High Energy Materials

A Brief History and Chemistry of Fireworks and Rocketry

Vedang Naik and K C Patil

Propellants used in rockets, pyrotechnics used in festivities, explosives used for military purposes, blasting chemicals used in construction activities, etc., are high energy materials. There is a lot of fascinating chemistry and interesting history behind them. This article gives an overview of these aspects, with somewhat more emphasis on propellants and working of rockets, and the chemistry of fireworks.


(left) Vedang Naik is 14 years old and a student of 9th Standard at National Public School, Bengaluru. He is interested in chemistry, aerospace, as well as engineering.

(right) K C Patil was a Professor in the Inorganic and Physical Chemistry Department, Indian Institute of Science, Bengaluru and retired in 1997. He is currently Vice President of the Karnataka Association for Advancement of Science, Bengaluru, which organises programmes in schools and colleges to popularise science.

1. Introduction

High energy materials are compounds which store chemical energy. They are either single compounds like trinitrotoluene (TNT) containing both an oxidizing group, $-NO_2$ and a reducing group or a mixture of an oxidizer and fuel elements, e.g., gun powder (KNO_3 + C + S). Such materials, on stimulation by mechanical, thermal or electrical devices, undergo rapid decomposition giving out heat, light, sound and large volumes of gases. The amount of energy released varies with the properties of the material such as composition, structure, density, heat of formation and decomposition, etc. High energy materials are classified as explosives, propellants[1] and fireworks[2] depending upon their properties and applications. This article aims to understand the chemistry of these materials.

[1] These are chemical compounds or their mixtures that rapidly produce large volumes of hot gases when properly initiated.

Keywords
Explosives, propellants, pyrotechnics, fireworks.

2. Explosives

2.1 *History*

Explosives have been around for a long time, the first one used being gunpowder. It was invented in China or India sometime around 1000 AD. In the 13th and 14th centuries, Roger Bacon and the Earl of Warwick introduced gunpowder to Europe. They used it for developing firearms and cannons. From then on until the 1800s, no major

[2] Pyrotechnics is the art of manufacturing or setting off fireworks using redox mixtures like gun powder with additives (e.g., metal salts) to create colourful displays.

developments took place in the field of explosives. But during the 19th century, many new materials such as nitric acid ester, nitrated paper (flash paper), nitrocotton (NC guncotton), smokeless nitrocellulose, wood powder, blasting gelatine, picric acid and trinitrotoluene (TNT, $C_7H_5N_3O_6$) were developed. The 20th century saw the development of many new and more powerful explosives, such as RDX ($C_3H_6N_6O_6$), HMX ($C_4H_8N_8O$), ADN ($NH_4N(NO_2)_2$), TNAZ ($C_3H_4N_3O_6$) and the latest and the most powerful explosive, HNIW ($C_6N_{12}H_6O_{12}$). *Table* 1 summarizes the history of explosives.

2.2 *Classification of Explosives*

Explosives are classified on the basis of chemical composition, properties and applications.

A. Composition

- Nitramines
- Nitric esters
- Derivatives of chloric and perchloric acid
- Azides: Heavy metal azides
- Others: Fulminates, styphnates, peroxides, ozonides, acetylides.

B. Properties

On the basis of intensity of explosion, explosives are classified as follows:

(i) primary or low explosives or initiators – these are normally employed as propellants. They burn rapidly at rates of up to 400 m/s, and

(ii) secondary or high explosives – these detonate[3] at 1000–8500 m/s. Primary explosives are very sensitive to heat, impact and friction, while secondary or high explosives are less sensitive and usually burn in small, unconfined space. However, there is no clear demarcation between primary and secondary explosives.

[3] Detonation is a chemical reaction involving an explosive substance which produces a shock wave. High temperature and pressure gradients are generated in the wave front so that the chemical reaction is initiated spontaneously with a velocity of detonation (VOD) ~1500–9000 m/sec.

C. Applications: Civil and Military

Explosives are classified according to applications either for

Name	Inventor(s)	Country	Year
Gunpowder	Anonymous	China or India	~1000 AD
Gun powder (a mixture of 75% KNO_3, 15% charcoal and 10% sulphur by weight)	Roger Bacon	United Kingdom	13th century
Gun powder in cannon	Earl of Warwick	United Kingdom	14th century
Nitric acid ester of starch	Henri Braconnot	France	19th century
Nitrated paper	Theophile J Pelouze	France	19th century
Nitrocotton (NC) (guncotton)	Christian Schoenbein	Germany	19th century
Wood powder	Major E Schultze	Germany	19th century
Blasting gelatine	Alfred Nobel[1]	Sweden	19th century
Picric acid	Hermann Sprengel	Germany	19th century
Smokeless NC	Paul Vieille	France	19th century
TNT (Trinitrotoluene)	Julius Wilbrand	Germany	19th century
Pyrocellulose + diphenylamine	EI DuPont de Nemours	USA	20th century
RDX (Research Department Explosive or Royal Demolition Explosive)		United Kingdom	20th century
HMX (Her Majesty's or High Melting Exposive)		United Kingdom	20th century
ADN (Ammonium dinitramide)	Robert Schmitt and Jeffrey C Bottars	United Kingdom United Kingdom	20th century 20th century
TNAZ (Trinitroazetidine)	Kurt Bann and Tom Archibald		
HNIW (Hexanitrohexaza isowurtzitane)	Arnold Nielsen	United Kingdom	20th century

civilian use such as demolition of old buildings, construction of bridges, roads, tunnels and mining or for military purposes like bombs, landmines, etc.

Table 1. A brief history of explosives.

2.3 *Tests for Explosives*

In order to determine if a substance is an explosive or not, the following standard tests are conducted:

(i) Test for impact or friction sensitivity: A weight (100 g steel ball) is dropped upon the sample (few milligrams) from a height. If the substance explodes, it is sensitive to impact. Friction test is carried out by putting the sample between two steel plates along with sand and rotating the upper plate against the fixed lower plate.

(ii) Thermal stability: A 20 mg sample of the substance is kept in a constant temperature bath. If it explodes within 10 seconds, it is sensitive to heat.

(iii) Velocity of detonation[4]: Direct flame photography, high speed photography and counter chronographs[5] are used to measure the velocity of detonation of an explosive.

[4] The velocity at which the shock wavefront travels through a detonated explosive is called the velocity of detonation.

[5] A counter chronograph is a timer device which measures the distance in metres/second for a shockwave to travel between two fixed points.

(iv) Destruction power: It is carried out by the so-called lead block test. In this test, a 10 gram sample of the explosive is put into a hole drilled in the middle of the lead block (*Figure* 1). Sand is then poured over the explosive, sealing the explosive in the centre of the block. Then the explosive is detonated. The power of the explosive is determined by measuring the volume of hole in the lead block. The bigger the volume, the more powerful is the explosive.

Some properties of well-known explosives are listed in *Table* 2.

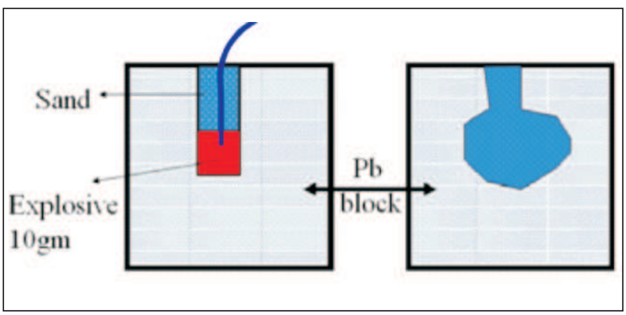

Figure 1. The lead block test.

Explosive/Density	Lead Block Volume cm^3/10 g	Velocity of Detonation (m/s)
TNT (1.65g/cm^3)	300	6700
Picric acid (1.76 g/cm^3)	315	4500
ANFO	316	3000
NC	373	7200–7300
Dynamite	412	
RDX (1.82 g/cm^3)	483	8200
PETN (1.77 g/cm^3)	520	8300
NG (1.6 g/cm^3)	530	
NC + NG	600	

Table 2. Properties of some common explosives.

3. Propellants

3.1 *History*

The first rockets were simple fireworks used by the Chinese to celebrate happy occasions and to frighten evil spirits. They later realised that rockets could be used as weapons to frighten and kill the enemy. In India, the Mysore rocket[6] using gun powder invented by Tipu Sultan was used in Srirangapattana war against British. Later, Sir William Congreve developed it in Europe in 1804. Robert Goddard in USA investigated liquid propellants and improved them in many ways. In World War II, Wernher von Braun designed the V-2 rockets which were the first inter-continental ballistic missiles (ICBMs). After the war, the Allied Powers captured German rocket scientists and made many developments in rocket technology, including the breaking of the sound barrier in a rocket-propelled plane called the Bell X-1. The Russians developed their versions of the V-2 rocket under the leadership of Sergei Korolev. Soon after, in 1981, followed the Space Shuttle, and after that, a wide range of advanced ICBMs, guided missiles and space launch vehicles. *Table* 3 summarizes the history of rocketry.

[6] Mysore rockets or Tipu rockets were the first iron-cased rockets stabilized by bamboo sticks. They consisted of an iron combustion chamber which was filled with compressed gunpowder. A pound of gunpowder could propel the rocket to almost 900 metres.

3.2 *Propellant Families*

There are several classes of propellants, e.g., monopropellants

Rocket invention/discovery	Inventor/discoverer	Year
First rockets used in artillery	Chinese	~1000 AD
The Mysore rocket	Tipu Sultan	1780s
Congreve rocket	Sir William Congreve	1804
Theory of interplanetary flight	Konstantin Tsiolkovsky	1903
First serious analysis of rockets	Robert Goddard	1912
V-2 rockets	Wernher von Braun	1920s-1930s
First ICBMs and SLBMs Germany	1942	
Bell X-1	USA	1948 (first test flight)
R-1, R-3. R-5 and R-7	Sergei Korolev (leader)	
First Moon landing	USA	1969
Space Shuttle	USA	1969 (idea), 1981 (first test flight)
Guided missiles, advanced IRBM, ICBM space rockets	Worldwide	Present day

Table 3. A brief history of rocketry.

(N_2H_4, H_2O_2), solid propellants, liquid propellants and hybrid propellants. Here, we shall discuss the two common classes, namely the solid and the liquid propellants.

A. Solid Propellants

A solid propellant is made from low or diluted high explosives which are deflagrated[7] instead of detonated. They consist of a fuel, an oxidiser and a binder and are in the form of grains. The earliest rockets were solid-fuel-propelled. Solid propellants are easy to use and can be stored for a longer time, and are thus, mainly used by the military in missiles. However, their low performance does not allow them to be used in space rockets as they do not produce sufficient thrust. *Table* 4 gives the composition of some typical solid propellants.

[7] Slower explosive reactions propagated by thermal conduction and radiation are known as deflagration. The combustion (burning/reaction) is very rapid with VOD $\approx 10^{-2}$ to 10^{2} ms^{-1}.

B. Liquid Propellants

A liquid propellant, as the name indicates, is in liquid form. Liquids are favoured over solid fuels, because their high energy (I_{sp}) allows for smaller tanks. For the combustion to take place, the fuel and the oxidizer are mixed in a combustion chamber. Liquid propellant rockets can be monopropellant, bipropellant or tripropellant. Bipropellant rockets usually use a liquid fuel and a liquid oxidizer, such

Propellant name	General Information
Gun powder or black powder	One of the oldest solid propellants, this compound is easy to make and use. The fuel consists of a block which is made of finely compressed powder.
Double-based (DB) propellants	These contain two monopropellant fuels in which one acts as a high-energy unstable propellant and the other as a stabilizing agent. They are used where minimal smoke and medium power is needed. (NC + NG)
Composite propellants	These are made of a powdered fuel and an oxidizer held by a binder which also acts as a fuel. They are usually ammonium perchlorate (APCP) or ammonium nitrate (ANCP) based.
High-energy composites (HEC) or HMX in them.	They are composite propellants with a few crystals of RDX
Composite modified double-based propellants	These are propellants which are made by modifying a mixture of composite and double-based propellants. (NC + NG +Al powder)
Smokeless propellants	They have been developed using HNIW. This explosive has 14% more energy per mass and 20% more energy density than HMX. It is also very shock-insensitive and non-polluting.

Table 4. Composition of solid propellants.

as liquid hydrogen and liquid oxygen.

Solid propellants are stable and can be stored for use in warfare whereas liquid propellants are energetic and, being cryogenic, are mostly used in satellite launch vehicles.

A huge number of liquid fuel and liquid oxidizer combinations have been tried over the years. Some of them are:

- Liquid oxygen (LOX) and liquid hydrogen (LH_2)
- LOX and highly refined kerosene (commonly called RF-1)
- LOX and alcohol (C_2H_5OH)
- LOX and gasoline

3.3 *Rockets*

The working principle of rockets is briefly mentioned here. All rockets are based on Newton's Third Law: an action will always have an equal and opposite reaction. In a rocket, the thrust

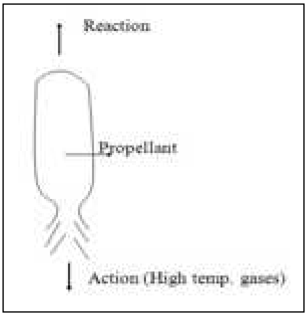

Figure 2. Schematic diagram of a rocket.

produced by the propellant is directed downward so that the rocket is pushed upwards. Fins or stabilizers on the sides of the rocket prevent it from turning suddenly in mid-air. To increase the thrust produced by the propellant, a de Laval nozzle is attached to the exhaust port. This nozzle forces the exiting hot gases into a small space, forcing them to increase their speed (*Figure* 2). This, in turn, increases the thrust. Guided missiles work in the same way, but have on-board computers to steer them in mid-air to their designated targets.

3.3 *Rocket Performance*

A. Oxygen Balance

All rockets and fireworks must have stochiometric amounts of fuel and oxidizer to work properly. When the oxidizer to fuel ratio is unity, the energy released is maximum; whereas, if it is greater or less than 1, the combustion is incomplete and various gases (CO, NOx, hydrocarbons), which cause environmental pollution, are formed.

Fuel-to-oxygen ration is the ratio of fuel elements to oxygen. Oxygen balance is the amount of oxygen required for complete combustion of all the carbon atoms to carbon dioxide and hydrogen atoms to water as shown in the equation. The formula for calculating oxygen balance[8] is

$$\text{Oxygen Balance} = \frac{1600}{\text{Molecular Weight of Fuel}}\left(Z - 2X - \frac{Y}{2}\right).$$

Here, X = number of carbon atoms, Y = number of hydrogen atoms, and Z = number of oxygen atoms.

[8] +ve oxygen balance: The amount of oxygen is more than enough for the reaction.
-ve oxygen balance: The amount of oxygen is not sufficient for the reaction.

B. Thrust and Specific Impulse

Thrust: Thrust is a force which is used to get a body from a stationary to a moving position. It is used to oppose drag and overcome the weight of a rocket.

Specific Impulse (I_{sp}): This is used to describe the efficiency of a rocket. It represents force with respect to the amount of propellant used in a unit of time. The more the specific impulse of an engine or propulsion method, the less propellant it uses per unit time.

The specific impulse of a rocket can be calculated by the following formula:

$$\text{Specific Impulse} = \frac{\text{Thrust (Force in lbs)}}{\text{lbs of propellant used in 1 second}} .$$

Specific impulse is also calculated by the following formula:

$$I_{sp} = \sqrt{\frac{\text{Chamber Temperature}}{\text{Avg Mol Wt of Combustion Products}}} .$$

The values of specific impulse for some solid and liquid propellants are given in *Table* 5.

Oxidizer	**Fuel**	I_{sp} **(sec)**
Liquid oxygen	Liquid H_2	390
	RP-1	300
	UDMH	310
	(unsymmetrical	280
	dimethyl hydrazine)	
	Alcohol	
Liquid F_2	Liquid H_2	410
	RP-1	320
	UDMH	340
RFNA(Red fuming	RP-1	270
nitric acid)	UDMH	275
N_2O_4	UDMH	285
	N_2H_4	290
Black powder	_	40–80
NH_4ClO_4+Al+CTPB	_	240

Table 5. I_{sp} values of some solid and liquid propellants.

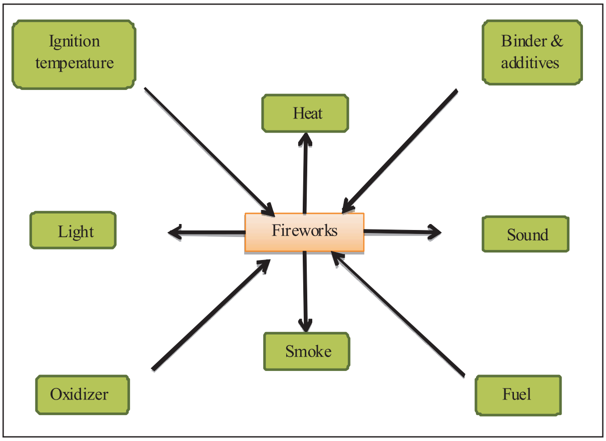

Figure 3. The fireworks square.

4. Pyrotechnics – The Art of Making Fireworks

Fireworks are a class of explosive pyrotechnic devices used for aesthetic, cultural, and religious purposes. The fireworks are designed to burn with flames and sparks of many hues and patterns. The square diagram of *Figure* 3 presents composition and outcome of fireworks ignition.

4.1 *History*

The first fireworks were invented by the Chinese sometime before 1000 AD. They later adapted them for military applications, and advanced the technology of making normal fireworks, including the invention of a crude version of the aerial fireworks we see today. Fireworks reached Italy during the Renaissance, where it was improved and evolved into an art. The development of the quick match[9], colours for use in rockets and flash powder took place in Italy from the 1700s to the 1850s. A brief history of fireworks is given in *Table* 6.

[9] A quick match is a gunpowder-coated string wrapped in paper which acts as a wick.

Table 6. A brief history of fireworks.

Firework/modification/event	**Inventor/discoverer**	**Year**
First fireworks	Chinese	Circa10th century AD
Fire arrows and fire lances	Chinese	10th century AD
Modification of gunpowder	Chinese	11th century AD
Aerial fireworks	Chinese civilian firework makers	Around 1200 AD
Firework shells, fountains and wheels	Italians	Renaissance Period
Quick match		Around 1730s
Fireworks in the new world	Settlers	1600s
New colours and the usage of potassium perchlorate	Southern Italy	1830s
Flash powder	Southern Italy	1830s

4.2 *How Fireworks Work*

Fireworks consist of a fuel, an oxidizer, a binder and additives for colours, (*Figure* 3). The most common oxidizer is potassium nitrate, and the fuel is usually charcoal or sulphur (gun powder). Gun powder is very sensitive to sparks and ignites instantly causing fire in fireworks factories and storehouses. Efforts to replace it with safer alternatives have not been successful so far! The binder can be sugar or starch, usually dextrin. When mixed, they form a kind of paste, which hardens around anything coated with it. A sparkler is made by dipping a wire of desired length into the slurry of this mixture. *Table* 7 lists various chemicals used in fireworks as fuels, oxidizers, binders, special effect initiators and their percentage weight in a standard skyrocket.

Rocket fireworks (or skyrockets) work much in the same way that space rockets do. A skyrocket consists of a cylinder packed

Table 7. Chemicals used in fireworks along with their function.

Fuels	Oxidizer	Binders
Aluminium,	Potassium nitrate	Dextrin
Charcoal,	/chlorate/perchlorate,	Red gum
Dextrin,	Barium nitrate/chlorate	Synthetic
Magnesium,	Ammonium perchlorate,	polymers
Red gum,	Strontium nitrate	
Sulphur,		
Titanium,		
Antimony sulphide,		
Polyvinyl chloride		

Chemicals for special effects

Red flame: strontium nitrate/chlorate, **Green flame:** barium nitrate/chlorate
Blue flame: copper chlorate/sulphate/oxide, **Yellow flame:** sodium oxalate, cryolite (Na_3AlF_6)
White flame: magnesium and aluminium, **Gold sparks:** iron filings and charcoal
White sparks: aluminium, magnesium, aluminium-magnesium alloy and titanium
Whistle effect: potassium benzoate or sodium salicylate, **White smoke:** potassium nitrate or sulphur mix
Coloured smoke: potassium chlorate/sulphate/organic dye mixture

with gunpowder and additives for specific colour(s). On ignition they propel themselves into the sky and then burst into one or more colours and patterns.

4.3. *Classification of Fireworks*

A. Single-colour Skyrockets

A single-colour skyrocket consists of just a tube filled with gunpowder, the chemical(s) needed for that particular colour, a delay fuse and a long stick to stabilize it while taking off and flying. The propellant is at the bottom and the additives that burst into stars are packed at the upper part (*Figure* 4). When the fuse is lit, it burns, igniting the propellant first and then the additives burst into stars, creating a colourful display.

B. Multi-colour Rockets

Multi-colour rockets work in stages, just like the now outdated Saturn-V space rockets used to. In a multistage space rocket, each stage falls away as it finishes its load of fuel. Similarly, in a multi-colour rocket, each stage contains the chemicals for a different colour, which explode one after the other. Each segment

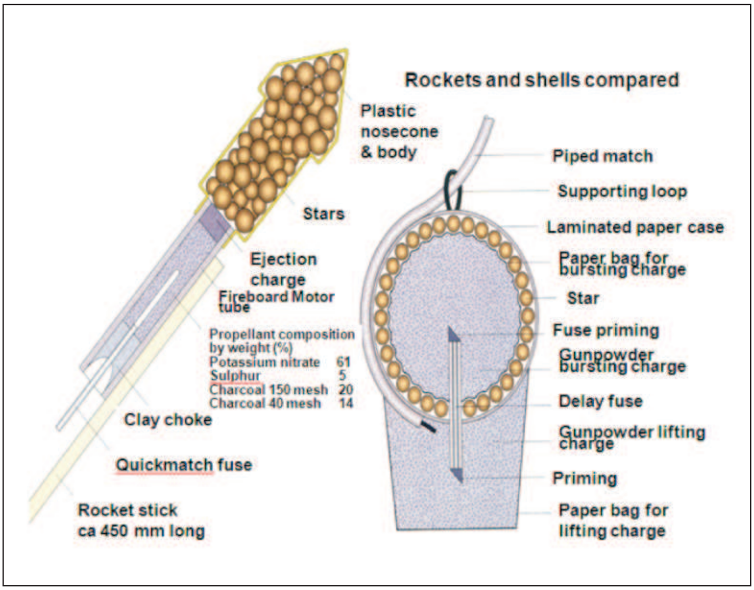

Figure 4. Comparison of a single-colour skyrocket and shell [1].

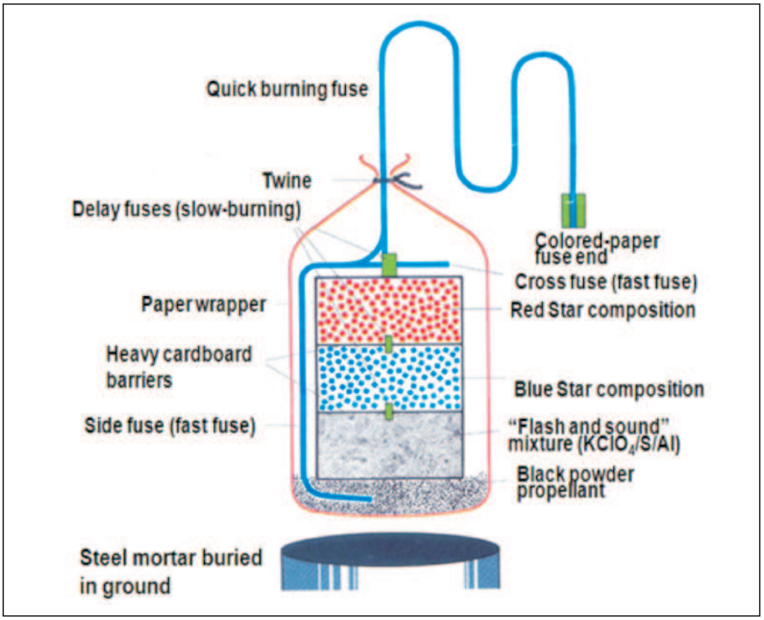

Figure 5. Schematic diagram of a multi-colour rocket [2].

of chemicals is separated from the next one by a sheet of cardboard, with the propellant being packed at the bottom of the rocket. There are many fuses in a multi-colour rocket. When the wick is lit, a fast-burning fuse ignites the propellant first, which subsequently propels the rocket high into the atmosphere. A slower, delay fuse then ignites the colour-stages in sequence, with the topmost one bursting first, followed by one or more colours exploding one after another in the sky (*Figure* 5). *Table* 8 gives a summary of some chemicals used for generating different colours in a multi-colour rocket.

Table 8. Chemicals used in a multi-colour rocket. Percentage of chemicals by weight in a standard sky rocket

Red Star	Blue Star	Cone Fountain	Green Fire
$KClO_3$ (64%)	$KClO_4$ (38%)	KNO_3 (53%)	NH_4ClO_4 (50%)
$SrCO_3$ (19%)	NH_4ClO_4 (29%)	Fe (32%)	$Ba(NO_3)_2$ (34%)
Red gum (13%)	$CuCO_3$ (14%)	S (8%)	Fine sawdust (8%)
Dextrin (4%)	Red gum (14%)	C (2%)	Shellac (8%)
Cone Foundatin	Dextrin (5%)	A1 (4%) Stearic acid (1%)	

5. Conclusion

Scientists over many centuries have developed chemicals which are used as explosives in warfare, civilian application and fanciful fireworks display. Wicked and misguided people have been using them in mindless destruction of humans, which has marred the far more important application of these materials for constructive and recreational purposes. Alfred Nobel [3], who made explosives safe to handle for constructive use, repented his invention of dynamite when it was used for killing and destruction.

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Address for Correspondence
Vedang Naik
K C Patil*
* Department of Inorganic and Physical Chemistry
Indian Institute of Science
Bengaluru 560 012
Email: kcpatil37@yahoo.co.in

Suggested Reading

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