
4. U. C. Durgapal et al., Study of zirconium-potassium perchlorate pyrotechnic system, presented at Proceedings of the 13th International Pyrotechnics Seminar, Grand Junction, CO, 1988.
5. *Recommendations on the transport of dangerous goods—Tests and criteria*, 2nd ed., published on behalf of the United Nations by Labelmaster, Chicago, 1990, and subsequent editions.
6. P. S. Wang and G. F. Hall, Friction, impact, and electrostatic discharge sensitivities of pyrotechnic materials: A comparative study, presented at Proceedings of the 13th International Pyrotechnics Seminar, Grand Junction, CO, 1988.
7. D. Skinner, D. Olson, and A. Block-Bolten, Electrostatic discharge ignition of energetic materials, *Propellants, Explosives, Pyrotechnics*, 23, 34 (1998).
8. R. K. Wharton, R. J. Rapley, and J. A. Harding, The mechanical sensitiveness of titanium/black powder pyrotechnics compositions, *Propellants, Explosives, Pyrotechnics*, 18, 25 (1993).
9. A. Bailey et al., The handling and processing of explosives, presented at Proceedings of the 18th International Pyrotechnics Seminar, Breckenbridge, CO, 1992.

7 Heat Compositions

Ignition Mixes, Delays, Thermites, and Propellants



BURNING NITROCELLULOSE: (See color insert after page 112) Nitrocellulose, produced by the reaction of nitric acid with cellulose, provided the first new propellant material since the development of black powder. Introduced in the late nineteenth century, this material served as the primary ingredient for smokeless powders, and revolutionized the propellant industry. Nitroglycerine, another energetic material developed in the nineteenth century, was combined with nitrocellulose to make other smokeless propellants, as well as used by itself to make Alfred Nobel's dynamite, which revolutionized the blasting industry. (Photo by Tim Wade and Dennis King, courtesy of MP Associates.)

One thing all energetic materials have in common is the fact that they are exothermic and self-propagating in their conversion from starting materials to reaction products. Once an initial ignition stimulus is successfully applied, burning continues without the need for any additional external energy, and heat is produced. One of the best analogies to use with ignition and propagation is starting a warm wood fire in the fireplace on a cold winter day. Wet wood is difficult to light, small slivers of wood ignite more readily than a large-diameter log, and no additional crumpled newspaper is required once the wood fire is under way.

HEAT PRODUCTION

All pyrotechnic compositions evolve heat upon ignition, and this release of energy can be used to produce color, motion, smoke, and noise. There are applications as well for the chemically produced heat itself, and these will be addressed in this chapter. Propellants are also discussed in this chapter, with emphasis on those with a composition similar to traditional pyrotechnic formulations—oxidizer, fuel, and binder. Propellants can also be formulated from energetic materials that more closely resemble high explosives than pyrotechnics, with nitrocellulose, nitroglycerine, and the somewhat newer nitramine explosives RDX, and HMX (containing energetic N-NO₂ functional groups) used in a variety of propellant formulations. These will not be discussed in detail in this book, but there are a number of excellent books in print covering the field of propellants from the viewpoint of the chemist and the engineer.¹

The use of incendiary mixtures in warfare can be traced back to ancient times, when fireballs provided an effective means of assaulting well-fortified castles. Naval warfare was revolutionized by the use of propelled objects (such as cannon balls) to attack wooden ships, and much effort was put into improving the heat output, range, portability, and accuracy of these thermal weapons.

As both weaponry and the use of explosives for blasting developed, the need for safe, reliable ways to ignite these devices became obvious, and the concepts of an ignition fuse and a pyrotechnic delay emerged. A variety of terms are used for materials that either ignite or provide a delay period between ignition of a device and the production of the main explosive or pyrotechnic effect. These include:

1. *Fuse*: A train of pyrotechnic composition (usually black powder), often covered with twine, thread, or twisted paper, as well as waterproofing material. Fuses are lit by a safety match or other hot object, and provide a time delay to permit the person igniting the device to retreat to a safe distance. This term should not be confused with *fuze*, which is a device used to initiate a military explosive device such as a bomb.
2. *Electric match* (often inaccurately referred to as a *squib*): A device containing a thin metal wire, termed a bridgewire, that is coated with a dab of heat-sensitive pyrotechnic composition. An electric current is passed through the bridgewire, using a wire circuit, and a temperature rise occurs in the bridgewire that ignites the small dab of match composition. A burst of flame is produced that ignites a section of fuse or a charge of pyrotechnic composition. Electric match compositions sometimes contain potassium chlorate (low ignition temperatures!). Lead mononitrosorsinate (LMNR) is also included in some electric match mixtures. Several electric match formulas are listed in Table 7.1.
3. *First fire*: An easily ignited composition that is pressed, coated, or otherwise placed in limited quantity on top of the main pyrotechnic mixture. The first fire is reliably ignited by a fuse or electric match, and the flame and hot residue that is produced then ignites the main charge. Black powder,

TABLE 7.1
Electric Match (Squib) Compositions

Component	Formula	% by Weight
1. Potassium chlorate	KClO_3	8.5
Lead mononitroresorcinate	$\text{PbC}_6\text{H}_3\text{NO}_4$	76.5
Nitrocellulose	—	15
2. Potassium chlorate	KClO_3	55
Lead thiocyanate	$\text{Pb}(\text{SCN})_2$	45
3. Potassium perchlorate	KClO_4	66.6
Titanium	Ti	33.4

Source: F. L. McIntyre, *A Compilation of Hazard and Test Data for Pyrotechnic Compositions*, Report ARLCD-CR-80047, U.S. Army Armament Research and Development Command, Dover, NJ, 1980.

moistened with water containing a binder such as dextrine, is often used in the fireworks industry as a first fire, and also helps secure the fuse to the item. First fires are often referred to as primes—a term similar to another with a distinct meaning (see number 5 below).

4. *Delay composition*: A general term for a mixture that burns at a reliable, reproducible rate, thereby providing a time delay between activation of a device and production of the main effect. A fuse containing a core of fine-grain black powder is an example of a delay. Highly reproducible delay mixtures are needed for military applications, and much research effort has been put into developing reliable compositions that are effective under a wide range of temperature and pressure.
5. *Primer (a common version is the percussion primer)*: A term for the device used to ignite smokeless powder in small arms ammunition or other propellant applications. An impact-sensitive composition is typically used. When struck by a metal firing pin, a primer emits a burst of flame and hot particulates capable of rapidly igniting the propellant charge. Several typical primer mixtures are given in Table 7.2.
6. *Friction igniter*: A truly self-contained device should be ignitable without the need for a safety match, battery, or other type of external energy source. Highway flares (fusees), other types of distress signals, and some military devices use a friction ignition system. The fusee uses a two-part igniter; when the two surfaces are rubbed together, a flame is produced and the main composition is ignited. Typically, the scratcher portion of these devices contains red phosphorus and an abrasive, gritty material like pumice, and the matchhead mixture contains potassium chlorate (KClO_3) and

TABLE 7.2
Typical Primer Mixtures

Component	Formula	% by Weight	Notes
1. Potassium chlorate	KClO ₃	45	Stab primer
Lead thiocyanate	Pb(SCN) ₂	33	
Antimony sulfide	Sb ₂ S ₃	22	
2. Potassium chlorate	KClO ₃	33	Stab primer
Antimony sulfide	Sb ₂ S ₃	33	
Lead azide	Pb(N ₃) ₂	29	
Carborundum		5	
3. Potassium chlorate	KClO ₃	50	Percussion primer
Lead peroxide	PbO ₂	25	
Antimony sulfide	Sb ₂ S ₃	20	
Trinitrotoluene	C ₇ H ₅ N ₃ O ₆	5	
4. Potassium perchlorate	KClO ₄	50	ZPP
Zirconium	Zr	50	Percussion primer

Source: F. L. McIntyre, *A Compilation of Hazard and Test Data for Pyrotechnic Compositions*, Report ARLCD-CR-80047, U.S. Army Armament Research and Development Command, Dover, NJ, 1980.

a good fuel-binder material. Several friction igniter systems are given in Table 7.3.

7. *Squib*: A device containing an electric match and a small quantity of black powder output charge. The electric match ignites the black powder, which in turn produces a flame and sparks to ignite the propellant or other pyrotechnic composition.
8. *Igniter*: A general term for devices used to initiate pyrotechnic or propellant systems. Igniters are typically initiated electrically, and produce a high-temperature output consisting of flame and hot particulates. Some common ignition compositions are given in Table 7.4.
9. *Detonator*: An explosive device used to produce a detonation in a high explosive material. Detonators typically contain an ignition mixture, a sensitive primary explosive that detonates from the ignition stimulus, and a high explosive output charge that is taken to detonation by the shock from the detonation of the small amount of primary explosive (which is usually lead azide, Pb(N₃)₂). Detonators are used with explosive devices—they are *not* components of propellant and pyrotechnic systems. The blasting cap is a common type of detonator.

TABLE 7.3
Friction Igniter Mixtures

Component	Formula	% by Weight	Reference
1. Main composition:			4
Potassium chlorate	KClO ₃	60	
Antimony sulfide	Sb ₂ S ₃	30	
Resin	—	10	
Striker:			
Red phosphorous	P	56	
Ground glass	SiO ₂	24	
Phenol/formaldehyde resin	(C ₁₃ H ₁₂ O ₂) ₇	20	
2. Main composition:			3
Shellac	—	40	
Strontium nitrate	Sr(NO ₃) ₂	3	
Quartz	SiO ₂	6	
Charcoal	C	2	
Potassium perchlorate	KClO ₄	14	
Potassium chlorate	KClO ₃	28	
Wood flour	—	5	
Marble dust	CaCO ₃	2	
Striker:			
Lacquer	—	61	
Pumice	—	2.2	
Red phosphorous	P	26	
Butyl acetate	C ₆ H ₁₂ O ₂	10.8	

DELAY COMPOSITIONS

The purpose of a delay composition is obvious—to provide a time delay between the ignition action and the delivery of the main effect. Crude delays can be made from loose powder, but a compressed column is capable of much more reproducible performance. The burning rates of delay mixtures range from very fast (millimeters/millisecond) to slow (millimeters/second).

Black powder was the sole pyrotechnic delay mixture available for several centuries. The development and use of a safety fuse containing a black powder core significantly improved the safety record of the blasting industry. However, the development of modern, long-range, high-altitude projectiles created a requirement for a new generation of delay mixtures. Black powder, under specified conditions, gives fairly reproducible burning rates at ground level. However, it produces a considerable quantity of gas upon ignition (approximately 50% of the reaction products are gaseous), and its burning rate will therefore show a significant dependence on external pressure (burning faster as

TABLE 7.4
Ignition and First-Fire Formulations

Mixture	Component	Formula	% by Weight	Note
I.	Barium peroxide	BaO ₂	80	4 Solid BaO particles aid in ignition
	Magnesium	Mg	18	
	Binder	—	2	
II.	Iron oxide	Fe ₂ O ₃	25	A-1A mixture, a gasless igniter 2
	Zirconium	Zr	65	
	Diatomaceous earth	—	10	
III.	Black powder	KNO ₃ /S/C	75	4
	Potassium nitrate	KNO ₃	12	
	Zirconium	Zr	13	
IV.	Potassium nitrate	KNO ₃	71	4
	Boron	B	24	
	Rubber	—	5	
V.	Red lead oxide	Pb ₃ O ₄	50	2
	Titanium	Ti	25	
	Silicon	Si	25	
VI.	Sodium nitrate	NaNO ₃	47	2
	Sugar	C ₁₂ H ₂₂ O ₁₁	47	
	Charcoal	C	6	
VII.	Barium peroxide	BaO ₂	88	4 Thermite igniter
	Magnesium	Mg	12	

the external pressure increases). To overcome this pressure dependence, researchers set out to develop gasless delays—mixtures that evolve heat and burn at reproducible rates with the formation of almost *exclusively* solid and liquid products. Such mixtures will be expected to show little, if any, variation of burning rate with pressure.

One could begin a development project for a new delay system by setting down the requirements for an ideal delay mixture:⁵

1. The mixture should be stable during preparation and storage. Materials of low hygroscopicity (that is, do not tend to pull moisture from the ambient air) must be used.
2. The mixture should be readily ignitable from a modest ignition stimulus.
3. There must be minimum variation in the burning rate of the composition with changes in external temperature and pressure. The mixture must readily ignite and reliably burn at low temperature and pressure.
4. There should be a minimum change in the burning rate with small percentage changes in the various ingredients.

5. Reproducible burning rates must be achievable in manufacturing, both within one batch of composition and between batches made days and weeks apart.
6. The component chemicals are low in toxicity and environmentally friendly.

The standard gasless delays—for the past sixty years—have been some combination of a metal oxide or chromate with an elemental fuel. The fuels are generally metals or high heat-producing nonmetallic elements such as silicon or boron. If an organic binder (e.g., nitrocellulose) is used, the resulting mixture will be low gas rather than gasless, due to the carbon dioxide (CO₂), carbon monoxide (CO), and nitrogen (N₂) that will form upon combustion of the binder. If a truly gasless mixture is required, leave out all organic materials!

If a fast burning rate is desired, a metallic fuel with high heat output per gram should be selected, together with an oxidizer of relatively low decomposition temperature. The oxidizer should also have a minimally endothermic—or even better, exothermic—heat of decomposition. For slower delay mixtures, metals with less heat output per gram should be selected, and oxidizers with higher decomposition temperatures and more endothermic heats of decomposition should be chosen. By varying the oxidizer and fuel, as well as the ratio of oxidizer to fuel, it is possible to create delay compositions with a wide range of burning rates. Table 7.5 lists some representative delay mixtures.

TABLE 7.5
Typical Delay Compositions

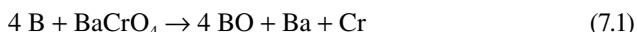
Component	Formula	% by Weight	Burning Rate, cm/s
1. Red lead oxide	Pb ₃ O ₄	85	1.7 (10.6 ml/g of gas)
Silicon	Si	15	
Nitrocellulose/acetone	—	1.8	
2. Barium chromate	BaCrO ₄	90	5.1 (3.1 ml/g of gas)
Boron	B	10	
3. Barium chromate	BaCrO ₄	40	— (4.3 ml/g of gas)
Potassium perchlorate	KClO ₄	10	
Tungsten	W	50	
4. Lead chromate	PbCrO ₄	37	0.30 (18.3 ml/g of gas)
Barium chromate	BaCrO ₄	30	
Manganese	Mn	33	
5. Barium chromate	BaCrO ₄	80	0.16 (0.7 ml/g of gas)
Zirconium-nickel alloy (50/50)	Zr-Ni	17	
Potassium perchlorate	KClO ₄	3	

Source: F. L. McIntyre, *A Compilation of Hazard and Test Data for Pyrotechnic Compositions*, Report ARLCD-CR-80047, U.S. Army Armament Research and Development Command, Dover, NJ, 1980.

Using this approach, lead chromate (melting point 844°C) would be expected to produce faster burning mixtures than barium chromate (which has a higher melting point), and barium peroxide (melting point 450°C) should react more quickly than iron oxide (Fe_2O_3 , melting point 1,565°C). Similarly, boron (heat of combustion = 14.0 kcal/gram) and aluminum (7.4 kcal/gram) should form quicker delay compositions than tungsten (1.1 kcal/gram) or iron (1.8 kcal/gram). Tables 3.2, 3.4, and 3.5 can be used to estimate the relative burning rates of various delay candidates. For high reactivity, look for low melting points, exothermic or minimally endothermic heat of decomposition (in the oxidizer), and high heat of combustion (in the fuel).

The ratio of oxidizer to fuel can be altered for a given binary mixture to achieve substantial changes in the rate of burning. The fastest burning rate would be expected, chemically, to correspond to an oxidizer/fuel ratio near the stoichiometric point, with neither component present in excess. Data have been published for the barium chromate–boron system. Table 7.6 gives the burn time and heat output per gram for this system.⁵

McLain has proposed that the maximum in performance, centered at approximately 15% boron by weight, indicates that the principal pyrotechnic reaction for the BaCrO_4/B system is



Although B_2O_3 is the expected oxidation product from boron in a room temperature situation, the lower oxide, BO, appears to be more stable at high reaction temperatures of the burning delay mixture.³

TABLE 7.6
The Barium Chromate–Boron System: Effect of
Percent Boron on Burning Time

% Boron	Average Burning Time, seconds/gram	Heat of Reaction, calories/gram
3	3.55	278
5	0.51	420
7	0.33	453
10	0.24	515
13	0.21	556
15	0.20	551
17	0.21	543
21	0.22	526
25	0.27	497
30	0.36	473
35	0.64	446
40	1.53	399
45	3.86	364

Source: U.S. Army Material Command, *Engineering Design Handbook: Theory and Application*, Military Pyrotechnic Series, Part One, Washington, DC, 1967 (AMC Pamphlet 706–185).

In practice, it has been observed in numerous systems that using a percentage of fuel in excess of the stoichiometric amount increases the burning rate for many delay mixtures, presumably through increased thermal conductivity for the composition (since most of the fuels used in delay mixtures are significantly better thermal conductors than the oxidizers). The propagation of burning is enhanced by the better heat transfer resulting from the additional fuel, especially in the absence of substantial quantities of hot gas to aid in the propagation of burning. Air oxidation of the excess fuel can also contribute additional heat to increase the reaction rate if the burning composition is exposed to the atmosphere.

The rate of burning of ternary mixtures can similarly be affected by varying the percentages of the components. Table 7.7 presents data for a three-component delay composition. In this study, a decrease in the burning rate (in centimeters/second) is observed as the metal percentage is lowered (giving poorer thermal conductivity) and the percentage of higher-melting oxidizer (BaCrO_4) is increased at the expense of the lower-melting, more reactive lead chromate, PbCrO_4 .

Table 7.8 illustrates this same concept for the molybdenum–barium chromate–potassium perchlorate system. Here, KClO_4 is the better oxidizer. An interesting study on this system showed that even when the excess metal in it is inert silver powder, rather than molybdenum, the burn rate is still enhanced, indicating that the enhanced thermal conductivity due to the excess metal is indeed a significant factor.⁶

Contrary to the behavior expected for gassy mixtures, the rate of burning for gasless compositions is expected to *increase* (in units of grams reacting per second) as the *consolidation pressure* is increased. Gasless delays propagate via heat transfer down the column of pyrotechnic material, and the thermal conductivity of the mixture plays a significant role. As the density of the mixture increases due to the increased loading pressure, the components are pressed closer together and better heat transfer occurs. Table 4.6 presents data for the barium chromate–boron system, showing the modest rate increase (in grams/second) that occurs as the loading pressure is raised. When significant gas products are produced, propagation of burning is enhanced by the movement/diffusion of the hot gaseous products into the unreacted material. In this case, high loading pressures block the penetration of the hot

TABLE 7.7
A Ternary Delay Mixture: The PbCrO_4 - BaCrO_4 -Mn System

Mixture	% Mn	% Lead Chromate	% Barium Chromate	Burning Rate, cm/s
I.	44	53	3	0.69
II.	39	47	14	0.44
III.	37	43	20	0.29
IV.	33	36	31	0.19

Source: J. H. McLain, *Pyrotechnics from the Viewpoint of Solid State Chemistry*, Franklin Institute Press, Philadelphia, 1980. Data from H. Ellern, *Military and Civilian Pyrotechnics*, New York: Chemical Publishing Co., 1968.

TABLE 7.8
The BaCrO₄-KClO₄-Mo System

Mixture	% Barium Chromate	% Potassium Perchlorate	% Molybdenum	Burning Rate, cm/s
I.	10	10	80	25.4
II.	40	5	55	1.3
III.	55	10	35	0.42
IV.	65	5	30	0.14

Source: G Rajendran et al., A Study of the Molybdenum/Barium Chromate/Potassium Perchlorate Delay System, *Propellants, Explosives, Pyrotechnics*, 14, 113 (1989).

gases into the unreacted material, thereby decreasing the rate of heat transfer, and a decrease in burn rate may be observed.

The obvious twenty-first-century problem with the standard delay mixtures that have been in use for over sixty years is the fact that the oxidizers tend to contain blends of lead, hexavalent chromium (Cr with a +6 valence), and barium. These are obviously materials that do not meet several of the stated criteria for green pyrotechnics. One major issue with finding replacements for these standard delay compositions is the fact that we have a long history of manufacturing the standard compositions, and the effects of changes in particle size, percent composition, homogeneity, and moisture content are fairly well known. With new delay compositions, we must go through the learning curve all over again to acquire knowledge of the art of producing these new compositions to achieve reproducible performance. Delay systems like iron(III) oxide with silicon or boron meet many of the twenty-first-century requirements, but their reproducibility in manufacturing and long-term storage stability needs to be verified.⁷

It is also possible that more use will be made in the future of electronic delays containing no pyrotechnic delay component, particularly in more sophisticated devices. These electronic delays should provide higher precision and avoid the manufacturing variability that is inherent with the production of pyrotechnic devices. Delays of this type have already been introduced in commercial blasting detonators to achieve improved blasting results via precise delay intervals (for more information, do a web search for the term *electronic delay detonators*).

IGNITION COMPOSITIONS AND FIRST FIRES

Compositions with high ignition temperatures (i.e., above 600°C) can be difficult to ignite using solely the spit from a black powder fuse or similar mild ignition stimulus. In such situations, an initial charge of a more readily ignitable material, called a *first fire*, is frequently used. The requirements for such a mixture include:⁴

1. Reliable ignitability itself from a small thermal impulse, such as a fuse, black powder, or a primer. The ignition temperature of a first fire should be 500°C or less for best results.

2. The mixture should attain high reaction temperature, well above the ignition temperature of the main composition. Metal fuels are usually used when *high* reaction temperatures are needed.
3. A mixture that forms a hot, liquid slag or solid particulates is preferred. Such slag will provide considerable surface contact with the main composition, facilitating ignition. The production of hot gas will usually produce good ignition behavior on the ground, but reliability may deteriorate at higher altitudes. Liquid and solid products provide better heat retention to aid ignition under these conditions.

A somewhat slower-burning ignition mixture is often preferred over a more rapid one, and especially over an explosive one. The shattering effect from an overenergetic ignition composition can cause the surface you are trying to light to crumble, and yield ignition failures. The slower release of energy allows for better heat transfer to the main composition. Also, most first fires are pressed into place or added as moist pastes (that harden on drying), rather than used as faster-burning loose powders. Obviously, though, when you are igniting a device that must function very quickly (such as an air bag system), a very fast and energetic ignition material will be required. Then it is up to the engineer to figure how to harness the output from the energetic ignition material and still achieve high reliability in the end item.

The pyrotechnic engineer must balance the need for speed in the overall ignition process against possible explosive behavior from the ignition composition. To achieve this, potassium nitrate—a moderate oxidizer—is frequently used in ignition compositions and first fires. Compositions made with this oxidizer tend to have low ignition temperatures (typically below 500°C), and yet the mixtures are reasonably safe to prepare, use in production, and store. In addition, they tend to be a bit less explosive in their output than potassium perchlorate compositions blended with the same fuel. Potassium chlorate formulations also tend to have low ignition temperatures, but they are considerably more sensitive, explosive, and hazardous, and thus are not widely used. Table 7.4 illustrates a range of ignition compositions.

Potassium nitrate mixed with charcoal can be used for ignition, as can black powder worked into a paste with water and a little dextrine. Shidlovskiy reports that the composition

KNO ₃	75
Mg	15
Iditol	10 (iditol is a phenol/formaldehyde resin)

works well as an igniter mixture.⁴ The solid magnesium oxide (MgO) residue aids in igniting the main composition, and the resin helps to waterproof the magnesium.

Boron mixed with potassium nitrate is a frequently used, fast, effective igniter mixture, known in the industry as B/KNO₃. The boron must be watched closely for particle size and oxidation (particularly from exposure to moisture), and mixtures in the 70/30 potassium nitrate/boron range are quite energetic in output and may be spark sensitive in manufacturing and handling.⁸

The ultimate ignition compositions in use at the present time are materials containing an oxidizer blended with zirconium metal as the fuel. One such composition is a blend of iron(III) oxide with zirconium metal and diatomaceous earth—commonly known as A1A ignition mixture. Even more energetic and faster burning is the ignition composition blended from zirconium and potassium perchlorate, known as ZPP.⁹ The zirconium-based ignition compositions tend to produce flame temperatures and hot particulate products in excess of 4,000°C. Due to the extreme electrostatic spark sensitivity of fine zirconium and its pyrotechnic compositions, these materials must be worked with under very controlled manufacturing conditions, and in a damp state whenever possible, with a full static protection program in place. Limited quantities of material, appropriate personal protective equipment (PPE), and barricading for workers must also be considered under the process hazard analysis (PHA) for operations involving zirconium. However, if you do need to light something really fast, zirconium may be the material for the job. Ignition compositions can be quite energetic; Table 7.9 lists a variety of current ignition formulations, along with their approximate flame temperatures (computed) at atmospheric pressure.¹⁰

TABLE 7.9
Flame Temperatures of Some Igniter Compositions

Composition		Percent by Weight	Flame Temperature, °C ^a
A1A	Zirconium	65	4,400
	Iron(III) oxide	25	
	Diatomaceous earth	10	
ZPP ^b	Zirconium	46	4,400
	Potassium perchlorate	53	
	Graphite	1	
BKNO ₃	Boron	24	3,000
	Potassium nitrate	71	
	Laminac [®] binder	5	
MTV	Magnesium	54	2,300
	Teflon [®]	30	
	Viton [®]	16	
Black powder	Potassium nitrate	75	1,500
	Charcoal	15	
	Sulfur	10	

Source: L. V. De Yong and F. J. Valenta, *Evaluation of Selected Computer Models for Modeling Pyrotechnic and Propellant Devices*, Indian Head Technical Report 1279, Indian Head, MD, Naval Ordnance Station, September 8, 1979.

^a Computed values at approximately 40 atm.

^b Very dangerous to prepare and handle, not recommended unless very fast ignition is needed.

THERMITE MIXTURES

Thermite mixtures produce a high heat concentration, usually in the form of molten reaction products. Thermite compositions contain a metal oxide as the oxidizer and a metal—usually aluminum—as the fuel, although other active metals may be used.

A minimum amount of gas is produced by these reactions, enabling the heat of reaction to concentrate in the solid and liquid products. High reaction temperatures can be achieved in the absence of volatile materials; typically, values of 2,000°C to 2,800°C are reached.⁴ A metal product such as iron (from an iron oxide), with a wide liquid range (melting point 1,535°C, boiling point 2,800°C), produces excellent thermite behavior. Upon ignition, a thermite mixture will form aluminum oxide and the metal corresponding to the starting metal oxide:



Thermite mixtures have found application as incendiary compositions and spot-welding mixtures. They are also used for the intentional demolition of machinery and for the destruction of documents. Thermites are usually produced without a binder (or with a minimum of binder), because the gaseous products resulting from the combustion of the organic binder will carry away heat, cool the reaction, and possibly produce blast effects under confinement.

Iron oxide (either Fe_2O_3 or Fe_3O_4) with aluminum metal forms the classic thermite mixtures. The particle size of the aluminum is important, and should be somewhat coarse to prevent the reaction from being too rapid. Thermites tend to be quite safe to manufacture, and they are rather insensitive to most ignition stimuli. In fact, the major problem with most thermites is getting them to ignite, and a strong first fire is usually needed. Calorific data for a variety of aluminum thermite mixtures are given in Table 7.10.

TABLE 7.10
Calorific Data for Thermite Mixtures

Oxidizers	Formula	% Active Oxygen by Weight	% Al by Weight in Thermite Mixture	$\Delta H_{\text{reaction}}$ kcal/gram
Silicon dioxide	SiO_2	53	37	0.56
Chromium (III) oxide	Cr_2O_3	32	26	0.60
Manganese dioxide	MnO_2	37	29	1.12
Iron oxide	Fe_2O_3	30	25	0.93
Iron oxide	Fe_3O_4	28	24	0.85
Cupric oxide	CuO	20	19	0.94
Lead oxide (red)	Pb_3O_4	9	10	0.47

Source: A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)

PROPELLANTS

The production of hot gas to lift and move objects, using a pyrotechnic system, began with the development of black powder. Rockets were in use in Italy in the fourteenth century,¹¹ and cannons were developed at about the same time. The development of aerial fireworks, along with muskets, was a logical extension of cannon technology.

The goal with a propellant is to maximize the volume, and temperature, of the hot gases produced from each gram of composition. Propellant theory predicts that the maximum thrust that can be obtained from a propellant is a function of the flame temperature and the average molecular weight of the exhaust gases produced when the propellant burns.¹ Propellants generate a large volume of gas upon ignition, and they thereby tend to show a significant increase in burn rate when confined. This is represented by the equation

$$\text{Burn rate} = aP^n \quad (7.3)$$

where a is a constant determined by the propellant chemistry as well as manufacturing and testing variables, P is the pressure in the reaction chamber, and n is the exponential effect of a change in confinement pressure on burn rate. In general, the gassier the propellant, the higher the n value will be. Some representative values for propellant formulations are given in Table 7.11.¹²

Black powder remained the sole propellant available for military and civilian applications until well into the nineteenth century, and the production of the material

TABLE 7.11
Propellant Pressure Exponents

Material	Pressure Exponent, n
I. Black powder	0.165
II. Ammonium perchlorate PBAN, ^a Al composite	0.39
III. Ammonium nitrate HTPB ^b Mg	0.51
IV. M10 single base smokeless propellant ^c	0.70
V. M8 double base ^d smokeless propellant	0.83

Source: P. Cooper, *Introduction to the Technology of Explosives*, New York: Wiley-VCH, 1996.

^a Polybutadiene–acrylonitrile fuel–binder.

^b Hydroxy-terminated polybutadiene.

^c Nitrocellulose plus additives.

^d Nitrocellulose (52%), nitroglycerine (43%), plus additives.

flourished around the world. However, a number of problems associated with the manufacturing and use of black powder stimulated efforts to locate replacements. The issues included:

1. Substantial variation in burning behavior from batch to batch. The better black powder factories produced good powder if they paid close attention to the purity of their starting materials, used one source of charcoal, and did not vary the extent of mixing or the amount of residual moisture in their product.
2. Black powder has a relatively low gas output, on a per gram basis. Only about 50% of the products are gaseous; the remainder are solids.
3. The solid residue from black powder is highly alkaline (strongly basic), and it is quite corrosive to many materials.
4. Black powder is a fairly low-energy composition, with a heat of combustion of approximately 0.66 kcal/gram. In order to manufacture a quick energetic material from a composition with an energy output value this low, it is necessary to optimize the homogeneity of the material during the manufacturing process by a lengthy grinding operation involving a damp cake of powder. The consequence of this energetic mixing and grinding has been a large number of accidents and explosions at black powder manufacturing sites. A 60:40 potassium perchlorate:aluminum flash powder, in contrast, will produce about 2.4 kcal/gram of heat output, and therefore requires minimal mixing to yield a fast, energetic composition. Flash powders have low gas output, though, thereby precluding the use of these materials as propellants.

Replacement efforts have been aimed at finding replacements for black powder that can give both enhanced performance and enhanced manufacturing safety. Pyrodex[®], the oldest and probably the best selling of the replacement materials, is a patented pyrotechnic composition designed to fulfill many of the functions of black powder. It contains some of the ingredients found in black powder plus binders and burning rate modifiers that make the material somewhat less sensitive and slower burning at ambient pressure. A greater degree of confinement is required to obtain performance comparable to normal black powder.¹³

The advantages of black powder, and Pyrodex, include good ignitibility, moderate cost, ready availability of the ingredients, and a wide range of uses (fuse powder, delay mixture, propellant, and explosive), depending on the degree of confinement.

As propellant technology developed, the ideal features for a better material became evident:

1. A propellant that can safely be prepared from readily available materials at moderate cost
2. A material that readily ignites, but yet is stable during storage
3. A mixture that forms the maximum quantity of low molecular weight gases upon burning, with minimum solid residue
4. A mixture that burns at the highest possible temperature to provide maximum thrust

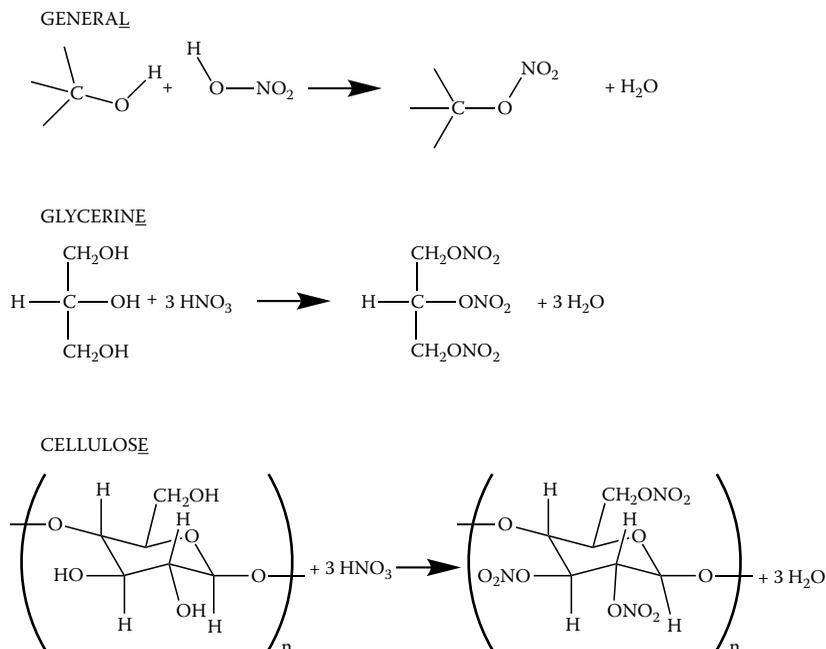


FIGURE 7.1 The nitration reaction. Organic compounds containing the $-\text{OH}$ (hydroxyl) functional group are termed *alcohols*. These compounds react with nitric acid to produce a class of compounds known as nitrate esters. Nitroglycerine and nitrocellulose are among the numerous explosive materials produced using this reaction.

The late nineteenth century saw the development of a new family of smokeless powders, as modern organic chemistry blossomed and the nitration reaction (formation of a nitrate ester between the hydroxyl group of an alcohol and nitric acid) became commercially feasible to chemists around the world. Two nitrate esters—nitrocellulose (NC) and nitroglycerine (NG)—became the major components of these new propellants (as well as components in new explosive formulations). Figure 7.1 illustrates the formation of NC and NG from nitric acid and the precursor alcohols cellulose and glycerine.

It might at first seem impossible that nitroglycerine, used to make the first modern blasting explosive, dynamite, could also be used safely to make propellants. Nitroglycerine requires the shock from a blasting cap (or detonator) to cause reliable detonation of the material. When blended with less explosive materials and ignited with flame rather than shock, it is capable of burning, and was found to be quite usable and effective in propellant formulations.

Nitrocellulose consists of a chain of glucose molecules linked together to form a polymer chain. There are three hydroxyl ($-\text{OH}$) groups per glucose unit that are available for nitration. Full nitration results in a nitrogen content in the NC of approximately 14% by weight; material with a nitrogen content of 12.6% or better is generally considered to be energetic material. The heat of explosion of nitrocellulose is approximately 0.97 kcal/gram (50% higher than the 0.66 kcal/gram value for black powder), and the combustion products are 100% gases.¹⁴

Single-base smokeless powder contains only nitrocellulose as an energetic material. Double-base smokeless powder is a blend of nitrocellulose and nitroglycerine—the solid nitrocellulose is gelatinized by the liquid nitroglycerine. The heat of explosion for nitroglycerine is 1.5 kcal/gram, and again, the combustion products are all gases. The double-base powders are the most energetic of the smokeless powders because of their nitroglycerine content, and the propellant energy increases as the nitroglycerine content is increased. Some double-base powders have a nitroglycerine content of greater than 40%,⁵ and some of the double-base powders are blasting cap sensitive and classed as 1.1 or high explosives. Triple-base smokeless powder, containing nitroguanidine as a third component, along with nitroglycerine and nitrocellulose, is also manufactured; it is the coolest burning of the three types of smokeless powder, and was developed for use in, and to extend the lifetime of, large, expensive metal gun barrels. The heat of explosion for nitroguanidine is 0.89 kcal/gram—lower than either nitrocellulose or nitroglycerine. All of the smokeless powders also contain an assortment of stabilizers, processing aids, flash inhibitors, and burn rate catalysts.^{1,14}

An advantage of the smokeless powders is their ability to be *extruded* during the manufacturing process. Perforated grains can be produced that simultaneously burn inwardly and outwardly such that variable burning surface area and variable gas production vs. time are achieved.¹

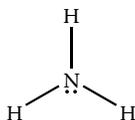
Nitrocellulose does not contain sufficient internal oxygen for complete combustion to CO₂, H₂O, and N₂, while nitroglycerine contains excess oxygen. The double-base smokeless propellants therefore achieve a slightly more complete combustion and benefit from the substantial exothermicity of NG (approximately 1.5 calories/gram).¹⁴

The smokeless powders were found to be much safer to manufacture than black powder, were more energetic per gram than black powder, and produced essentially 100% gas products with a minimum of smoke (and no corrosive solid products) when ignited. They burned much slower than black powder at standard atmospheric pressure, a safety feature in manufacturing. Under confinement, due to their large amount of gas products, they increased sharply in burn rate and were found to be noticeably faster—and performed better—than black powder at the typical high pressures found in gun barrels.

The only real downside to the nitrocellulose-containing powders was their inherent chemical instability. Traces of residual acid from the manufacturing process were difficult to completely remove from cellulosic materials, and this acid catalyzed the decomposition of the nitrate ester linkages in the nitrocellulose during storage. Small amounts of smokeless powder lost their ballistic performance over time as a result. Large amounts of smokeless powder stored in sealed containers could undergo accelerating self-heating, since both the heat that was generated and the additional acid catalyst generated during the decomposition of the nitrate ester linkages caused rate acceleration in the center of large containers. If the temperature inside a drum of smokeless powder reached the low (approximately 200°C) ignition temperature of the material, ignition—leading to an explosion—could result, and a warehouse would disappear.

This problem was eventually solved—in a classic example of applied acid-base chemistry—by the incorporation (at a 1 to 2% level) of a small percentage of an antacid into the smokeless propellant composition. The material used for over a

AMMONIA



DIPHENYLAMINE

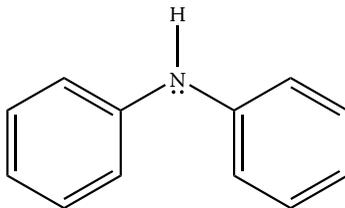


FIGURE 7.2 Molecular structures for ammonia (a gas at ambient conditions), and its nitrocellulose-storage stabilizing derivative diphenylamine (a solid at ambient conditions). The basic nitrogen acts as a base for hydrogen ions, and the benzene rings will absorb nitrogen oxides. Diphenylamine saved the infant smokeless powder industry by making nitrocellulose safer in storage.

century to stabilize single-base smokeless powder is diphenylamine, $C_{12}H_{11}N$ —a solid derivative of ammonia, with two 6-carbon benzene rings replacing hydrogen atoms on the ammonia molecule, as shown in Figure 7.2. The basic nitrogen in the diphenylamine molecule picks up any acidic hydrogen ions, H^+ , that are produced upon decomposition of the nitrocellulose, and the six-carbon benzene rings are effective absorbers of nitrogen oxides, also generated during the decomposition of nitrocellulose. The removal of these chemical species by the diphenylamine stabilizer blocks any acceleration of the rate of decomposition of the nitrocellulose, extending the lifetime of the smokeless powder for many years. Similar chemical stabilizers are added to double-base and triple-base smokeless powders as well. Diphenylamine is not normally used with these materials, however, as it is too basic to be compatible in storage with nitroglycerine. Weaker organic bases are used instead.

Smokeless powders are widely used today as the propellants for small arms ammunition as well as for artillery projectiles. Black powder use fell dramatically as the twentieth century began, with the introduction of the smokeless propellants, but it remains the primary propellant used by the fireworks industry for sky rockets and for aerial shells fired from mortars, and is still used for a variety of military applications as well.

The larger rockets and missiles used by the military and in the space program require tremendous thrust to lift off successfully, and combinations of liquid fuel engines (e.g., liquid hydrogen peroxide (H_2O_2) and hydrazine (N_2H_4), or liquid hydrogen with liquid oxygen) with solid propellant pyrotechnic boosters are used to lift enormous vehicles such as the Space Shuttle.

Modern solid propellants for rocket and missile technology have relied for quite a few decades now on composite propellants that appear pyrotechnic in their makeup. They are usually based on ammonium perchlorate (NH_4ClO_4) as the oxidizer. Various polybutadiene (synthetic rubber) derivatives are commonly used as the primary fuel, and also play a role as a binder for the compositions. Ammonium perchlorate produces 100% gas products during its thermal decomposition, and therefore is

an excellent choice for use in solid propellants. The pyrotechnic boosters used for these launches typically contain:

1. *A solid oxidizer:* Ammonium perchlorate (NH_4ClO_4) is the current favorite due to the high percentage of gaseous products it forms upon reaction with a fuel.
2. *An organic fuel that also serves as binder and gas former:* Liquids that polymerize into solid masses are preferred, for simpler processing, and a binder with low oxygen content is desirable to maximize heat production per pound.
3. *A small percentage of light, high-energy metal:* This metal produces solid combustion products that do not aid in achieving thrust, but the considerable heat evolved by the burning of the metal raises the temperature of the other gaseous products. Another very significant role played by the metal fuel is that of a thermal conductor, capturing some of the heat produced as the propellant burns and effectively conducting this heat into the column of unburned propellant. The thermal conductivity of the metal helps smooth out the burning of the propellant as well. Aluminum and magnesium are the metals that have been most commonly used.

The formulation for the Space Shuttle booster rockets is as follows:¹⁵

Ammonium perchlorate	70
Polybutadiene polymer*	12
Aluminum	16
Epoxy	2
Iron oxide	0.17
* A polybutadiene–acrylic acid–acrylonitrile terpolymer.	

The iron oxide serves as a burn rate catalyst, speeding up the thermal decomposition of the ammonium perchlorate. Other metal oxides have been shown to also display catalytic effects with AP. Little use of catalysts is otherwise seen with pyrotechnic-type compositions, where the goal is to control, rather than maximize, burn rate.

Each booster on the Space Shuttle contains 1 million pounds of solid propellant, meaning a total of 2 million pounds of propellant functions each time the Space Shuttle is launched.¹⁶

A negative oxygen balance (i.e., a fuel-rich composition with positive net Pyro Valence) is frequently designed into these propellant mixtures to obtain CO gas in addition to CO_2 . CO is lighter and will produce greater thrust, all other things being equal. However, the full oxidation of carbon atoms to CO_2 evolves more heat, so some trial and error is needed to find the optimum ratio of oxidizer and fuel.

More recent propellant research has focused on the use of the nitramine explosives RDX and HMX as energetic materials. Like nitrocellulose, these materials will ignite and burn in a controlled manner from a flame stimulus, and yet detonate when a shock of sufficient energy is applied. RDX ($\text{C}_3\text{H}_6\text{N}_6\text{O}_6$, Pyro Valence to $\text{CO}_2 = +6$) and its chemical first-cousin HMX ($\text{C}_4\text{H}_8\text{N}_8\text{O}_8$, Pyro Valence to $\text{CO}_2 = +8$) are both slightly fuel rich to produce carbon dioxide as a reaction product, but are oxygen

balanced (Pyro Valence = 0) to form water, nitrogen, and carbon monoxide, CO, as combustion products. These high explosives are blended with a binder and, in some cases, ammonium perchlorate, to produce propellant formulations. The binders in these propellants are selected to also serve to desensitize these propellants to impact and shock, and make them safer to handle, transport, and store.

Propellant compositions are also used in automobile air bags, as well as in numerous other gas generator devices, where the production of gas pressure is used to drive pistons, trigger switches, eject pilots from aircraft, and perform an assortment of other critical functions. The military and the aerospace industry use many of these items, which can be designed to function rapidly and can be initiated remotely.

Research continues in efforts to produce propellant materials that meet all of the requirements of the twenty-first century—superior performance, safety in manufacturing and storage, and environmental compatibility.

REFERENCES

1. N. Kubota, Propellant chemistry, in *Pyrotechnic chemistry, Journal of Pyrotechnics*, Whitewater, CO, 2004, chaps. 11 and 12.
2. F. L. McIntyre, *A compilation of hazard and test data for pyrotechnic compositions*, Report ARLCD-CR-80047, U.S. Army Armament Research and Development Command, Dover, NJ, 1980.
3. J. H. McLain, *Pyrotechnics from the viewpoint of solid state chemistry*, Philadelphia: Franklin Institute Press, 1980.
4. A. A. Shidlovskiy, *Principles of pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)
5. U.S. Army Material Command, *Engineering design handbook: Theory and application*, Military Pyrotechnic Series, Part One, Washington, DC, 1967 (AMC Pamphlet 706-185).
6. G. Rajendran et al., A study of the molybdenum/barium chromate/potassium perchlorate delay system, *Propellants, Explosives, Pyrotechnics*, 14, 113 (1989).
7. P. Elischer et al., Evaluation of a low toxicity delay composition, presented at Proceedings, 11th International Pyrotechnics Seminar, Vail, CO, 1986.
8. E. L. Charsley et al., The properties and reactions of the boron-potassium nitrate pyrotechnic system, presented at Proceedings, 11th International Pyrotechnics Seminar, Vail, CO, 1986.
9. U. C. Durgupal et al., Study of the zirconium-potassium perchlorate pyrotechnic system, presented at Proceedings, 13th International Pyrotechnics Seminar, Grand Junction, CO, 1988.
10. L. V. De Yong and F. J. Valenta, *Evaluation of selected computer models for modeling pyrotechnic and propellant devices*, Indian Head Technical Report 1279, Naval Ordnance Station, Indian Head, MD, September 8, 1979.
11. J. R. Parington, *A history of Greek fire and gunpowder*, Cambridge, UK: W. Heffer & Sons, Ltd., 1960.
12. P. Cooper, *Introduction to the technology of explosives*, New York: Wiley-VCH, 1996.
13. G. D. Barrett, *Venting of pyrotechnics processing equipment*, Proceedings, Explosives and Pyrotechnics Applications Section, American Defense Preparedness Association, Los Alamos, NM, October 1984.
14. *Military explosives*, U.S. Army and U.S. Air Force Technical Manual TM 9-1300-214, Washington, DC, 1967.
15. www.nasa.gov/returntoflight/system/system_SRB.html.
16. R. Seltzer, Impact widening from explosion of Nevada rocket oxidizer plant, *Chemical and Engineering News*, August 8, 1988.

8 Color and Light Production



BURNING RED STAR: (See color insert following page 112) Colors are produced in burning pyrotechnic compositions by the use of specific chemical elements, and began to find wide use in pyrotechnics by the beginning of the nineteenth century. Strontium, as strontium nitrate or strontium carbonate, will impart a beautiful red color to the flame of a burning pyrotechnic material. The effect is used for entertainment, and for emergency signaling in both military and civilian applications. (Photo by Tim Wade and Dennis King, courtesy of MP Associates.)

No one appreciates a fireworks display as much as a chemist does. When a beautiful red shell explodes up in the sky, 99% of the audience goes “oooooh.” The chemist says “aah, strontium.”

INTRODUCTION

The production of bright light, often with vivid color, is the primary purpose of many pyrotechnic compositions. Light emission has a variety of applications, ranging from military signals and illuminating devices to highway distress flares to spectacular aerial fireworks and theatrical pyrotechnics. The basic theory of light emission was discussed in Chapter 2, and several good articles have been published dealing with the chemistry and physics of colored flames.^{1,2}

Color compositions can be pressed into tubes to produce flares of varying burn times, or the compositions can be pressed into pellets and fired or expelled into the air. The aerial pellets are referred to as stars, and a large star fired singly is often referred to as a *comet*. Very small stars are also now widely used in fireworks fountains, where an expelling charge of a black-powder-type composition sprays small microstars into the air to produce spark-type effects of various colors.³

The instrumentation used for the analysis of the light emission from pyrotechnic mixtures has continued to get better and better, providing scientists with more and more information regarding the molecular and atomic origin of light emission. The quantitative measurement of light intensity (candlepower) at any instant and the light integral (total energy emitted, with units of candle-seconds/gram) can be affected by a variety of test parameters, such as container diameter, burning rate, and the measuring equipment. Therefore, comparisons between data obtained from different reports—using either different equipment or a different test procedure—should be viewed with caution.

WHITE LIGHT COMPOSITIONS

INTRODUCTION

For white light emission, a mixture is required that burns at high temperature (typically greater than 3,000°C), creating a substantial quantity of excited atoms or molecules in the vapor state together with incandescent solid or liquid particles. Incandescent particles emit a broad range of wavelengths in the visible region of the electromagnetic spectrum, and white light is perceived by the viewer. Intense emission from sodium atoms in the vapor state, excited to higher-energy electronic states by high flame temperature, is the principal light source in the sodium nitrate–magnesium–organic binder flare compositions widely used by the military.^{4,5}

Magnesium or aluminum is found as a fuel in most white light compositions. These metals evolve substantial heat upon oxidation, and the high-melting magnesium oxide (MgO) and aluminum oxide (Al₂O₃) reaction products are good light emitters at the high reaction temperatures that can be achieved using these fuels. Titanium and zirconium metals are also good fuels for white light compositions, but their spark sensitivities require caution in manufacturing if fine fuel particles are used.

In selecting an oxidizer and fuel for a white light mixture, a main consideration is maximizing heat output. A value of 1.5 kcal/gram has been given by Shidlovskiy as the minimum for a usable illuminating composition.⁶ Black powder produces a heat output of approximately 0.66 kcal/gram, whereas sodium nitrate–magnesium and potassium perchlorate–aluminum compositions produce a heat output in excess of 2 kcal/gram and are noticeably brighter and whiter in their flame color.

A flame temperature of less than 2,000°C will produce a minimum amount of white light by emission from incandescent particles or from excited gaseous sodium atoms.

Therefore, the initial choice for an oxidizer is one with an *exothermic* heat of decomposition such as potassium chlorate (KClO₃). However, binary mixtures containing either a chlorate and perchlorate salt with active metal fuels are usually

considered too ignition sensitive for commercial use, and the less reactive, but safer nitrate compounds are usually selected. Potassium perchlorate is used with aluminum and magnesium in some photoflash mixtures; these are extremely reactive compositions, with velocities in the explosive range and intense white light output. Care in manufacturing and small quantities in process at any given time are usually employed—and strongly recommended—with these mixtures.

The nitrates are considerably endothermic in their decomposition, and therefore deliver less heat per mole than chlorates or perchlorates, but they can be used with somewhat less fear of accidental ignition. However, if fine metal fuel particles are used, static electricity is always a concern regardless of the oxidizer that is used.

Barium nitrate is often selected for use in white light mixtures. The barium oxide (BaO) product formed upon reaction is a good, broad-range molecular emitter in the vapor phase (the boiling point of BaO is ca. 2,000°C), and condensed particles of BaO found in the cooler parts of the flame are also good emitters of incandescent light.

Sodium nitrate is another frequent choice for white light production. It is quite hygroscopic, however, so precautions must be taken during production and storage to exclude moisture. Sodium nitrate produces good heat output per gram due to the low atomic weight (23) of sodium, and the intense flame emission from atomic sodium in the vapor state contributes substantially to the total light intensity. Potassium nitrate, on the other hand, is not a good source of intense atomic or molecular emission, and it is rarely (if ever) used as the sole oxidizer in white light compositions.

Magnesium metal is the fuel found in most military illuminating compositions, as well as in some special effects devices. However, it is rarely used in fireworks, due to moisture concerns. Aluminum and titanium metals, the magnesium-aluminum alloy magalium, and antimony sulfide (Sb₂S₃) are used for white light effects in many fireworks mixtures. Several published formulas for white light compositions are given in Table 8.1.

Extremely bright compositions can be produced using an oxidizer with zirconium as the fuel. The high boiling point of zirconium oxide, well in excess of 4,000°C, allows the flame temperature to rise to extraordinary levels approaching 5,000°C, producing a brilliant white light. This effect has seen little commercial application, however, due to the extreme spark sensitivity associated with compositions containing zirconium powders.

The ratio of ingredients, as expected, will affect the performance of the composition. Optimum performance is anticipated near the stoichiometric point, but an excess of metallic fuel usually increases the burning rate and light emission intensity. The additional metal increases the thermal conductivity of the mixture, thereby increasing the burn rate, and the excess fuel, especially a volatile metal such as magnesium (boiling point 1,107°C), can vaporize and burn with oxygen in the surrounding air to produce extra heat and light. The sodium nitrate–magnesium system is extensively used for military illuminating compositions. Data for this system are given in Table 8.2. The anticipated reaction between sodium nitrate and magnesium is



For a stoichiometric mixture, 121.5 grams of magnesium and 170 grams of sodium nitrate correspond to the balanced chemical equation (41.6% magnesium and 58.4%

TABLE 8.1
White Light Compositions

Oxidizer (% by weight)	Fuel (% by weight)	Other (% by weight)
I. Barium nitrate, Ba(NO ₃) ₂	Magnesium, Mg	Wax
Potassium nitrate, KNO ₃		Oil
38.3	26.9	6.7
25.2		2.9
II. Sodium nitrate, NaNO ₃	Magnesium, Mg	Laminac
44	50	6
III. Teflon, (-CF ₂ -CF ₂) _n	Magnesium, Mg	Nitrocellulose
46	54	2.6
IV. Sodium nitrate, NaNO ₃	Aluminum, Al	VAAR resin
53	35	5
	Tungsten, W	7
V. Potassium perchlorate, KClO ₄	Antimony, Sb	Gum
64	13	10
Potassium nitrate, KNO ₃		
13		
VI. Potassium nitrate, KNO ₃	Sulfur, S	Fine black powder
65	20	5
	Antimony, Sb	10
VII. Ammonium perchlorate, NH ₄ ClO ₄	Antimony sulfide, Sb ₂ S ₃	Wood meal
40	14	5
Potassium perchlorate, KClO ₄	Starch	
30	11	

Source: Formula I: U.S. Army Material Command, *Engineering Design Handbook: Theory and Application Military Pyrotechnic Series*, Part One, Washington, DC, 1967 (AMC Pamphlet 706-185).¹⁹
 Formulas II-IV: F. L. McIntyre, *A Compilation of Hazard and Test Data for Pyrotechnic Compositions*. Report ARLCD-CR-80047, U.S. Army Armament Research and Development Command, Dover, NJ, 1980.²²
 Formulas V-VII: T. Shimizu, in R. Lancaster, *Fireworks: Principles and Practice*, New York: Chemical Publishing Co., 1972.⁷

TABLE 8.2
The Sodium Nitrate–Magnesium System

	% Sodium Nitrate	% Magnesium	Linear Burning Rate, mm/s	Heat of Reaction, kcal/g
A.	70	30	4.7	1.3
B.	60	40	11.0	2.0
C.	50	50	14.3	2.6

Source: A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)

sodium nitrate by weight). Formula A in Table 8.2 therefore contains an excess of oxidizer. It is the slowest-burning mixture and produces the least heat. Formula B is very close to the stoichiometric point. Formula C contains excess magnesium and is the most reactive of the three; the burning of the excess magnesium in the air appears to contribute substantially to the performance of this composition.

A significant altitude effect will be shown by these illuminating compositions, especially those containing excess metal. The decreased atmospheric pressure, and also the resulting decrease in oxygen concentration, at higher altitudes will slow the burning rate as the excess fuel will not be consumed as efficiently by the lower concentrations of atmospheric oxygen, and the reduced atmospheric pressure will not hold the heat at the reaction surface as effectively as a higher pressure does.

Illuminant compositions are typically mixtures of an oxidizer, metal fuel, and binder. They provide a classic example of how to modify the performance of a pyrotechnic mixture. For a faster (and brighter) reaction, several options are available: use a higher percentage of the metal fuel, use a finer particle size metal, or reduce the binder content to raise the heat output. Criteria such as cost, performance, and specification limitations will determine which approach is best for a given situation.

PHOTOFLASH MIXTURES

To produce a burst of light of short duration, a composition is required that will react very rapidly. Fine particle sizes are used for the oxidizer and fuel to increase reactivity, but sensitivity is also enhanced at the same time. Therefore, these mixtures are quite hazardous to prepare, and mixing operations should always be carried out remotely. Several representative photoflash mixtures are given in Table 8.3.

An innovation in military photoflash technology was the development of devices containing fine metal powders *without* any oxidizer. A high-explosive bursting charge is used instead. This charge, upon ignition, scatters the metal particles at high temperature, and they are then air oxidized to produce light emission. No hazardous mixing of oxidizer and fuel is required to prepare these illuminating devices.

TABLE 8.3
Photoflash Mixtures

Oxidizer (% by weight)		Fuel (% by weight)		Reference	
I.	Potassium perchlorate, KClO_4	40	Magnesium, Mg Aluminum, Al	34 26	19
II.	Potassium perchlorate, KClO_4	40	Magnalium, Mg/Al	60	19
III.	Potassium perchlorate, KClO_4 Barium nitrate, $\text{Ba}(\text{NO}_3)_2$	30 30	Aluminum, Al	40	19
IV.	Barium nitrate, $\text{Ba}(\text{NO}_3)_2$	54.5	Magnalium Aluminum	45.5 4	22

Energetic photoflash compositions require a minimum of mixing in order to create highly reactive oxidizer-fuel blends. It is possible to mix these compositions in the actual end item by placing layers of oxidizer and fuel in the device, sealing the units, and then gently tumbling or rotating the devices, in a remote location, to achieve an acceptable degree of homogeneity for the powder inside the device. Similarly, flash powders used in the entertainment industry as special effect materials are shipped and stored as separate, premeasured containers of oxidizer and fuel. Right before “show time,” the chemicals are carefully blended, loaded into holders, positioned for use, and then electrically fired at the proper moment during a show, producing a concussive audible effect and a flash of light.

Flash powders are among the most energetic, sensitive, and explosive of all pyrotechnic compositions. There is sometimes debate and friendly discussion about whether or not very reactive flash powders function by a deflagration or detonation mechanism. It is truly an academic argument—there is no question that they can explode violently, whatever the reaction process is.

SPARKS

The production of brilliant sparks is one of the principal effects available to the fireworks manufacturer and to the special effects industry. Sparks occur during the burning of many pyrotechnic compositions, and they may or may not be a desired feature.

Sparks are produced when liquid or solid particles, either original components or reaction products created at the burning surface, are ejected from the composition by gas pressure produced during the high-energy reaction. These particles, heated to incandescent temperatures, leave the flame area and proceed to radiate light as they cool off or continue to react with atmospheric oxygen. The particle size of the fuel will largely determine the quantity and size of sparks; the larger the particle size, the larger the sparks are likely to be. A combination consisting of fine fuel particles for heat production blended with larger fuel particles for the spark effect is a technique that has been used by some manufacturers.

TABLE 8.4
Spark-Producing Compositions

Composition	% by Weight	Effect	Reference
I. Potassium nitrate, KNO_3	58	Gold sparks	7
Sulfur	7		
Pure charcoal	35		
II. Barium nitrate, $\text{Ba}(\text{NO}_3)_2$	50	Gold sparks (sparkler)	7
Steel filings	30		
Dextrine	10		
Aluminum powder	8		
Fine charcoal	0.5		
Boric acid	1.5		
III. Potassium perchlorate, KClO_4	42.1	White sparks	23
Titanium	42.1		
Dextrine (make a paste from dextrine and water, then mix in oxidizer and fuel)	15.8		
IV. Potassium perchlorate, KClO_4	50	White sparks "waterfalls"	7
Bright Al powder	25		
Flitter Al, 30–80 mesh	12.5		
Flitter Al, 5–30 mesh	12.5		

Metal particles, especially aluminum, titanium, and magnalium alloy, produce good sparks that are white in appearance. Charcoal of sufficiently large particle size also works well, producing sparks with a characteristic orange color. Sparks from iron particles vary from gold to white, depending on the reaction temperature; they are the source of many of the brilliant sparks seen in the popular gold sparkler ignited by millions of people on the Fourth of July.

Magnesium metal does not produce a good spark effect unless large particle size metal is used. The metal has a low boiling point ($1,107^\circ\text{C}$), and therefore tends to vaporize and completely react in the pyrotechnic flame.⁷ Magnalium can produce good sparks that burn in the air with a novel, crackling sound. Several spark-producing formulas are given in Table 8.4. Remember, the particle size of the spark-producing material is very important in generating sparks in a pyrotechnic flame; experimentation is needed to find the ideal size for a given effect. For a good spark effect, the fuel must contain particles large enough to escape from the flame prior to complete combustion. Also, the oxidizer must not be too effective, or complete reaction may occur in the flame, and little or no spark effect will be observed. Charcoal sparks are difficult to achieve with the hotter oxidizers; potassium nitrate (KNO_3), with its lower flame temperatures, often works best. Some gas production is required to achieve good spark effects by assisting in the ejection of particles from the flame. Charcoal, other organic fuels and binders, and the nitrate ion can provide gas for this purpose.

FLITTER AND GLITTER

Several interesting visual effects can be achieved by careful selection of the fuel and oxidizer for a spark-producing composition. Several thorough review articles discussing this topic in detail, with numerous formulas, have been published.^{8,9}

Flitter refers to the large white sparks obtained from the burning of large aluminum flakes. These flakes burn continuously upon ejection from the flame, creating a beautiful white effect, and they are used in a variety of fireworks items.

Glitter is the term given to the effect produced by molten droplets that, upon ejection from the flame, ignite in air to produce a brilliant flash of light. A nitrate salt (KNO_3 is best) and sulfur or a sulfide compound appear to be essential for the glitter phenomenon to be achieved. It is likely that the low melting point (334°C) of potassium nitrate produces a liquid phase that is responsible, at least in part, for this effect. Several glitter formulas are given in Table 8.5.

The ability of certain compositions containing magnesium or magnalium alloy to burn in a pulsing, strobe light manner is a novel phenomenon believed to involve

TABLE 8.5
Glitter Formulas

Composition	% by Weight	Effect	Note
I. Potassium nitrate, KNO_3	55	Good white glitter	Used in aerial stars
Bright Al powder	5		
Dextrine	4		
Antimony sulfide, Sb_2S_3	16		
Sulfur	10		
Charcoal	10		
II. Potassium nitrate, KNO_3	55	Gold glitter	Used in aerial stars
Bright Al powder	5		
Dextrine	4		
Antimony sulfide, Sb_2S_3	14		
Charcoal	8		
Sulfur	8		
III. Potassium nitrate, KNO_3	55	Good white glitter	Used in fountains
Sulfur	10		
Charcoal	10		
Atomized aluminum	10		
Iron oxide, Fe_2O_3	5		
Barium carbonate, BaCO_3	5		
Barium nitrate, $\text{Ba}(\text{NO}_3)_2$	5		

Source: R. M. Winokur, The Pyrotechnic Phenomenon of Glitter, in *Pyrotechnica II*, Pyrotechnica Publications, Austin, TX, 1978.

TABLE 8.6
Strobe Compositions

Material	Strobe Color (% by weight)		
	Red	Green	White
Ammonium perchlorate	50	60	60
Strontium sulfate	20		
Barium sulfate		17	15
Magnesium	30	23	
Magnalium alloy			25
Potassium dichromate ^a	+5	+5	+5

Source: T. Shimizu, Studies on Strobe Light Pyrotechnic Compositions, in *Pyrotechnica VIII*, Pyrotechnica Publications, Austin, TX, 1982.

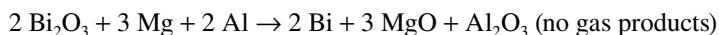
^a Potassium dichromate is coated on the metal fuel as a stabilizer.

two distinct reactions. A slow, dark process occurs until sufficient heat is generated to initiate a fast, light-emitting reaction. Dark and light reactions continue in an alternate manner, generating the strobe effect.^{10,11} Some strobe formulations are given in Table 8.6. The strobing light production from these compositions can be used for entertainment, but it also offers some interesting possibilities for emergency signaling flares.

CRACKLE EFFECTS

A relatively new effect in the field of entertainment pyrotechnics is a crackling spark effect produced by a thermite-type reaction between a metal oxide and a metal. The original crackle compositions that were introduced into the fireworks market by China contained lead tetroxide—or “red lead” oxide—with formula Pb_3O_4 , and magnalium as the fuel. Replacement formulations, again based on thermite-type metal oxide–metal reactions, have been developed using bismuth(III) oxide and copper(II) oxide in place of lead tetroxide, again with magnalium as the fuel.¹² The addition of coarse (>100 mesh) titanium metal particles with the compositions produces a spectacular white spark effect in addition to the crackling effect.¹³

While an audible effect is produced when granules of crackling composition ignite, there is very little gas pressure produced from the thermite-type reaction, and consequently, the small granules have little to no explosive effect on the surroundings. Bulk amounts of the crackling compositions in the manufacturing workplace, though, will burn very hot and very fast, and caution is definitely required when working with such mixtures. The reaction of bismuth oxide with a 50/50 alloy of magnalium is similar to



A typical lead-free crackling composition is as follows:

Bismuth oxide, Bi ₂ O ₃	50
Copper oxide, CuO	15
Magnalium (Mg/Al) alloy	20
Titanium (>100 mesh)	15
Binder/solvent	As needed

This composition would be blended with solvent, and the damp material would be tumbled or screened to form small granules, which are then dried for use.

COLOR

INTRODUCTION

Certain elements and chemical compounds, when heated to high temperature and present in the pyrotechnic flame in the vapor phase, have the unique property of emitting lines or narrow bands of light in the visible region (380 to 780 nanometers) of the electromagnetic spectrum. This emission is perceived as color by an observer, and the production of colored light is one of the more important goals sought by the pyrotechnic chemist. Table 8.7 lists the colors associated with the various regions of the visible spectrum. The *complementary* colors, perceived if white light *minus* a particular portion of the visible spectrum is viewed, are also given in Table 8.7. The dyes used to produce colored smoke work by this latter principle—absorbing a portion of visible light and scattering the remainder.

TABLE 8.7
The Visible Spectrum

Wavelength (nanometers)	Emission Color	Observed Color—If This Wavelength Is Removed from White Light
<380	None (ultraviolet region)	—
380–435	Violet	Yellowish green
435–480	Blue	Yellow
480–490	Greenish blue	Orange
490–500	Bluish green	Red
500–560	Green	Purple
560–580	Yellowish green	Violet
580–595	Yellow	Blue
595–650	Orange	Greenish blue
650–780	Red	Bluish green
>780	None (infrared region)	—

Source: H. H. Bauer, G. D. Christian, and J. E. O'Reilly, *Instrumental Analysis*, Boston: Allyn & Bacon, 1979.

To produce color in a pyrotechnic flame, heat (from the reaction between an oxidizer and a fuel) and a color-emitting species are required. Sodium compounds added to a heat mixture will impart a yellow-orange color to the flame. Strontium salts will yield red, barium and copper compounds can give green, and certain copper-containing mixtures will produce blue. Color can be produced by emission of a narrow band of light (e.g., light in the range 435 to 480 nanometers is perceived as blue), or by the emission of several ranges of light that combine to yield a particular color. For example, the mixing of blue and red light in the proper proportions will produce a purple-violet flame effect. Color theory is a complex topic, but it is one that should be studied by anyone desiring to produce colored flames.²

The production of a vividly colored flame is a much more challenging problem than creating white light. A delicate balance of factors is required to obtain a satisfactory effect:

1. An atomic or molecular species that will emit the desired wavelength, or blend of wavelengths, must be present in the pyrotechnic flame.
2. The emitting species must be sufficiently volatile to exist in the vapor state at the temperature of the pyrotechnic reaction. The flame temperature will range from 1,000 to 2,000°C (or more), depending on the particular composition used.
3. Sufficient heat must be generated by the oxidizer-fuel reaction to produce the excited electronic state of the emitter. A minimum heat requirement of 0.8 kcal/gram has been mentioned by Shidlovskiy.⁶
4. Heat is necessary to volatilize and excite the emitter, but you must not *exceed* the dissociation temperature of molecular species (or the ionization temperature of atomic species) or color quality will suffer. For example, green emitter BaCl is unstable above 2,000°C, and the best blue emitter, CuCl, should not be heated above 1,200°C.⁶ A temperature *range* is therefore required, high enough to achieve the excited electronic state of the vaporized species but low enough to minimize dissociation.
5. The presence of incandescent solid or liquid particles in the flame will adversely affect color quality. The resulting black body emission of white light will enhance overall emission intensity, but the color quality will be lessened. A washed-out color will be perceived by the viewers. The use of magnesium or aluminum metal in color compositions will yield high flame temperatures and high overall intensity, but broad emission from incandescent magnesium oxide or aluminum oxide products may lower color purity.
6. Every effort must be made to minimize the presence of unwanted atomic and molecular emitters in the flame. Sodium compounds, even as impurities, must be avoided, or at least minimized, in any color mixtures except yellow. The intense yellow-orange atomic emission from sodium (589 nanometers) will overwhelm other colors.

Potassium emits weak violet light (near 450 nanometers), but good red and green flames can be produced with potassium compounds present in the mixture. Ammonium perchlorate is advantageous for color compositions because it contains no metal ion

to interfere with color quality. The best oxidizer to choose, therefore, should contain the metal ion whose emission, in atomic or molecular form, is to be used for color production, *if* such an oxidizer is commercially available, works well, and is safe to use. Using this logic, the chemist would select barium nitrate or barium chlorate for green flame mixtures. Strontium nitrate, although hygroscopic, is frequently selected for red compositions. The use of a salt other than one with an oxidizing anion (e.g., strontium carbonate for red) may be required by hygroscopicity, burn rate, and safety considerations. However, these inert ingredients will tend to lower the flame temperature, and therefore lower the emission intensity. If so, a metal fuel may be required to raise flame temperature and offset this effect. A lower percentage of color ingredient may also be required in such cases to produce a satisfactory color.

A binder may be required in a colored flame mixture if the composition will be pelleted or formed into stars. If so, the minimum percentage of binder should be used. Carbon-containing compounds can produce an orange flame color. The use of a binder that is already substantially oxidized (one with a high oxygen content, such as dextrine) can minimize this problem. Binders such as paraffin that contain little or no oxygen should be avoided unless a hot, oxygen-rich composition is being prepared.

OXIDIZER SELECTION

The numerous requirements for a good oxidizer were discussed in detail in Chapter 3. An oxidizer for a colored flame composition must meet all of those requirements, and in addition must either emit the proper wavelength light to yield the desired color or not emit any light that interferes with the color produced by other components.

In addition, the oxidizer must react with the selected fuel to produce a flame temperature that yields the maximum emission of light in the proper wavelength range. If the temperature is too low, not enough excited molecules are produced and weak color intensity is observed. A flame temperature that is too hot may decompose the molecular emitter, destroying color quality.

Table 8.8 gives some data on flame temperatures obtained by Shimizu for oxidizer-shellac mixtures. Sodium oxalate was added to yield a yellow flame color and permit temperature measurement by the line reversal method.¹⁴

The data in Table 8.8 show that potassium nitrate, with its highly endothermic heat of decomposition, produces significantly lower flame temperatures with shellac than the other three oxidizers. The yellow light intensity will be substantially less for the nitrate compositions.

In order to use potassium nitrate in bright-colored flame mixtures, it is usually necessary to include magnesium or magnalium as a fuel to raise the flame temperature. A source of chlorine is also helpful for formation of volatile BaCl (green), or SrCl (red) emitters. The presence of chlorine in the flame also aids by hindering the formation of magnesium oxide and strontium or barium oxide, all of which will hurt the color quality. Shidlovskiy suggests a minimum of 15% chlorine donor in a color composition when magnesium metal is used as a fuel.⁶

However, chlorine is not necessary in order to produce color flames. It has been shown that a series of colors—except blue—can be produced successfully using nitrate oxidizers without the use of any metallic fuels or chlorine-containing

TABLE 8.8
Flame Temperatures for Oxidizer-Shellac Mixtures

Composition		Flame Temperatures for Various Oxidizers (°C)			
		Potassium Perchlorate, KClO ₄	Ammonium Perchlorate, NH ₄ ClO ₄	Potassium Chlorate, KClO ₃	Potassium Nitrate, KNO ₃
I.	75% oxidizer 15% shellac 10% sodium oxalate ^a	2,250	2,200	2,180	1,675
II.	70% oxidizer 20% shellac 10% sodium oxalate	2,125	2,075	2,000	1,700
III.	65% oxidizer 25% shellac 10% sodium oxalate	1,850	1,875	1,825	1,725

Source: T. Shimizu, *Fireworks: The Art, Science and Technique*. Tokyo: T. Shimizu, 1981.

^a The sodium oxalate (Na₂C₂O₄) produces a yellow flame. Analysis of the yellow-orange light (sodium) emission at 589 nm can be used to determine the flame temperature.

compounds.¹⁵ The use of chlorine-containing compounds and metal fuels does aid in expanding the burn rate range for color compositions and in expanding the range of flame temperatures that can be achieved with color compositions.

FUELS AND BURNING RATES

Applications involving colored flame compositions will require either a long-burning composition or a mixture that burns rapidly to give a burst of color. Highway flares (fusees) and the lances used to create fireworks set pieces require long burning times ranging from 1 to 30 minutes. Fast fuels such as metal powders and charcoal are usually not included in these slow mixtures. Partially oxidized organic fuels such as dextrine can be used. Coarse oxidizers and fuel particles can also retard the burning rate. Highway flares often contain sawdust as a coarse, slow-burning retardant and wax as a low-melting heat sink to help achieve lengthy burning times.

To achieve rapid burning, such as in the brightly colored stars used in aerial fireworks and Very pistol cartridges, compositions will contain charcoal or a metallic fuel. Fine particle sizes will be used, and all ingredients will be well mixed to achieve a very homogeneous and fast-burning mixture.

Military color flare compositions have traditionally used magnesium as a fuel, to maximize flame temperature and candlepower.¹⁶ When magnesium is used, however, moisture is always a concern. If compositions containing magnesium are not thoroughly dried in the manufacturing process, and end items are not well sealed, the storage lifetime of the end items will be adversely affected by slow oxidation of the magnesium. Burn rates will slow up and candlepower will decrease over time.

Fireworks color effects have become noticeably brighter in recent years, largely due to an innovation from China. The Chinese factories in the 1970s pioneered the use of magnalium alloy in color compositions. The alloy used in fireworks is typically a 50/50 ratio of the two metals, and consists of a solution of Al_3Mg_2 dissolved in Al_2Mg_3 .^{2,14} Magnalium ages much better than magnesium metal by itself in color compositions, and the lower amount of aluminum does not interfere with the production of color in the flame. The magnalium fuel raises the flame temperature significantly over that of nonmetallic color compositions, and an entire range of colors can now be produced using magnalium-based compositions. A series of color compositions based on a basic set of starting chemicals was developed by master pyrotechnician Robert Veline, who generously published his formulations for hobbyists (and others) to use. Table 8.9 contains the Veline color system, for both pure colors and the wider range of colors that can be obtained by mixing colors in the pyrotechnic flame.¹⁷

COLOR INTENSIFIERS

Chlorine is one of the keys to the production of good red, green, and blue flames, and its presence is often required in a pyrotechnic mixture to achieve a good output,

TABLE 8.9
The Veline Color Series

	Prime	Red	Orange	Green	Blue
Red gum		9	9	5	9
Charcoal	20				
Magnalium	5	6	6	11	6
Potassium perchlorate	55	55	55	30	55
Barium nitrate				24	
Red iron oxide	5				
Strontium carbonate		15			
Calcium carbonate			15		
Barium carbonate				15	
Copper carbonate					15
Parlon		15	15	15	15
Wood meal (70 mesh)	6				
Dextrine	+4	+4	+4	+4	+4
Composite Colors (made by mixing the percentages of the prime colors above)					
Yellow			45	55	
Chartreuse			20	80	
Aqua				80	20
Turquoise				55	45
Magenta		50			50
Maroon		85			15
Peach		25	60		15
Purple		15	5		80

TABLE 8.10
Chlorine Donors for Pyrotechnic Mixtures

Material	Formula	Melting Point, °C	% Chlorine by Weight
Polyvinyl chloride (PVC)	$(-\text{CH}_2\text{CHCl}-)_n$	Softens ca. 80, decomposes ca. 160	56
Parlon (chlorinated polyisopropylene)	—	Softens 140	ca. 66
Hexachlorobenzene	C_6Cl_6	229	74.7
Dechlorane (hexachloropentadiene dimer)	$\text{C}_{10}\text{Cl}_{12}$	160	78.3
Hexachloroethane	C_2Cl_6	185	89.9

at a specific burn rate, of these colors. Chlorine serves two important functions in a pyrotechnic flame. It forms volatile chlorine-containing molecular species with the color-producing metals, ensuring a sufficient concentration of emitters in the vapor phase. Also, these chlorine-containing species are good emitters of narrow bands of visible light, producing the observed flame color. Without both of these properties, volatility and light emission, good colors would be difficult to achieve.

The use of chlorate or perchlorate oxidizers (KClO_3 , KClO_4 , etc.) is one way to introduce chlorine atoms into the pyrotechnic flame. Another method is to incorporate a chlorine-rich organic compound into the mixture. Table 8.10 lists some for the chlorine donors commonly used in pyrotechnic mixtures. A dramatic increase in color quality can be achieved by the addition of a small percentage of one of these materials into a mixture. Shimizu recommends the addition of 2% to 3% organic chlorine donor into compositions that don't contain a metallic fuel, and the addition of 10% to 15% chlorine donor into the high-temperature mixtures containing metallic fuels.¹⁴

Shimizu attributes much of the value of these chlorine donors in magnesium-containing compositions to the production in the flame of hydrogen chloride, which reacts with magnesium oxide to form volatile MgCl molecules¹⁴. The incandescent emission from MgO particles is thereby reduced by the reaction



and color quality improves significantly. Carefully check all proposed chlorine donors for their latest carcinogenic and toxicological information. Example: hexachlorobenzene, shown in Table 8.10, is now a material to avoid due to apparent harmful properties.

RED FLAME COMPOSITIONS

The best flame emission in the red region of the visible spectrum is produced by molecular strontium monochloride, SrCl . This species, unstable at room temperature, is generated in vapor phase in the pyrotechnic flame by a reaction between strontium and chlorine atoms. Strontium(II) chloride, SrCl_2 , would appear to be a logical precursor to SrCl , and it is readily available commercially, but it is much too hygroscopic to use in pyrotechnic mixtures.

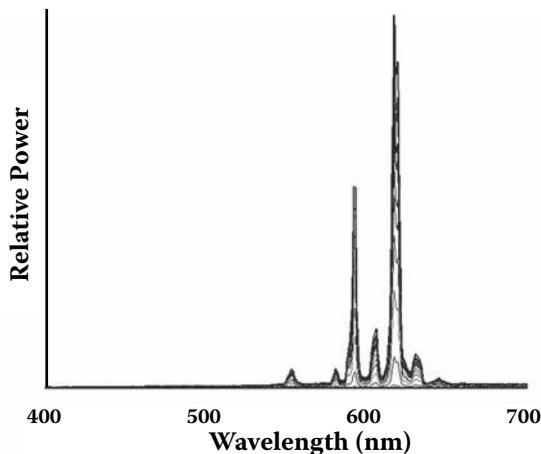
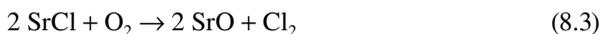


FIGURE 8.1 Emission spectrum of a red flare. Emission is concentrated in the 600 to 650 nm region. The primary emitting species are SrCl and SrOH molecules in the vapor state.

The SrCl molecule emits a series of bands in the 620- to 680-nanometer region, the deep red portion of the visible spectrum. Other peaks are also observed. Strontium monohydroxide, SrOH, is another substantial emitter in the red and orange-red regions.^{1,2} The emission spectrum of a red flare is shown in Figure 8.1.

Strontium nitrate, Sr(NO₃)₂, is often used as a combination oxidizer–color source in red flame mixtures. A hotter oxidizer, such as potassium perchlorate, is frequently used in addition to help achieve higher temperatures and faster burning rates. Strontium nitrate is rather hygroscopic, and water should not be used to moisten a binder for mixtures using this oxidizer. Strontium carbonate is much less hygroscopic and can give a beautiful red flame under the proper conditions. However, it contains an inert anion, the carbonate ion CO₃²⁻, and low percentages must be used to avoid burning difficulties.

To keep the SrCl from oxidizing in the flame, Shidlovskiy recommends using a composition containing a negative oxygen balance (excess fuel). Such a mixture will minimize the reaction



and enhance color quality.⁶ Several red formulas are presented in Table 8.11.

GREEN FLAME COMPOSITIONS

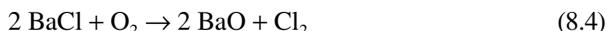
Pyrotechnic compositions containing a barium compound and a good chlorine source can generate barium monochloride, BaCl, in the flame, and the emission of green light will be observed. BaCl, an unstable species at room temperature, is an excellent emitter in the 505- to 535-nanometer region of the visible spectrum, the deep green portion.^{1,2} The emission spectrum of a green flare was shown in Figure 4.1.

TABLE 8.11
Red Flame Compositions

Composition	% by Weight	Use	Reference
I. Ammonium perchlorate, NH_4ClO_4	70	Red torch	7
Strontium carbonate, SrCO_3	10		
Wood meal (slow fuel)	20		
II. Potassium perchlorate, KClO_4	67	Red fireworks star	7
Strontium carbonate, SrCO_3	13.5		
Pine root pitch	13.5		
Rice starch	6		
III. Potassium perchlorate, KClO_4	45	Red fireworks star	Unpublished
Magnalium alloy (100/200 mesh)	18		
Shellac binder (dissolved in alcohol)	8		
Polyvinyl chloride	9		
Strontium carbonate, SrCO_3	20		
IV. Potassium perchlorate, KClO_4	44	Red signal flare (very little residue)	Unpublished
Strontium nitrate, $\text{Sr}(\text{NO}_3)_2$	31		
Epoxy (fuel/binder)	25		

Barium nitrate, $\text{Ba}(\text{NO}_3)_2$, and barium chlorate, $\text{Ba}(\text{ClO}_3)_2$, are used most often to produce green flames, serving as both the oxidizer and color source. Barium chlorate can produce a deep green flame, but it is somewhat unstable (and acid sensitive) and can form explosive mixtures with good fuels. Barium nitrate produces an acceptable green color, and it is considerably safer to work with due to its high decomposition temperature and endothermic heat of decomposition. Barium carbonate (BaCO_3) is another possibility, but it must be used in low percentage due to its inert anion, CO_3^{2-} .

An oxygen-deficient flame is required for a good quality green flame. Otherwise, barium oxide (BaO) will form and emit a series of bands in the 480- to 600-nanometer range, yielding a dull, yellowish green color. The reaction



will shift to the left-hand side when chlorine is present in abundance and oxygen is scarce, and a good green color will be achieved. A flame temperature that is too high will decompose BaCl , however, so metal fuels must be held to a minimum, if they are used at all.

This temperature dependence and the value of a chlorine source are important to remember. A binary mixture of barium nitrate and magnesium or magnalium metal

TABLE 8.12
Green Flame Compositions

Composition	% by Weight	Use	Reference
I. Ammonium perchlorate, NH_4ClO_4	50	Green torch	7
Barium nitrate, $\text{Ba}(\text{NO}_3)_2$	34		
Wood meal	8		
Shellac	8		
II. Barium chlorate, $\text{Ba}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$	65	Green torch	Unpublished
Barium nitrate, $\text{Ba}(\text{NO}_3)_2$	25		
Red gum	10		
III. Potassium perchlorate, KClO_4	46	Green fireworks star	7
Barium nitrate, $\text{Ba}(\text{NO}_3)_2$	32		
Pine root pitch	16		
Rice starch	6		
IV. Barium nitrate, $\text{Ba}(\text{NO}_3)_2$	59	Russian green flare	6
Polyvinyl chloride	22		
Magnesium	19		

will produce a brilliant white light upon ignition, from a combination of MgO and BaO emission at the high temperature achieved by the mixture. Addition of a chlorine-containing organic fuel to lower the temperature and provide chlorine atoms to form BaCl can produce a green flame. Several green flame compositions are given in Table 8.12.

BLUE FLAME COMPOSITIONS

The generation of an intense, deep blue flame represents the ultimate challenge to the pyrotechnic chemist. A delicate balance of temperature and molecular behavior is required to obtain a good blue, but it can be done if the conditions are right.

The best flame emission in the blue region of the visible spectrum (435 to 480 nanometers) is obtained from copper monochloride, CuCl . Flame emission from this molecular species yields a series of bands in the region from 428 to 452 nanometers, with additional peaks between 476 and 488 nanometers.^{1,2}

In an oxygen-rich flame, and at temperatures above $1,200^\circ\text{C}$, CuCl is unstable and will react to form CuO and CuOH . CuOH emits in the 525- to 555-nanometer region (green), and substantial emission may overpower any blue effect that is also present. Copper oxide, CuO , emits a series of bands in the red region, and this reddish emission is often seen at the top of blue flames, where sufficient oxygen from the atmosphere is present to convert CuCl to CuO .¹⁴

Paris green, copper acetoarsenite, $(\text{CuO})_3\text{As}_2\text{O}_3 \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)$, was widely used in blue flame mixtures until a few years ago. It produces a good blue flame, but it has all but vanished from commercial formulas because of the health hazards associated with its use. (It contains arsenic!)

TABLE 8.13
Blue Flame Compositions

Composition	% by Weight	Use	Reference
I. Potassium perchlorate, KClO_4	68.5	Blue flame—excellent	18
Polyvinyl chloride	6		
Copper oxide, CuO	15		
Red gum	7.5		
Rice starch	+5%		
II. Potassium perchlorate, KClO_4	40	Blue flame	7
Ammonium perchlorate, NH_4ClO_4	30		
Copper carbonate, CuCO_3^a	15		
Red gum	15		
III. Potassium perchlorate, KClO_4	68	Blue flame—excellent	18
Copper carbonate, CuCO_3^a	15		
Polyvinyl chloride	11		
Red gum	6		
Rice starch	+5%		
IV. Ammonium perchlorate, NH_4ClO_4	70	Blue fireworks star (with charcoal tail)	Reference ^b
Red gum	10		
Copper carbonate, CuCO_3^a	10		
Charcoal	10		
Dextrine (moisten with isopropyl alcohol)	+5%		

^a Material is actual basic copper carbonate, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$.

^b In J. Stone, *Cut Star Making, Pyrotechnica I, Pyrotechnics*. Austin, TX: Publications, 1977.

Copper oxide (CuO), basic copper carbonate $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, and copper sulfate, available commercially as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, are among the materials used in blue flame mixtures. Potassium perchlorate and ammonium perchlorate are the oxidizers found in most blue compositions. Potassium chlorate would be an ideal choice because of its ability to sustain reaction at low temperatures (remember, CuCl is unstable above $1,200^\circ\text{C}$), but copper chlorate is an extremely reactive material. The chance of it forming should a blue mixture get wet precludes the commercial use of KClO_3 .

Several formulas for blue flame compositions are given in Table 8.13. An extensive review of blue and purple flames, concentrating on potassium perchlorate mixtures, has been published by Shimizu.¹⁸

PURPLE FLAME COMPOSITIONS

A purple flame, a relative newcomer to pyrotechnics, can be achieved by the correct balance of red and blue emitters. The additive blending of these two colors produces a range of colors in the purple/lilac/violet/magenta family as perceived

TABLE 8.14
Purple Flame Compositions

Composition	% by Weight	Comment ^a
I. Potassium perchlorate, KClO_4	70	Excellent
Polyvinyl chloride	10	
Red gum	5	
Copper oxide, CuO	6	
Strontium carbonate, SrCO_3	9	
Rice starch	+5%	
II. Potassium perchlorate, KClO_4	70	Excellent
Polyvinyl chloride	10	
Red gum	5	
Copper powder, Cu	6	
Strontium carbonate, SrCO_3	9	
Rice starch	+5%	

^a T. Shimizu, Studies on Blue and Purple Flame Compositions Made with Potassium Perchlorate, in *Pyrotechnica VI*, Austin, TX: Pyrotechnica Publications, 1980.

by the observer. Several comprehensive review articles on purple flames have been published. The compositions given in Table 8.14 received an excellent rating in the review article written by Shimizu.¹⁸

YELLOW FLAME COMPOSITIONS

A yellow-orange flame color is easily achieved by atomic emission from sodium. The emission intensity at 589 nanometers increases as the reaction temperature is raised; there is no molecular emitting species here to decompose. Ionization of sodium atoms to sodium ions will occur at very high temperatures, however, so even here there is an upper limit of temperature that must be avoided for maximum color quality.

A purer canary yellow can be achieved pyrotechnically by blending green and orange. Pyrotechnic compositions that contain a barium compound (for green emission) and a calcium or sodium compound for yellow/orange color, can achieve some beautiful color effects in the yellow region. Trial and error is probably the best method to use in finding the perfect mix for a desired hue.

Most sodium compounds tend to be quite hygroscopic, and therefore simple compounds such as sodium nitrate (NaNO_3), sodium chlorate (NaClO_3), and sodium perchlorate (NaClO_4), combining the oxidizing anion with the metallic emitter, cannot be used unless precautions are taken to protect against moisture before, during, and after the manufacturing process. Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) and cryolite (Na_3AlF_6) are lower in hygroscopicity, and they are therefore the color agents used in most

TABLE 8.15
Yellow Flame Compositions

Composition	% by Weight	Use	Reference
I. Potassium perchlorate, KClO_4	70	Yellow fireworks star	7
Sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$	14		
Red gum	6		
Shellac	6		
Dextrine	4		
II. Potassium perchlorate, KClO_4	75	Yellow fire	7
Cryolite, Na_3AlF_6	10		
Red gum	15		
III. Sodium nitrate, NaNO_3	56	Russian yellow fire	6
Magnesium	17		
Polyvinyl chloride	27		
IV. Potassium nitrate, KNO_3	37	Russian yellow fire	6
Sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$	30		
Magnesium	30		
Resin	3		
V. Barium nitrate, $\text{Ba}(\text{NO}_3)_2$	17	Yellow flare	22
Strontium nitrate, $\text{Sr}(\text{NO}_3)_2$	16		
Potassium perchlorate, KClO_4	17		
Sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$	17		
Hexachlorobenzene, C_6Cl_6	12		
Magnesium	18		
Linseed oil	3		

commercial yellow flame mixtures. Some representative yellow compositions are given in Table 8.15.

It must be remembered that a little bit of sodium goes a long way in affecting flame color, due to the fact that sodium is an atomic, rather than a molecule emitter. A molecular emitter must form in the flame via a reaction between two chemical species. An atomic emitter requires no such flame chemistry to vaporize the atomic material, and it is ready to emit its atomic spectrum immediately upon vaporization in the pyrotechnic flame. A low percentage of a sodium impurity in a chemical can cause that chemical to affect flame color efforts to a significant extent, so quality control of raw materials is important when the production of a pure color is the goal.

A set of U.S. Navy flare compositions, containing magnesium metal, is given in Table 8.16, showing formulas for bright red, green, and yellow flares.¹⁶

TABLE 8.16
U.S. Navy Flare Formulas

Material	Weight %		
	Red	Green	Yellow
Magnesium	24.4	21.0	30.3
Potassium perchlorate, KClO_4	20.5	32.5	21.0
Strontium nitrate, $\text{Sr}(\text{NO}_3)_2$	34.7		
Barium nitrate, $\text{Ba}(\text{NO}_3)_2$		22.5	20.0
Polyvinyl chloride	11.4	12.0	
Sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$			19.8
Copper powder, Cu		7.0	
Asphaltum	9.0		3.9
Binder		5.0	5.0

^a H. A. Webster III, Visible Spectra of Standard Navy Colored Flares, *Propellants, Explosives, Pyrotechnics*, 10, 1 (1985).

BEYOND THE VISIBLE REGION

As the twentieth century proceeded, and modern technology for the detection and analysis of the light output from pyrotechnics and other light-emitting articles continued to improve, interest on the military side moved from the visible into the infrared region of electromagnetic radiation.

Infrared radiation is emitted as a continuum from warm and hot objects,¹⁹ and it is also emitted in discrete wavelengths (or frequencies, which some scientists prefer to use to describe electromagnetic radiation) from molecular species in association with vibrational and rotational activity involving the chemical bonds in the molecules. Chemical bonds either absorb infrared radiation of the proper wavelength to undergo a transition from a ground state vibrational state to an excited state, or the bonds are first thermally excited to a higher vibrational level, and return to the ground state with the emission of a photon of infrared radiation. This emission of infrared radiation can be used to detect objects that are warmer than their background, and thereby provides a means of targeting those warm objects.

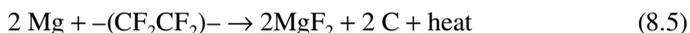
Night vision technology is one application of this area of technology. The detection of diesel engines, jet engines, and other hot spots that stand out from their background is another area of very active research interest, and pyrotechnic articles have been used to provide protection for hot objects that might be detectable due to infrared emission, and therefore be in harm's way in a combat setting.

Infrared radiation ranges from 0.80 microns (or 800 nm—the long-wavelength end of visible light) to 300 microns, where the microwave region begins. Warm objects emit a thermal fingerprint of infrared radiation that is a function of temperature and the types of chemical bonds, if any, that are emitting the radiation. Spikes of intensity from molecular vibrational activity are superimposed on the continuum

from black body radiation from solids and liquids. Countermeasures that can be used to protect against a thermal detector include:

1. A pyrotechnic flare that emits a high-intensity output of visible and infrared radiation, to dazzle the detector
2. Use of a pyrotechnic smoke, where the smoke particles absorb and scatter the radiation that is emitted by the warm target object, causing it to not be distinguishable from the background
3. The use of multiple decoys that are emitting infrared radiation of a type and energy output that mimics what the detector is specifically looking for, and thereby divert attention away from the target

Much of the countermeasure technology for the protection of aircraft from heat-seeking missiles for the past fifty years has used method 3, and has focused on a pyrotechnic system consisting of magnesium fuel with polytetrafluoroethylene (Teflon[®]) as the reactive system. Upon ignition of the composition, in a flare, the fluorine atoms are released from the carbon skeleton of the polymer at elevated temperature and react vigorously with the magnesium fuel to produce magnesium fluoride (MgF₂), with carbon produced as another reaction product.²⁰



In an effort to maintain the proper signature, the binder that is used with this technology is also a highly fluorinated species containing enough residual hydrogen atoms to be soluble in a solvent such as acetone. The trade name for the polymer is Viton[®], and the resulting blend of magnesium, Teflon, and Viton is known in the industry as a MTV composition. The mixture burns fast and hot, and has also found some applications as an ignition composition.²¹ Obviously, much of the specifics of these compositions remain classified at this time.

As factories geared up to produce this vital composition for the defense industry, a number of tragic accidents occurred involving ignition of the mix during the post-blending handling process. Investigations revealed that the composition had very unique electrostatic properties that resulted in the composition retaining an electrostatic charge that developed during the production process for a long period of time. Measures were instituted to help disperse the accumulated charge, and the material was allowed to sit for a longer than normal time after consolidation operations were performed, in an effort to help prevent manufacturing accidents with this critical material. The technology in this area continues to evolve as detection methods and countermeasures get more and more sophisticated.

REFERENCES

1. B. E. Douda, *Theory of colored flame production*, RDTN 71, Crane, IN: U.S. Naval Ammunition Depot, 1964.
2. K. L. Kosanke and B. J. Kosanke, The chemistry of colored flames, in *Pyrotechnic chemistry*, *Journal of Pyrotechnics*, Whitewater, CO, 2004, chap. 9.

3. T. Shimizu, Studies on microstars, in *Pyrotechnica X*, Austin, TX: Pyrotechnica Publications, 1985.
4. B. E. Douda, Spectral observations in illuminating flames, In *Proceedings, First International Pyrotechnics Seminar*, Denver Research Institute, Estes Park, CO, August 1968, 113 (available from NTIS as AD 679 911).
5. D. R. Dillehay, Illuminanta and illuminant research, in *Pyrotechnic Chemistry, Journal of Pyrotechnics*, Whitewater, CO, 2004, chap. 10.
6. A. A. Shidlovskiy, *Principles of pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)
7. T. Shimizu, in R. Lancaster, *Fireworks principles and practice*, New York: Chemical Publishing Co., 1972.
8. R. M. Winokur, The pyrotechnic phenomenon of glitter, in *Pyrotechnica II*, Pyrotechnica Publications, Austin, TX, 1978.
9. C. Jennings-White, Glitter chemistry, in *Pyrotechnic chemistry, Journal of Pyrotechnics*, Whitewater, CO, 2004, chap. 14.
10. T. Shimizu, Studies on strobe light pyrotechnic compositions, in *Pyrotechnica VIII*, Austin, TX: Pyrotechnica Publications, 1982.
11. C. Jennings-White, Strobe chemistry, in *Pyrotechnic chemistry, Journal of Pyrotechnics*, Whitewater, CO, 2004, chap. 15.
12. C. Jennings-White, Lead-free crackling microstars, in *Pyrotechnica XIV*, Austin, TX: Pyrotechnica Publications, 1992.
13. T. Shimizu, Studies on mixtures of lead oxides with metals (magnalium, aluminum, or magnesium), in *Pyrotechnica XIII*, Austin, TX: Pyrotechnica Publications, 1990.
14. T. Shimizu, *Fireworks: The art, science and technique*, Tokyo: T. Shimizu, 1981.
15. C. Jennings-White, Nitrate colors, in *Pyrotechnica XV*, Austin, TX: Pyrotechnica Publications, 1993.
16. H. A. Webster III, Visible spectra of standard navy colored flares, *Propellants, Explosives, Pyrotechnics*, 10, 1, 1985.
17. R. Veline, self-published paper on color compositions, readily available on the Internet by searching for "Veline color."
18. T. Shimizu, Studies on blue and purple flame compositions made with potassium perchlorate, in *Pyrotechnica VI*, Austin, TX: Pyrotechnica Publications, 1980.
19. U.S. Army Material Command, *Engineering design handbook: Theory and application*, Military Pyrotechnic Series, Part One, Washington, DC, 1967 (AMC Pamphlet 706-185).
20. N. Kubota, Combustion process of Mg/TF pyrotechnics, *Propellants, Explosives, Pyrotechnics*, 12, 145, 1987.
21. E.-C. Koch, Magnesium-fluorocarbon pyrolants. III. Development and application of magnesium/Teflon/Viton (MTV), *Propellants, Explosives, Pyrotechnics*, 27, 262, 2002.
22. F. L. McIntyre *A compilation of hazard and test data for pyrotechnic compositions*, Report ARLCD-CR-80047. Dover, NJ: U.S. Army Armament Research and Development Command, 1980.
23. Anonymous, *Pyrotechnica IV*, Austin, TX: Pyrotechnica Publications, 1978.

9 Smoke and Sound



GREEN SMOKE: (See color insert following page 112) Pyrotechnically generated smoke is used for civilian and military applications. Colored smokes, such as the green smoke shown here, are used for entertainment as well as for military applications. The smoke is produced by the sublimation of a volatile dye in a burning pyrotechnic composition. The temperature of the composition must be high enough to vaporize the dye, but not so hot that the dye molecules are destroyed and the color is lost. (Photo by Tim Wade and Dennis King, courtesy of MP Associates.)

The entire world appears to have a fascination with fireworks, and most countries have at least one special day each year where the sky explodes in bright colors and noise. Man has had a fascination with—and been in awe of—fire as well as loud, bright bursts in the night sky going way back in time. What is the appeal of fireworks? Yes, they are entertaining, but there is surely something deeper in the human soul that relates to our attraction to these bright explosions.

SMOKE PRODUCTION

Most explosive and pyrotechnic reactions produce significant quantities of smoke, and this visible phenomenon may or may not be desirable. Smoke can obscure colored flames, and therefore attempts are made to keep the production of smoke to a minimum

in such mixtures, and active research and development efforts are under way around the world to produce low-smoke pyrotechnics.¹ Smoke is normally a nuisance. In a confined area, it can be undesirable and unhealthy. But if you are in an armored vehicle and someone is aiming a heat-seeking missile in your direction, a good cloud of the right smoke at the right time can be a true lifesaver. A variety of smoke-producing compositions are purposefully manufactured for use in daytime signaling and protective obscuration, as well as for amusement and entertainment purposes.

Two basic processes are used to create smoke clouds: the condensation of vaporized material and the dispersion of solid or liquid particles. Materials can be either released slowly via a pyrotechnic reaction or instantaneously scattered using an explosive bursting charge. Technically, a dispersion of fine solid particles in the air is termed *smoke*, while liquid particles in the air create a *fog*. A smoke is created by particles in the 10^{-5} to 10^{-9} meter range, while larger suspended particles create a *dust*.² Pyrotechnic smoke compositions must meet all of the standard requirements for an acceptable energetic device (good performance, safety, storage, etc.) that have been discussed in previous chapters.

A variety of events that will lead to smoke production can occur in the pyrotechnic flame. Incomplete burning of an organic fuel will produce a black, sooty flame (mainly atomic carbon). A highly oxidized fuel such as a sugar is not likely to produce carbon. Materials such as naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$)—volatile solids with high carbon content—are good candidates for soot production. Several mixtures that will produce black smokes are listed in Table 9.1.

The heat from the reaction between an oxidizer and fuel can vaporize a volatile ingredient, with no chemical change occurring in the vaporized material. The vaporized component, which was part of the original mixture, then condenses as fine, solid particles upon leaving the reaction zone and a smoke is created. Volatile organic dyes, ammonium chloride, and sulfur can be used to create smokes using this method.

TABLE 9.1
Black Smoke Compositions

Composition	% by Weight	Reference
I. Potassium chlorate, $KClO_3$	55	2
Anthracene, $C_{14}H_{10}$	45	
II. Potassium chlorate, $KClO_3$	45	2
Naphthalene, $C_{10}H_8$	40	
Charcoal	15	
III. Potassium perchlorate, $KClO_4$	56	3
Sulfur	11	
Anthracene, $C_{14}H_{10}$	33	
IV. Hexachloroethane, C_2Cl_6	62	3
Magnesium, Mg	16	
Naphthalene (or anthracene)	23	

Alternately, the pyrotechnic reaction can occur in a separate container, and the heat that is produced volatilizes a smoke-forming component contained in an adjacent compartment. The vaporization and dispersion of heavy oils to create white smoke can be accomplished using this technique.

Finally, a product of a pyrotechnic reaction may vaporize from the reaction zone and subsequently condense as fine particles in air, creating a smoke. Potassium chloride (boiling point 1,407°C) produces smoke in many potassium chlorate and potassium perchlorate compositions, although smoke is usually not a goal that is intentionally sought from these mixtures.

A good white smoke can be obtained by the formation of zinc chloride, $ZnCl_2$, from a reaction between zinc metal and a chlorinated organic compound (the chlorine-containing species serves as the oxidizer). Reaction products that strongly attract moisture (such as $ZnCl_2$) will have an enhanced multiplier smoke effect in humid atmospheres. The burning of elemental phosphorus, producing phosphorus oxides, can also be used to create dense white smoke as the oxides attract moisture to form acids such as phosphoric acid, H_3PO_4 .

COLORED SMOKE MIXTURES

The generation of colored smoke by the volatilization of an organic dye is a fascinating pyrotechnic problem. The military and the fireworks and entertainment industries rely on this technique for the generation of copious quantities of brilliant colored smoke. The requirements for an effective colored smoke composition include:

1. The mixture must produce sufficient heat to vaporize the dye, as well as a sufficient volume of gas to disperse the dye into the surrounding space.
2. The mixture must ignite at a low temperature and continue to burn smoothly at low temperature (well below 1,000°C). If the temperature is too high, the dye molecules will decompose, and the color quality as well as volume of the smoke will deteriorate. Metal fuels are not used in colored smoke mixtures because of the high reaction temperatures they produce.
3. Although a low ignition temperature is required, the smoke mixture must be *stable*, and not ignite, during manufacturing and storage over the expected range of ambient temperatures.
4. The molecules creating the colored smoke must be of low toxicity (including low carcinogenicity). Further, they must readily sublime without decomposition at the temperature of the pyrotechnic reaction to yield a dense smoke of good color quality.⁴

When requirements that include low ignition temperature and reliable propagation of burning at low reaction temperature are considered, the choice of oxidizer rapidly narrows to one candidate: potassium chlorate, $KClO_3$. The ignition temperature of potassium chlorate combined with sulfur or many organic fuels is below 250°C. Good heat production is achieved with such mixtures, in part due to the exothermic decomposition of $KClO_3$ at a temperature below 400°C, forming KCl and oxygen gas.

A mixture consisting of 70% KClO_3 and 30% sugar ignites near 220°C and has a heat of reaction of approximately 0.8 kcal/gram.⁷ Both chlorate-sulfur and chlorate-sugar mixtures are used in commercial and military colored smoke compositions. Sodium bicarbonate (NaHCO_3) is added to KClO_3/S mixtures to neutralize any acidic impurities that might stimulate premature ignition of the composition, and it also acts as a coolant by decomposing endothermically to evolve carbon dioxide gas (CO_2), which further aids the system by dispersing the vaporized dye. Magnesium carbonate (MgCO_3) can also be used as a coolant and acid neutralizer, absorbing heat to decompose into magnesium oxide (MgO) and CO_2 . Varying the amount of coolant can be used to help obtain the desired rate of burning and the correct reaction temperature—if a mixture burns too rapidly, more coolant should be added.⁶

The ratio of oxidizer to fuel will also affect the amount of heat and gas that is produced. A stoichiometric mixture of KClO_3 and sulfur (Equation [9.1]) contains a 2.55:1 ratio of oxidizer to fuel, by weight. Colored smoke mixtures in use today contain ratios very close to this stoichiometric amount. The chlorate-sulfur reaction is not strongly exothermic, and a stoichiometric mixture is needed to generate the heat necessary to volatilize the dye.



The reaction requires 71.9% potassium chlorate and 28.1% sulfur (by weight), a 2.55 to 1.00 ratio.

The reaction of potassium chlorate with a carbohydrate (e.g., lactose) will produce carbon monoxide (CO), carbon dioxide (CO_2), or a mixture, depending on the oxidizer/fuel ratio. The balanced equations are given as Equations (9.2) and (9.3). (Lactose occurs as a hydrate—one water molecule crystallizes with each lactose molecule.)

CO_2 product:



The reaction uses 73.1% potassium chlorate and 26.9% lactose hydrate (by weight), a 2.72 to 1.00 ratio. The heat of reaction is 1.06 kcal/gram.²

CO product:



The reaction uses 57.6% potassium chlorate and 42.4% lactose hydrate (by weight), a 1.36 to 1.00 ratio. The heat of reaction is 0.63 kcal/gram.²

The amount of heat can be controlled by adjusting the KClO_3 /sugar ratio. Excess oxidizer should be avoided; it will encourage oxidation of the dye molecules. The quantity (and volatility) of the dye will also affect the burning rate. The greater the quantity of dye used, the slower will be the burning rate—the dye is a diluent in these mixtures. Typical colored smoke compositions contain 40%–60% dye, by weight. Table 9.2 shows a variety of colored smoke compositions.

In colored smoke compositions, the volatile organic dye sublimates out of the reacting mixture and then condenses in air to form small solid particles. The dyes are strong *absorbers* of visible light. The light that is reflected off these particles is *missing* the

TABLE 9.2
Color Smoke Compositions

Composition	% by Weight	Reference
Green smoke		10
Potassium chlorate, KClO_3	25.4	
Sulfur	10.0	
Green dye	40.0	
Sodium bicarbonate, NaHCO_3	24.6	
Red smoke		10
Potassium chlorate, KClO_3	29.5	
Lactose	18.0	
Red dye	47.5	
Magnesium carbonate, MgCO_3	5.0	
Yellow smoke		6
Potassium chlorate, KClO_3	22.0	
Sucrose	15.0	
Chinoline yellow dye	42.0	
Magnesium carbonate, MgCO_3	21.0	

absorbed wavelengths, and the *complementary* hue is perceived by observers. This color-producing process is different from that of colored flame production, where the emitted wavelengths are perceived as color by the viewers. Table 8.7 lists the complementary colors for the various regions of the visible spectrum.

A variety of dyes have been used in colored smoke mixtures; many of these dyes have been under investigation for carcinogenicity and other potential health hazards because of their molecular similarity to known problem compounds.^{4,5} The materials that work best in colored smokes have several properties in common, including:

1. *Volatility*: The dye must convert to the vapor state on heating, without substantial decomposition. Only low molecular weight species (less than 400 grams/mole) are usually used; volatility typically decreases as molecular weight increases. Salts do not work well; ionic species generally have low volatility due to the strong interionic attractions present in the crystalline lattice. Therefore, functional groups such as $-\text{COO}^-$ (carboxylate ion) and NR_4^+ (a substituted ammonium salt) cannot be present.
2. *Chemical stability*: Oxygen-rich functional groups ($-\text{NO}_2$, $-\text{SO}_3\text{H}$) cannot be present to any significant extent. At the typical reaction temperatures of smoke compositions, these groups are likely to release their oxygen, leading to oxidative decomposition of the dye molecules. Groups such as $-\text{NH}_2$ and $-\text{NHR}$ (amines) are used, but one must be cautious of possible oxidative coupling reactions that can occur in an oxygen-rich environment.

Structures for some of the dyes used in colored smoke mixtures are given in Figure 9.1.

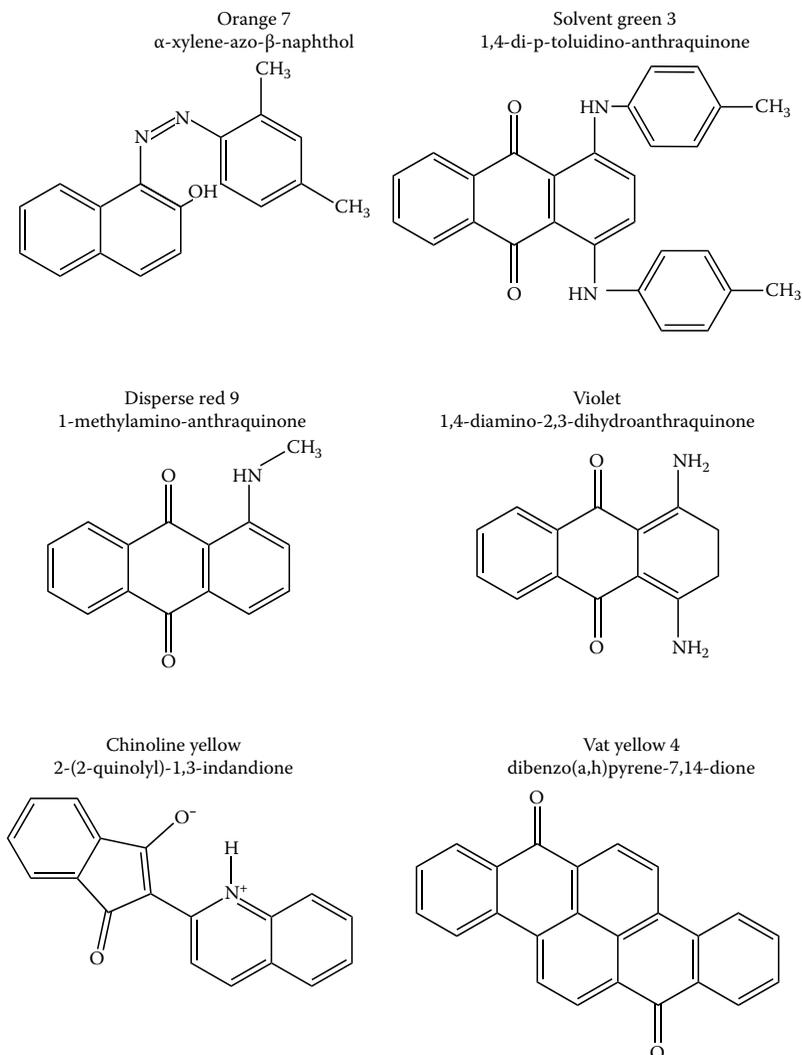


FIGURE 9.1 The chemical names and molecular structures of several dyes used in colored smoke composition. Smoke dyes must be stable at temperatures exceeding 200°C and must pass screening tests for carcinogenicity and other potential health hazards.

WHITE SMOKE PRODUCTION

The processes used to generate white smoke by means of a pyrotechnic reaction include:

1. *Sublimation of sulfur, using potassium nitrate as the oxidizer:* A fuel-rich ratio of sulfur to KNO_3 is used in such mixtures. *Caution:* Some toxic sulfur dioxide gas will be formed. Ignition and use of these mixtures must be done in a well-ventilated area (unless rodent control is a desired goal of the device).

TABLE 9.3
White Smoke Compositions

Composition	% by Weight	Note	Reference
I. Hexachloroethane, C ₂ Cl ₆	45.5	HC type C	8
Zinc oxide, ZnO	47.5		
Aluminum	7.0		
II. Hexachloroethane, C ₂ Cl ₆	34.4	Modified HC	8
Zinc oxide, ZnO	27.6		
Ammonium perchlorate, NH ₄ ClO ₄	24.0		
Zinc dust	6.2		
Laminac	7.8		
III. Red phosphorous	63	Under development	10
Butyl rubber, methylene chloride	37		
IV. Red phosphorous	51.0		6
Magnesium	10.5		
Magnesium dioxide, MgO ₂	32.0		
Magnesium oxide, MgO	1.5		
Microcrystalline wax	5.0		
V. Potassium nitrate, KNO ₃	48.5	Contains arsenic	11
Sulfur	48.5		
Arsenic disulfide, As ₂ S ₂	3.0		

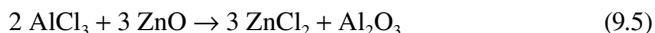
2. *Combustion of phosphorus*: White or red phosphorus burns to produce various oxides of phosphorus, which then attract moisture to form dense white smoke. Research and development work relating to red-phosphorus-based smoke mixtures is actively being pursued in the effort to find lower-toxicity substitutes for the zinc-containing white smokes, such as I & II in Table 9.3. An explosive bursting charge is often used with the very hazardous white phosphorus. *Caution*: Phosphorus-based smokes generate acidic compounds that may be irritating to the eyes, skin, and respiratory tract.
3. *Volatilization of oil*: A pyrotechnic reaction produces heat needed to vaporize high molecular weight hydrocarbons. The subsequent condensation of this oil in the air creates a white smoke cloud. With proper selection of a low-toxicity oil, the negative health effects of this smoke are probably the least of all the materials discussed here.
4. *Formation of zinc chloride (HC smokes)*: A reaction of the type



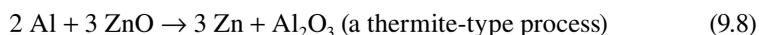
produces zinc chloride vapor, which condenses in the air and attracts moisture to create a very effective white-gray smoke. These mixtures have been widely used for over sixty years with an excellent safety record during the

manufacturing process. However, ZnCl_2 can cause headaches and other possible health concerns upon continued human exposure, and replacements for the HC smokes are actively being sought due to the concerns relating to the various reaction products.

The original HC smoke mixtures (type A) contained zinc metal and hexachloroethane (C_2Cl_6), but this composition is extremely moisture sensitive and can ignite spontaneously if moistened. An alternative approach involves adding a small amount of aluminum metal to the composition, and zinc oxide (ZnO) is used in place of the moisture-sensitive metal. Upon ignition, a sequence of reactions ensues of the following type:⁸

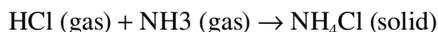


Alternatively, the original trigger reaction has been proposed to be⁹



In either event, the products are ZnCl_2 , CO , and Al_2O_3 , and the aluminum percentage in the composition will play a significant role in the overall burn rate. The zinc oxide cools and whitens the smoke by consuming atomic carbon in an endothermic reaction that occurs spontaneously above $1,000^\circ\text{C}$ (Equation [9.6]). The reaction with aluminum (Equations [9.4] or [9.8]) is quite exothermic, and this heat evolution controls the burning rate of the smoke mixture. A minimum amount of aluminum metal will yield the best white smoke. Several HC smoke compositions are listed in Table 9.3.

5. *Cold smoke*: White smoke can also be achieved by nonthermal means. A beaker containing concentrated hydrochloric acid placed near a beaker of concentrated ammonia will generate white smoke by the vapor phase reaction



Similarly, titanium tetrachloride (TiCl_4) rapidly reacts with moist air to produce a heavy cloud of titanium hydroxide— $\text{Ti}(\text{OH})_4$ —and HCl . Obviously, the hydrogen chloride gas that is produced will pick up moisture from the atmosphere to form hydrochloric acid, so this must be factored into decisions on where and how to deploy such a smoke cloud.

HC REPLACEMENT RESEARCH

A number of research programs have been carried out in recent years in efforts to develop white smoke screening compositions to replace HC smoke that are low in toxicity and meet all of the other requirements for a good pyrotechnic smoke. This

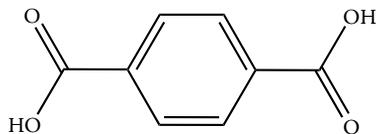


FIGURE 9.2 The chemical structure of terephthalic acid, used for the production of low toxicity, white smoke.

has proven to be a difficult challenge because of the excellent obscuration that is provided by the HC smoke system.

One system that has been developed functions in a manner similar to that of the colored smokes. A volatile organic compound is vaporized/sublimed using a potassium chlorate–sulfur or potassium chlorate–sugar composition, and a white smoke cloud is produced. One of the chemicals that has proven to be effective at white smoke generation by this method is terephthalic acid, $C_8H_6O_4$, a material widely used in the chemical industry for the production of plastics.⁵ It is therefore readily available in high purity, and moderate in cost. It sublimes readily at the potassium chlorate–sugar flame temperature to produce white smoke; the structure of terephthalic acid is shown in Figure 9.2.

A terephthalic acid smoke mixture is as follows:

Potassium chlorate, $KClO_3$	23%
Sucrose, $C_{12}H_{22}O_{11}$	14
Terephthalic acid, $C_8H_6O_4$	57
Magnesium carbonate, $MgCO_3$	3
Graphite	1
Nitrocellulose binder	2

While the TA (for terephthalic acid) smokes cannot match the HC smokes in obscuration on a pound-for-pound basis, it may well turn out to be the case that smoke devices for use in training will contain a low-toxicity composition like the TA smoke mixture, and the more highly obscuring HC smokes are reserved for use in true battlefield conditions.

NOISE PRODUCTION

Two basic audible effects are produced by pyrotechnic devices: a loud explosive noise and a whistling sound. In the terminology for noise effects, the sound effect itself is a report. The device that produces a report in the fireworks industry is a salute, and in the military it is a simulator. The typical composition used to produce a report, whether in civilian or military applications, is an oxidizer–metal mixture that is termed a *flash powder*.

A report is produced by igniting an explosive mixture, usually under confinement in a heavy-walled cardboard tube. Potassium chlorate and potassium perchlorate are the most commonly used oxidizers for report compositions. Report mixtures produce a flash of light and a loud bang upon ignition. Black powder under substantial confinement

also produces a report, but does not have the bright light emission of a flash powder. The key factors that cause a material to be considered a flash powder include:

1. When confined, even in small quantities, in a tube and ignited, a loud audible effect and a bright flash of light are observed (e.g., a firecracker).
2. The pyrotechnic composition contains an active oxidizer and a significant percentage of metal fuel in fine particle size (usually <270 mesh). Small to moderate amounts of additional chemicals, such as sulfur, may be present.
3. Flame temperatures are high, typically 3,000°C or greater.
4. The composition itself can mass explode in a manufacturing setting, with the quantity necessary for such an event depending on a number of factors, including the metal particle size, confinement, and oxidizer/fuel ratio.
5. Shipping cartons containing devices with significant charges of flash powder per unit can mass explode in transportation or storage. Again, what is a significant amount of powder per unit will depend on a number of factors, but the amount per unit can be as low as 1 gram or so for a heavily confined, energetic powder.

A proposed definition for a *flash powder* is the following: a type of explosive composition commonly used to produce a report in a fireworks device. Flash powder consists of at least one oxidizer (such as potassium perchlorate or barium nitrate) and 25% or more by weight (of the formulation) of a metal powder fuel (such as aluminum or magnalium) that is less than 53 microns in size (passes through a 270-mesh sieve). Other fuels, such as sulfur, may also be present.¹²

Flash powders are true explosives, and they will explode violently if a sufficient quantity of powder (perhaps 100 grams or more) is present in bulk form, even if unconfined! Again, do flash powders deflagrate or detonate? For everyone but scientists examining the science of the detonation process, the best answer may be: “Who cares? It explodes!” Flash powders are sensitive and highly energetic. Great care is needed when working with them.

Chlorate-based flash mixtures are considerably more hazardous than perchlorate compositions because of their substantially lower ignition temperatures. However, flash powders made with either oxidizer must be considered very dangerous. They have killed many people at fireworks manufacturing plants in the United States and abroad. Mixing should only be done using remote means, and the smallest feasible amount of composition should be prepared at one time. Bulk flash powder should *never* be stored anywhere near operating personnel.

The well-known Chinese firecracker has traditionally used a mixture of potassium chlorate, sulfur, and aluminum. The chlorate combined with sulfur makes this mixture doubly dangerous for the manufacturer. The ignition temperature of the potassium chlorate–sulfur system is less than 200°C! The presence of aluminum—an excellent fuel—guarantees that the pyrotechnic reaction will rapidly propagate once it begins. Safety data from China are unavailable, but one has to wonder how many accidents have occurred from the preparation of this firecracker composition. The preparation of potassium chlorate–sulfur compositions was banned in Great Britain in 1894 because of the numerous accidents associated with this mixture.

Why have Chinese factories used the potassium chlorate–aluminum–sulfur composition? One reason is regulatory in origin. Regulations of the U.S. Consumer

Product Safety Commission limit the explosive content of a consumer-type firecracker to a maximum of 50 milligrams of chemical composition.¹³ It is difficult to reliably produce a decent bang from a paper-wrapped firecracker with such a small amount of chemical composition. The chlorate-containing composition, with a fine aluminum or magnalium powder, can do it. The hope is that the 50-milligram explosive effect will satisfy the public's desire to make a noise on the Fourth of July, without the need for an emergency room visit if the device is misused in some way. Numerous tests on shipping cartons containing retail packages of 50-milligram firecrackers have demonstrated that these products, as packaged for transportation, do not pose a mass explosion hazard in a fire situation.

The standard American flash powder composition for aerial salutes is a blend of potassium perchlorate, sulfur or antimony sulfide, and aluminum. The ignition temperature of the formulation is several hundred degrees higher than that of chlorate-based mixtures, but these are still very dangerous compositions because of their extreme sensitivity to spark and flame. The spark sensitivity depends to a large extent on the particular metal powder that is used in the composition, with one study showing the spark sensitivity to be the greatest for very fine flake aluminum.¹⁴ Ignition of a small portion of a flash powder mixture will rapidly propagate through the entire sample. These mixtures should only be prepared remotely, by experienced personnel. Table 9.4 lists several flash powder formulas.

TABLE 9.4
Flash and Sound Compositions^a

Composition	% by Weight	Use	Reference
I. Potassium perchlorate, KClO_4	50	Military simulator	10
Antimony sulfide, Sb_2S_3	33		
Magnesium	17		
II. Potassium perchlorate, KClO_4	64	M-80 firecracker for military training	10
Aluminum	22.5		
Sulfur	10		
Antimony sulfide, Sb_2S_3	3.5		
III. Potassium chlorate, KClO_3	43	Japanese flash thunder for aerial fireworks	7
Sulfur	26		
Aluminum	31		
IV. Potassium perchlorate, KClO_4	50	Japanese flash thunder for aerial fireworks	7
Sulfur	27		
Aluminum	23		

^a These mixtures are explosive and *very* dangerous. They must only be prepared by trained personnel using adequate protection and should be mixed by remote mean.

WHISTLES

A unique whistling phenomenon can be produced by firmly pressing certain oxidizer-fuel mixtures into cardboard tubes and igniting the compositions. A detailed analysis of this phenomenon, from both a chemical and a physical view, has been published by Maxwell,¹⁵ and a more recent review of the whistle literature has also been published.¹⁶ Further whistle research has continued in efforts to fully understand the phenomenon.^{17,18} Without consolidation of the powder in a tube, whistle composition produces a rapid flash of light (in an explosive manner) and no whistle-like effect. The whistle effect is produced by compositions consisting of potassium chlorate or potassium perchlorate as the oxidizer, with a salt of benzoic acid or a substituted benzoic acid (e.g., potassium benzoate, sodium salicylate).

Whistle compositions were initially developed in the search for possible replacements for black powder in propellant applications. One can imagine the reaction of the first pyrotechnic chemist who blended what is now known to be a whistle composition in a research setting, pressed the powder into a tube to examine its propellant characteristics, and then heard a loud, piercing screech when the composition was ignited.

Devices producing a whistle-like effect have since found uses both in the civilian arena for fireworks effects and in military applications for simulators used in training exercises to simulate incoming rounds. Titanium particles (in particle sizes greater than 100 mesh) can be added in low (5% or so) amounts to a whistle composition to produce a spark effect to accompany the audible output.

A reaction that produces a whistling effect is burning intermittently from layer to layer in the pressed composition. A whistling reaction is on the verge of an explosion, so

TABLE 9.5
Whistle Compositions^a

Composition	% by Weight	Note	Reference
I. Potassium chlorate, KClO_3	73	Military simulator	10
Gallic acid, $\text{C}_7\text{H}_6\text{O}_5 \cdot \text{H}_2\text{O}$	24		
Red gum	3		
II. Potassium perchlorate, KClO_4	70	Perhaps the safest to prepare and use	7
Potassium benzoate, $\text{KC}_7\text{H}_5\text{O}_2$	30		
III. Potassium perchlorate, KClO_4	75	Hygroscopic—does not store well	7
Sodium salicylate, $\text{NaC}_7\text{H}_5\text{O}_3$	25		
IV. Potassium perchlorate, KClO_4	75	Chinese whistle composition	Unpublished
Potassium hydrogen phthalate, $\text{KC}_8\text{H}_5\text{O}_4$	25		

^a These mixtures are very sensitive ignition and can be quite dangerous to prepare. They should only be mixed by trained personnel using adequate protection.

these mixtures must be cautiously prepared and carefully loaded into tubes. Next to flash powders, whistle compositions are perhaps the most hazardous class of pyrotechnic compositions used by the fireworks industry. Large quantities of bulk powder should be avoided, and they should never be stored near operating personnel. Several formulas for whistle compositions are given in Table 9.5.

REFERENCES

1. D. E. Chavez, M. A. Hiskey, and D. L. Naud, High-nitrogen fuels for low smoke pyrotechnics, *Journal of Pyrotechnics*, 10, 17 (1999).
2. A. A. Shidlovskiy, *Principles of pyrotechnics*, 3rd ed., Moscow, 1964. (Translated by Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 1974.)
3. T. Shimizu, in R. Lancaster, *Fireworks principles and practice*, New York: Chemical Publishing Co., 1972.
4. A. Chin and L. Borer, Investigations of the effluents produced during the functioning of navy colored smoke devices, in *Proceedings, Eighth International Pyrotechnics Seminar*, ITT Research Institute, Steamboat Springs, CO, July 1982, 129.
5. J. A. Domanico, Using a standard test protocol to qualify candidate low toxicity colored smoke dyes, presented at Proceedings, 35th International Pyrotechnics Seminar, Fort Collins, CO, July 2008.
6. M. D. Smith and F. M. Stewart, Environmentally acceptable smoke munitions, in *Proceedings, Eighth International Pyrotechnics Seminar*, ITT Research Institute, Steamboat Springs, CO, July 1982.
7. T. Shimizu, *Fireworks: The art, science and technique*, Tokyo: T. Shimizu, 1981.
8. U.S. Army Material Command, *Engineering design handbook: Theory and application*, Military Pyrotechnic Series, Part One, Washington, DC, 1967 (AMC Pamphlet 706-185).
9. J. H. McLain, *Pyrotechnics from the viewpoint of solid state chemistry*, Philadelphia: Franklin Institute Press, 1980.
10. F. L. McIntyre, *A compilation of hazard and test data for pyrotechnic compositions*, Report ARLCD-CR-80047, Dover, NJ: U.S. Army Armament Research and Development Command, 1980.
11. R. Lancaster, *Fireworks principles and practice*, New York: Chemical Publishing Co., 1972.
12. J. A. Conkling, Regarding a default classification system for fireworks, presented at 9th International Symposium for Fireworks, Berlin, Germany, April 2006.
13. Title 16, U.S. Code of Federal Regulations, Part 1500.17(a)(8).
14. J. A. Conkling and D. Jacobson, Investigation of the spark sensitivity of oxidizer/aluminum compositions, presented at 5th International Symposium on Fireworks, Naples, Italy, April 2000.
15. W. R. Maxwell, Pyrotechnic whistles, in *4th Symposium on Combustion*, Baltimore: Williams and Wilkins, 1953, 906. (Reprinted in the *Journal of Pyrotechnics*, 4, 37 (1996).)
16. M. Davies, A review of the chemistry and dynamics of pyrotechnic whistles, *Journal of Pyrotechnics*, 21, 1 (2005).
17. J. A. Domanico et al., Pyrotechnic whistle performance variations, in *Proceedings, 22nd International Pyrotechnics Seminars*, Fort Collins, CO, 1996, 489.
18. M. Podlesak and M. Wilson, A study of the combustion behavior of pyrotechnic whistle devices, in *Pyrotechnic chemistry*, *Journal of Pyrotechnics*, Whitewater, CO, 2004, chap. 16.

Appendix A: Obtaining Pyrotechnic Literature

NTIS

Many of the technical reports and publications referenced in this book are available through the U.S. Department of Commerce's National Technical Information Service (NTIS) located in Springfield, Virginia.

Publications can be ordered from NTIS if the accession numbers are known; these are the numbers assigned by NITS to technical documents in their files. NTIS can supply you with an accession number if you provide them with the title and author of a document. NTIS has an online search service available at <http://www.ntis.gov>.

NTIS numbers for several of the major references used in this book are

- A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd edition, NTIS AD-A001859
- *Theory and Application*, Military Pyrotechnic Series, Part One, NTIS AD-817071
- *Properties of Materials Used in Pyrotechnic Compositions*, Military Pyrotechnic Series, Part Three, NTIS AD-830394
- F. L. McIntyre, *A Compilation of Hazard and Test Data for Pyrotechnic Compositions*, NTIS AD-A096248

INTERNATIONAL PYROTECHNIC SEMINARS

Copies of various Proceedings of the International Pyrotechnics Symposia are available for purchase. For information, prices, and order forms, go to www.ipsusa.org. Information on the IPS as well as membership in the IPS is available at www.intpyro.org.

JOURNAL OF PYROTECHNICS

Information regarding subscriptions to the *Journal of Pyrotechnics*, as well as the book *Pyrotechnic Chemistry* (which contains a series of review articles on various topics in the field of pyrotechnics) and additional publications they have available, can be obtained from the publisher, Bonnie Kosanke, at 1775 Blair Road, Whitewater, Colorado 81527, or by e-mail to bonnie@jpyro.com.

OTHER SOURCES

Another route to many of the references in this book, as well as to additional information on the various topics in this book, is to use an Internet search engine such as Google®. There is a wealth of information out there in cyberspace, but much of it has not been through any type of peer review or safety analysis—be *very* careful if you want to try anything you find out there that does not come from an identified, reputable source.

Appendix B: Mixing Test Quantities of Pyrotechnic Compositions

The pyrotechnic chemist always begins with a very small quantity of composition when carrying out initial experiments on a new formula. The preparation of 1 or 2 grams of a new mixture enables one to evaluate performance (color quality and intensity, smoke volume, etc.) without exposure to an unduly hazardous amount of material.

Eye protection, such as safety glasses or goggles, is mandatory whenever any pyrotechnic composition is being prepared or tested. Necessary equipment includes a mortar and pestle, a laboratory balance, a soft bristle brush, several 2- to 3-inch lengths of fireworks-type safety fuses (available from hobby stores), and a fireproof stone or composite slab on which to conduct burning tests.

Pregrind the components *individually* to fine particle size. Do not grind any oxidizer and fuel together—fire or explosion may result. Weigh out the proper amount of each component and combine the materials in the mortar. Carefully mix them together with the soft brush to obtain a homogeneous blend. *Caution:* Do not prepare more than 2 grams of any composition for evaluation purposes during this procedure.

Place a small pile of the mixed composition on the fireproof board, insert a selection of safety fuse into the base of the pile, and carefully light the end of the fuse with a match. Step back and observe the effect. Because of the generation of smoke by most pyrotechnic compositions, these tests are best conducted outdoors or in a well-ventilated area such as a laboratory fume hood. Be certain no flammable materials are near the test area, for sparks may be produced. Be sure to keep a bucket of water handy, just in case.

All testing of pyrotechnic compositions must be carried out under the direct supervision of a responsible adult well trained in standard laboratory safety procedures. Serious injury can result from working with larger amounts of composition or from the misuse of pyrotechnic mixtures, so caution and adequate supervision are mandatory. *Warning:* Do not attempt to prepare any of the explosive mixtures listed in Tables 9.4 and 9.5. These must be mixed only by remote means, or serious injuries might result. The color-producing compositions listed in the tables in Chapter 8 are recommended as a good starting point for persons preparing their first pyrotechnic compositions. The effects caused by variations from the specified percentages can easily be seen upon burning.

Finally, federal, state, and local laws may place restrictions on the preparation of energetic mixtures by individuals, such as license and storage requirements. Joining a group such as the Pyrotechnics Guild International (www.pgi.org), as well as a local affiliate group of people with an interest in the art and science of pyrotechnics, is recommended for anyone interested in pursuing an interest in the field of pyrotechnics.

CHEMISTRY

JOHN A. CONKLING
CHRISTOPHER J. MOCELLA

Chemistry of Pyrotechnics

Basic Principles and Theory

SECOND EDITION

Primarily driven by advancing technology and concerns for safety, advancement in the world of pyrotechnics and high-energy materials has exploded in the past 25 years. The promulgation of new government regulations places new and more stringent restrictions on the materials that may be used in energetic mixtures. These regulations now mandate numerous training programs and initiate other actions, such as OSHA's Process Safety Management standard, intended to eliminate accidents and incidents. Unfortunately, the United States lacks an organized, broad-range academic program to cover the science and use of energetic materials and educate the next generation of pyrotechnicians.

Designed as a bridge to provide a smooth and confident transition for personnel coming from a chemistry background into the practical world of high-energy materials, *Chemistry of Pyrotechnics: Basic Principles and Theory, Second Edition* emphasizes basic chemical principles alongside practical, hands-on knowledge in the preparation of energetic mixtures and examines the interactions between and adaptations of pyrotechnics to changing technology in areas such as obscuration science and low-signature flame emission.

Much more than a simple how-to guide, the book discusses chemical and pyrotechnic principles, components of high-energy mixtures, and elements of ignition, propagation, and sensitivity. It offers heat compositions, including ignition mixes, delays, thermites, and propellants and investigates the production of smoke and sound as well as light and color.

Promoting the growth and expansion of pyrotechnics as a science, *Chemistry of Pyrotechnics: Basic Principles and Theory, Second Edition* teaches practitioners how to apply chemical principles and logic to energetic materials and, thereby, make the field as productive, useful, and safe as possible.

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