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# PYROTECHNICS, PROPELLANTS AND EXPLOSIVES

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## **PYROTECHNICS, PROPELLANTS AND EXPLOSIVES**

### **CLASSIFICATION**

[Pyrotechnics](#) (from Greek  $\pi\rho\omicron\zeta$ , fire) refers to making fire by chemical reaction, with the goal to produce light, heat, noise, or gases. It is always done by combustion of a fuel and an oxidiser (a *red-ox* reaction), but distinguishes from normal combustion in the speed: combustion refers to slow processes whereas pyrotechnics is associated to almost instantaneous combustion (solid-rocket propellants being in between).

For pyrotechnics to be effective, fuel and oxidiser must be premixed (double-base pyrotechnics) or, even better, they should be part of the same molecule (single-base pyrotechnics) with zero or slightly positive oxygen balance, they should be highly exothermic, and they should be in condense form and generate a lot of gas. Nitrogen atoms are found in most explosives, because they yield nitrogen molecules that release great energy and expanding gases (the bond energy of  $N\equiv N$  is 941 kJ/mol).

In double-base pyrotechnics, the oxidising agents may be nitrates, chlorates, peroxides, oxides, chromates and perchlorates (the best), all providing oxygen. The reducing agents may be charcoal (carbon), sulfur, or metal powders. Notice that all practical double-base pyrotechnics are powder solids mixed-up, with some gluing agent to keep them bounded, because liquid mixtures are too unstable.

By physical state pyrotechnics may be grouped as:

- Solids. The majority of cases, because they are more stable and easier to handle.
- Liquids. Very unstable even if single-base, as nitrocellulose and nitroglycerine. Separate liquids, like LH2 and LOX used in cryogenic rockets, are treated as combustion processes.
- Gases. There are no single-base pyrotechnic gases (they would decompose), and premixed explosive gases are considered under normal combustion.

An explosion is a mechanical process generating a destructive high-pressure wave in a fluid; this shock wave (the blast caused by rapidly expanding gases), and the associate projection of entrained solid debris, cause mechanical damage by impact (besides other possible associated risks, as fires, toxic fumes, radioactive waste...). A container with pressurised gas, a confined mixture of premixed flammable gases, a mist of combustible particles in air, a high-explosive, a high-power electrical discharge in a solid, a nuclear reaction... all these systems may explode.

By use, pyrotechnics are grouped as:

- **Explosives.** Substances that, by chemical decomposition, generate a supersonic reaction wave, propagating at several km/s within the material, generating a lot of hot expanding gases. They are also called high-explosives, and the process is known as detonation; e.g. dynamite. Sensitive materials that can be exploded by a relatively small amount of heat or pressure are called primary explosives (e.g. nitroglycerine, lead azide), and more stable materials secondary explosives (e.g. TNT, ANFO).
- **Propellants.** Substances that, by chemical decomposition, generate a subsonic reaction wave, propagating at a few cm/s or m/s within the material, generating a lot of hot expanding gases. They are also called low-explosives, and the process is known as deflagration, as in combustion; e.g. black powder.

## **APPLICATIONS: BLASTERS, PROPELLANTS, AIRBAGS, SPARKLERS, MATCHES, FIREWORKS...**

According to their purpose, pyrotechnics may be classified as:

- Blasters, for mining, tunnelling, demolition, quick-release devices, and weaponry (warhead). They are high-explosives that undergo supersonic combustion when detonated by a low-explosive or shock-wave (they slowly burn if just approached by a flame). If the blast is just to cause an abrupt noise, with insignificant blasting, the device is called a firecracker (see below).
- Propellants, for rockets and weaponry. They generate a large gas stream (like all other pyrotechnics) that is channelled with one free end to give propulsive thrust to a projectile or to the combustor body. The main difference between rocket propellants and gun propellants is the working pressure reached, which in rockets is around 10 MPa, and in guns more than 100 MPa, with the consequent change in burning rate (recession speed  $v_r$  is modelled by Vieille's law,  $v_r \propto p^n$ , with  $0.4 < n < 0.7$ ).
- Gas generators, for airbag inflators. Airbags are car-safety-devices that use a pyrotechnic inflator. They commercially started in the late 1970s in USA and Germany, and widespread to all new cars in late 1990s. They were based on the combustion of sodium azide ( $\text{NaN}_3$ ) with an oxidiser, rapidly producing a great quantity of nitrogen gas that inflates a nylon or polyester bag in some 50 milliseconds (it inflates at 100 m/s); the bag is micro-perforated to allow progressive cushioning by deflation when the passenger-body hits it. A low combustion temperature (2000..2300 K) is preferable to avoid massive formation of toxic CO and NO. Airbag deployment is harsh: it generates some toxic substances (NaOH, a strong alkali that

cause eyes irritation), it generates a bang (some 170 dB, but too short to break eardrums) and white smoke of talcum powder (used to lubricate the deployment), and it usually causes burns to passengers, either by friction, chemical attack or high temperature. In case of accident, beware of un-deployed airbags. If  $\text{NaN}_3$  is exposed to water in a landfill, it is converted into hydrazoic acid, which is an extremely toxic, volatile liquid. Since most airbags will never be deployed and since each airbag contains between 50 and 150 grams of  $\text{NaN}_3$ , concerns have been raised regarding landfill pollution. Less dangerous pyrotechnics are taking over  $\text{NaN}_3$ , like triazole ( $\text{C}_2\text{H}_3\text{N}_3$ ), tetrazole ( $\text{CH}_2\text{N}_4$ ) and derivatives.

- Light generators (sparklers), for fireworks or for rescue signals. Some metal powders (Al, Fe, Zn, Mg, Na) are added to the black powder in order to create bright light (yellow-white by hot emission at  $>1500$  K) and coloured shimmering sparks (by actual particle burning and gas line-emission: yellow Na-line, orange CaCl-band, red SrCl-band, green BaCl-band, blue CuCl-band). Underwater torches use a mixture of high-gassing solid reactives that, when ignited, creates enough pressure gases to keep water away (they only work at small depths; a few meters).
- Fire generators, for domestic use (matches, fuel pellets for field stoves) or military purpose (incendiary grenades; thermite, a powder mixture of iron oxide and aluminium or magnesium dust, was used to spread fire by the splash of liquid iron generated:  $2\text{Al(s)} + \text{Fe}_2\text{O}_3\text{(s)} = \text{Al}_2\text{O}_3\text{(s)} + 2\text{Fe(l)}$ )).
- Heat generators. Aluminium has already been mentioned as an incendiary metal. Other incendiary metals include zirconium, magnesium, titanium, and depleted uranium. They all burn at very high temperatures. A particularly useful metallic incendiary is "thermite", which is a mix of ferrous oxide ( $\text{Fe}_2\text{O}_3$ , essentially rust) and aluminium. The thermite reaction is  $\text{Fe}_2\text{O}_3 + 2\text{Al} = \text{Al}_2\text{O}_3 + 2\text{Fe}$ . The reaction burns very hot and releases a tremendous amount of energy. Thermite is often used in demolition grenades to burn or melt down military gear that has to be abandoned to an enemy.
- Smoke generators, for rescue signals or military purpose (smoke grenades). Smoke from combustion is an aerosol formed by a suspension of microscopic solid particles from the poor combustion of carbonaceous fuels. Theatre 'smoke' is just a mist formed by condensation in the ambient of boiling glycol entrained by an air jet, or the condensation of water-vapour forced over dry ice or liquid nitrogen.
- Noise generators (firecrackers), for fireworks or for rescue signals. Black-powder slowly burns if in the open, but confined within the paper wrapping of a firecracker, it explodes (yields a high pressure pulse, but not supersonic combustion).

## EXPLOSIVES

CAUTION. The author reminds the reader that the information collected below is intended to satisfy human curiosity; as for children, it is better to educate on dangers, than to let them explore on their own. The author is wise enough to keep away of foreseeable dangers, and advises other people to be so prudent (simple things may kill if put to bad use, like the donkey bone in Cain and Abel story, but explosives are risky even if put to good use).

Fire was used by humans since 500 000 years ago, and it is known that little explosions may occur in the fireplace that cause a loud noise and throw sparks away, but control of 'sudden fires' is a very recent happening. One may find precedents in the incendiary substances developed in the Middle Ages.

Notice that an explosion is a sudden mechanical process causing rupture and noise, due to great pressure forces that may be originated chemically (e.g. from a confined combustion or detonation), thermally (as in boilers, even electrically heated), mechanically (as in a balloon or any other gas pressurised vessel), nuclearly, etc. An explosion creates a travelling wave with a sizeable pressure jump across; in air, a very loud noise (e.g. a close-up turbine) produce an acoustic wave with  $\Delta p < 0.1$  kPa, nearly hurting the ear; a 3 kPa jump may break window panes, a 10 kPa jump may throw down people, a 20 kPa jump may throw down thin walls and a 50 kPa jump thick walls; beyond  $\Delta p = 200$  kPa the wave becomes supersonic in ambient air, above  $\Delta p = 200$  kPa there may be some casualties, and at  $\Delta p = 400$  kPa more than 90 % people die. Detonations may arise in the typical condensed [explosives](#) (e.g. TNT), in confined fuel/oxidiser gas mixtures (e.g. [shock tube](#)), or in dispersion of particulate fuels in air, either confined (e.g. explosions in a flour industry), or in open air (e.g. [fuel-air bombs](#)).

### **Greek fire**

Greek fire is a water-resistant fuel-mix used by the Byzantines. With it, they manage to destroy the Arab's wooden ships during the siege of Constantinople in 670 a.D. Greek fire was a mixture of pitch, sulfur, petroleum and quicklime, that burned vigorously and could not be extinguished with water. Its present-time successor, Napalm (an acronym from naphtha and palmitic acid, or from sodium palmitate), is a highly incendiary jelly, usually consisting of a naphtha liquid made viscous and sticky with a thickener: a sodium soap, an aluminium soap, or polystyrene plastic beads). Another incendiary is FAE (acronym for fuel-air explosives) that sprays out an aerosol cloud of a hydrocarbon liquid, and then ignites it to create a flaming explosion over a wide area.

### **Black powder**

Black powder may be considered the first pyrotechnic. It was known in China more than 1000 years ago, and used to make firecrackers and rockets for public entertainment and to frighten enemies in combat. Black powder knowledge spreaded to the West in the Middle Ages. The English monk Roger Bacon described a formula for it in 1242; he wrote (in code because of the lethal nature of the material) that when heating a finely ground mixture of 6 weights of saltpetre with 5 weights of charcoal and 5 weights of sulphur, a vigorous flame suddenly appears. In the 14th century, black powder led to the development of fire weapons. Saltpetre is potassium nitrate, a shiny white crystalline material that could be found on the walls of caves or in well-aged manure piles. Charcoal is pyrolysed wood, often approximated as carbon, but it is really partially pyrolysed cellulose best approximated by the empirical formula  $C_7H_4O$ . Sulfur, found in volcanic deposits, decrease the ignition temperature (and provided additional fuel). Eventually, the formula for black powder was refined to a mix of saltpetre, charcoal, and sulfur, in the proportions 75:15:10 by weight. A simple approximate stoichiometry for its reaction is  $4KNO_3 + 7C + S = K_2CO_3(s) + K_2S(s) + 3CO_2(g) + 3CO(g) + 2N_2(g)$ . The large amount of solids formed (>50 % in mass) makes powder combustion very sooty; this fact, and the fact that moisture turned some of the

soot into a caustic corroding solution (with KOH), demanded a thorough cleaning of old fire arms for maintenance.

Black powder is an excellent pyrotechnic in many respects. Its raw materials are cheap, abundant, and reasonably safe: non-toxic ingredients easily shaped, non-detonating (it burns readily, but by deflagration, though it may explode under confinement), it can be stored indefinitely if kept very dry, and it can be easily ignited with a spark; but, on burning, it gives off a dirty smoke with a characteristic smell. A binder (e.g. a moistened starch or sugar slurry) is used to give shape to the mixture, and the compound slurry can easily coat a support wire or fill a tube. Black powder, also known as gunpowder, was used to propel ammunition until late 19th century, when cellulose nitrate (nitrocellulose,  $C_6H_7O_2(OH)_3+3HNO_3=C_6H_7O_2(ONO_2)_3+3H_2O$ , in concentrated sulfuric acid to get rid of water) was developed by F.A. Abel in 1865, giving way to smokeless powders (of which guncotton was the first, followed by cordite) that are used almost exclusively since then.

Magicians commonly use different forms of nitrocellulose (flash paper, flash cotton, flash string) to produce bright flashes of fire; less dangerous is lycopodium powder, custard powder and even powdered milk, used by fire-breathing magicians.

### **The match**

Up to the beginning of the XIX c., the usual way to start a fire was by striking a flint-stone with an iron to get a spark, close to an easily burning material (tinder). In the friction match (from Old French *meiche*), the piezoelectric spark is substituted by a low-temperature combustion process initiated by rub-heating of phosphorus or one of its compounds (pure white phosphorus catches fire spontaneously in air).

The first trial to make matches is due to R. Boyle, that in 1680 tried to enhance the old friction method of making fire, by using small wood-sticks impregnated with sulfur (used in black powder) and phosphorus (just discovered in 1669 by Hennig Brand, who extracted it by evaporating urine to dryness and distilling the residue with sand, looking for the philosopher's stone), rubbed against another wood, but it was not reliable. There were other chemically-ignited matches developed, as the one in Paris, in 1805, where a thin strip of wood or cardboard, tipped with a mixture of potassium chlorate and sugar, spontaneously ignited when brought into contact with sulfuric acid (soaked in asbestos inside a bottle), but the common friction match was invented by the English chemist John Walker in 1826 (it is said that he accidentally scraped the stick he was using to mix phosphorus with antimony sulphide and potassium chlorate over a rough surface and caught fire). Matches were produced on a commercial scale first in 1833 at Darmstadt (D), and the match box developed in late XIX c. in USA. The basic design of the match may be split in three parts: igniter (phosphorus in air), booster (potassium chlorate oxidiser mixed with sulfur fuel) and sustainer, the slow-burning splint to which the head is glued with a binder (such as gum arabic or wax, also preventing moisture). The ordinary yellow phosphorous initially used was highly poisonous to match-makers, producing necrosis of the jaw-bone and mental disorder. The match box widespread with smoker fashion in XX c., until development of the disposable gas-lighter in 1969. Burning a match releases around 1 kJ of heat.

Phosphorus (Gr. *phos*, light, and *phoros*, bearer; ancient name for the planet Venus when appearing before sunrise) can have several allotropic forms: white, red, violet ... The equilibrium phase at standard conditions is a transparent (whitish-yellow by impurities) soft crystalline solid named white phosphorus ( $M=0.031$  kg/mol,  $\rho=1820$  kg/m<sup>3</sup>,  $T_m=44$  °C,  $T_b=277$  °C, arranged as tetrahedral units of four atoms). Phosphorescence is the emission of light (the glow can only be seen in darkness) by slow oxidation of white phosphorus in air (red phosphorus does not phosphoresce). Transition from white to red phosphorous may occur by boiling or by exposure to sunlight. Red phosphorus is relatively stable and easy to handle (it is an amorphous solid with  $\rho=2340$  kg/m<sup>3</sup>, that sublimates at 417 °C), but white phosphorus is a deadly poison that spontaneously ignites at room temperature (it is kept under water). Black phosphorus is produced by heating white phosphorus in the presence of a mercury catalyst, and it is the least reactive and of least commercial value. Phosphorus is the most abundant mineral element in plants (0.7 %wt), and only second (after calcium) in animals (0.7 %; present in every cell, but 85 percent of the phosphorus is found in the bones and teeth). Phosphorus is commercially obtained from phosphate ores.

Safety matches, first patented by Pash in 1844 in Sweden, do not have the igniter (the phosphorus) in the same place as the booster (the head); i.e., the match-head must be rubbed against a special surface (glued on the package of matches) to get ignited. The striking surface is coated with powdered glass and red phosphorus mixed in a binder. When the match is scratched over it, the heat from friction causes some red phosphorus to become white phosphorus, which burns spontaneously in air, decomposing the potassium chlorate, liberating oxygen that quickly reacts with sulfur and lights the wood of the match, which has been dipped in a fireproofing agent to keep it from burning too easily. Matches and their boxes are tested to avoid burning problems as exploding heads, spitting heads, splint afterglow, heat resistance, friction resistance, etc., as well as non-combustion-related problems as splint strength, tray retention of the box, etc. Safety matches were slowly introduced into the market because technical difficulties in producing red phosphorus, and the ease-of-use of ‘strike-anywhere’ matches.

A few basic safety-rules on how to light a match should be pursued (at least for child education): 1) Verify there is no flammable substances nearby, 2) Take only one match, 3) Close the cover of the match box before striking the match, 4) Strike the match away from the direction of the body, holding the match an arm's length away, 5) Throw a match away only after the flame is extinguished and cool to the touch (a waste basket is not an ash tray), 6) Matches are fire-making tools, not toys (do not allow children to play with match-boxes or lighters, even when empty).

### **Nitroglycerine and dynamite**

Explosives may be grouped in low explosives (like black powder) and high explosives (like dynamite). In low or deflagrating explosives the explosion propagates through the material at subsonic speed through a sustained combustion process, whereas in high explosives the explosion propagates by a supersonic detonation.

The first commercial high explosive was found in 1846 by an Italian chemist named Ascanio Sobrero adding glycerol to a mixture of nitric and sulfuric acids, setting off an explosion that nearly killed him.

Glycerol, or glycerine,  $C_3H_8O_3$  (Fig. 1a) is a syrupy liquid, a by-product of soap manufacture. Sobrero decided that the liquid he called "nitroglycerine" was dangerous and tried to keep it a secret, but he failed: a Swedish chemical manufacturer, Alfred Nobel, began to produce nitroglycerine for rock blasting in 1863.

Nitroglycerine, the nitric acid triester of glycerol,  $CHONO_2(CH_2ONO_2)_2$ ,  $M=0.227$  kg/mol (Fig. 1b), is a dense oily liquid with a density of  $1600$  kg/m<sup>3</sup> that melts at  $80$  °C and detonates if heated to  $218$  °C or if subjected to mechanical shock, releasing a lot of gas and energy:



Nitroglycerine tablets and sprays are used as heart medication (diluted by inert matter and completely non-explosive). A tiny amount of nitroglycerine (<1mg) placed under the tongue causes blood vessels to dilate, instantly lowering blood pressure.

Alfred Nobel, began to produce nitroglycerine for rock blasting in 1863. Liquid nitroglycerine is very unsafe to handle (Nobel's brother Emile was killed while working with it). But he made two major findings:

- He found a stabiliser: nitroglycerine absorbed in diatomaceous earth (a porous clay that consisted of the deposits of the skeletons of tiny sea creatures laid down aeons before) is stable to shocks. This material could be packed into cardboard tubes and reliably transported, handled, and detonated. Nobel called it dynamite. Dynamite was particularly useful in coal-mine blasting, where the quick, cool flame was not likely to ignite the explosive methane-coal dust mixture in the tunnel.
- He found a detonator: dynamite could not be set off by a spark or a flame (it was even safer than black powder). In 1865 Nobel devised the first detonator, a blasting cap consisting of a small black powder charge with a cord fuse, to set it off. Nobel's detonator was a significant step forward in the development of modern explosives technology. Detonators have traditionally been made from fulminate of mercury,  $Hg(CNO)_2$ , or lead azide,  $Pb(N_3)_2$ . These are salts of hydrazoic acid ( $HN_3$ ), which is a dangerous and unstable liquid explosive, and have the respective formulas of  $Hg(N_3)_2$ , and  $Pb(N_3)_2$ .

Besides dynamite in 1867, Nobel developed in 1875 blasting gelatine (gelatinised nitroglycerine and nitrocellulose), that can be detonated underwater, and in 1887 ballistite, a smokeless powder (a mixture of nitrocellulose and nitroglycerine).

### **Trinitrotoluene (TNT)**

The first military high explosive to be put into service was picric acid,  $C_6H_2OH(NO_2)_3$ , a toxic yellow crystalline substance used by the French in 1885. However, picric acid has a high melting point, making the process of filling shells with it difficult; reacts with heavy metals to form very toxic compounds; and tends to be sensitive.

Another explosive, trinitrotoluene (TNT, trilitite, Fig. 1d), was first discovered in the 1860s, but was not used until the German military adopted it in 1902. It was widely used in World War I. It is relatively insensitive to chock and can be melted at low temperature to allow it to be poured into bombs and shells.

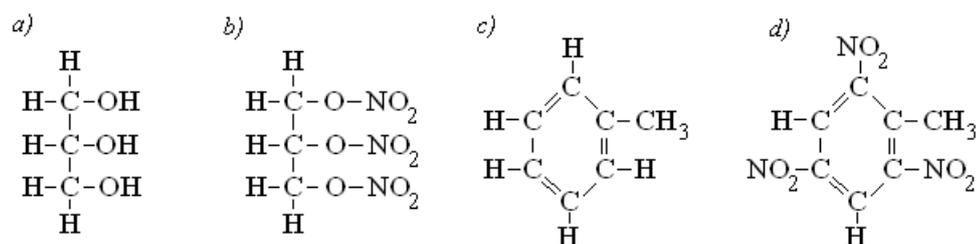


Fig. 1. a) glycerol (glycerine), b) trinitrolycerine, c) toluene, d) trinitrotoluene (trilitite, TNT).

### Ammonium nitrate

Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ,  $\rho=1750 \text{ kg/m}^3$ ,  $M=0.080 \text{ kg/mol}$ ,  $T_f=445 \text{ K}$ ,  $T_{\text{decomp}}=470 \text{ K}$ ) is a colourless odourless highly soluble crystalline solid, obtained by the reaction between gaseous ammonia and aqueous nitric acid, and used mainly as a fertiliser and in explosives. In the 1950's ammonium nitrate derivative explosives were commercialised. Ammonium nitrate is stable if pure, even in the molten state or in aqueous solutions, yielding  $\text{NH}_4\text{NO}_3=2\text{H}_2\text{O}+\text{N}_2\text{O}$  when slowly heated in the open, but violently exploding as  $\text{NH}_4\text{NO}_3=2\text{H}_2\text{O}+\text{N}_2+1/2\text{O}_2$  when subjected to hot confinement or a strong shock. Contaminants increase the explosion hazard, particularly if acid. If pure (<0.2 % wt combustible matter within) it is catalogued as a strong oxidiser by the U.S. Department of Transportation, but for >0.2 % of combustible substances as an explosive.

One of the worst blasts ever happened took place on 16 April 1947 on a French freighter docked at Texas City and loaded with ammonium nitrate fertiliser. The ship caught on fire in the morning and attracted a crowd of spectators along the shoreline, who believed they were a safe distance away. In mid-morning the ship exploded, killing hundreds with the tremendous blast, sending a tidal wave surging over the shoreline, and setting refineries on the waterfront on fire. A second ship loaded with fertiliser exploded after midnight, but emergency workers were given warning, they evacuated the vicinity of the vessel, and only two people were killed. Fires burned for six days after the disaster. Official casualty estimates came to a total of 567. An explosion in Toulouse on 21-09-2001 of some 250 tons of ammonium nitrate in a large fertiliser factory caused 31 deaths and more than 2000 injuries. A truck with 25 tonnes exploded in Spain on 09-03-2004 in a car accident, leaving 2 deaths and a 3 m diameter crater. ANFO, ammonium nitrate and fuel oil, is the most common explosive nowadays for surface-mine blasting, having practically replaced dynamite, due to lower cost and safer handling

In the early 1980s, US Army researchers experimented with "cubane" a cubical C-network hydrocarbon synthesised in 1960s of double the density of gasoline; its high density means faster propagation of breakdown reaction, leading to a more powerful and compact explosive. Octanitrocubane consists of a cubic core of eight carbon atoms, with an  $\text{N}_2\text{O}$  group attached to each corner of the cube; it seems to be very stable, twice as powerful as TNT and its breakdown products are non-toxic carbon and nitrogen compounds.

## PROPELLANTS

Propellants are used to force an object to move forwards, from a firework-rocket, to a rocket to put people on the Moon. As propellants must be carried aboard, condensed phase propellants (solid or liquid) are much preferable.

Liquid propellants may be grouped as:

- Single base liquids, such as hydrazine ( $\text{N}_2\text{H}_4(\text{l})$ ) and derivatives (as mono-methyl-hydrazine MMH  $\text{N}_2\text{H}_3\text{CH}_3(\text{l})$ ) and unsymmetrical-dimethyl-hydrazine UDMH  $\text{N}_2\text{H}_2(\text{CH}_3)_2(\text{l})$ ), or hydrogen peroxide ( $\text{H}_2\text{O}_2$  more than 70 % wt concentrated), that are stable at ordinary temperatures, but decompose into hot gases when exposed to suitable catalysts or high temperatures (e.g.  $2\text{N}_2\text{H}_4=2\text{NH}_3+\text{N}_2+\text{H}_2$ ).
- Double base liquids, stored apart. As oxidiser, liquid oxygen (LOX) or nitrogen tetroxide ( $\text{NO}_2$ ) may be used. As fuels, liquid hydrogen or kerosene may be used.

Solid propellants (they do not allow intermittent operation) are categorised as "single-base", "double-base", and "multi-base" or "composite" powders or pastes:

- Single-base powders, such as cordite, are mostly nitrocellulose (guncotton with some nitroglycerine). Black powder was used for solid-propellant rockets in the first third of the 20<sup>th</sup> c. They burn cool and cause little barrel wear in firearms. Double-base composite powders are now generally used as a propellant for solid-fuel rockets.
- Double-base powders are mixtures of nitroglycerine and nitrocellulose such as ballistite, and burn hotter.
- Composite powders are modern formulations that do not contain nitrocellulose or nitroglycerine, instead using more modern propellants that burn cool but are as powerful as double-base powder. Ammonium perchlorate composite propellant (APCP), one of the best solid rocket fuels, can be cast into shape (instead of pressed as a powder), making its setup more simple and reliable.

Hypergolic propellant are substance pairs that ignite upon contact with each other without a spark, heat or other external aid, such as  $\text{N}_2\text{H}_4/\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{H}_4/\text{NO}_2$ , aniline and red fuming nitric acid (concentrated nitric acid in which nitrogen dioxide is dissolved), etc.

### Shuttle fuels

The Shuttle (the Space Transportation System) has, for take-off, two solid rocket boosters (2 minutes burn) and three liquid-fuelled main engines, providing in total up to  $30 \cdot 10^6$  N thrust (80 % solid rockets, 20 % liquid rockets) to lift the  $2 \cdot 10^6$  kg total mass. Besides, the Orbiter (what most people call the Space Shuttle) has two propulsion systems: OMS (Orbital Manoeuvring System) used to change orbit and to return to earth, and the RCS (Reaction Control System) used for station-keeping and attitude control; both systems burn liquid hydrazine with cryogenic oxygen.

Each solid rocket is 45 m high and 3.7 m in diameter, has 500 000 kg of APCP-fuel (590 000 kg total mass) and yields  $13 \cdot 10^6$  N thrust during the first few seconds, slightly decreasing during the 2 minutes burn. The APCP propellant consists of a mixture of ammonium perchlorate powder ( $\text{NH}_4\text{ClO}_4$ , oxidant,

70 % by mass), aluminium powder (fuel, 16 %), and a dash of iron oxide powder (catalyst, 0.4 %), held together with a polymer binder (12 %) and curing epoxy resin (2 %). The burning reaction of ammonium perchlorate (AP) is basically  $\text{NH}_4\text{ClO}_4 = 2\text{H}_2\text{O} + 0.5\text{Cl}_2 + 0.975\text{O}_2 + 0.25\text{N}_2 + 0.25\text{N}_2\text{O} + 167.4 \text{ kJ}$ , i.e. a lower heating value of 1.42 MJ/kg, but the added fuel (Al-particles and binder) increases the heating value to about 4 MJ/kg. The white cloud formed at launch is due to the alumina particles formed ( $\text{Al}_2\text{O}_3$ ). Russians have always used liquid-fuel rockets boosters in their launchers.

The liquid rocket engines use liquid hydrogen and liquid oxygen contained in the external tank, the largest element of the Shuttle (8.4 m in diameter, 2000 m<sup>3</sup> of cryogenic propellants with a multilayer thermal protection 25 mm thick). Hydrogen is supplied from a 1450 m<sup>3</sup> bottom tank (106 t of LH<sub>2</sub> at 20.6 K and 300 kPa,  $\rho=73 \text{ kg/m}^3$ ), at a rate of 210 kg/s (3 m<sup>3</sup>/s), while oxygen is supplied from a 540 m<sup>3</sup> top tank (630 t of LOX at 90.6 K and 250 kPa,  $\rho=1150 \text{ kg/m}^3$ ), at a rate of 1300 kg/s (1.1 m<sup>3</sup>/s), both through 0.43 m diameter feed lines, during the 8.5 minutes burning time, positioning the Shuttle at 115 km height. Notice that for 1300 kg/s of LOX, the stoichiometric LH<sub>2</sub> is  $1300/8=163 \text{ kg/s}$ , but 210 kg/s is supplied, this excess hydrogen being used as coolant to protect the engine. Each of the three rockets yield up to  $2 \cdot 10^6 \text{ N}$  thrust.

### **Ariane fuel**

Ariane 5 has two solid boosters and two liquid-propellant stages, with a total thrust of  $11 \cdot 10^6 \text{ N}$  and a total take-off mass of  $750 \cdot 10^3 \text{ kg}$ . Each booster is 31 m long and 3 m in diameter, uses  $240 \cdot 10^3 \text{ kg}$  of a PCA + HTPB + aluminium solid mixture, yielding  $5 \cdot 10^6 \text{ N}$  thrust during 130 s (up to 55 km). Stage 1 is 31 m long and 5.4 m in diameter, using  $160 \cdot 10^3 \text{ kg}$  of LH<sub>2</sub>/LOX and yielding  $1 \cdot 10^6 \text{ N}$  thrust during 580 s; the combustion chamber is at 10 MPa. Stage 2 is 3.3 m long and 4 m in diameter, using  $10 \cdot 10^3 \text{ kg}$  of monomethyl hydrazine / nitrogen tetroxide and yielding  $27 \cdot 10^3 \text{ N}$  thrust during 1100 s.

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