

Propellant Chemistry

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Abstract: A systematic overview of the different types of solid propellants, their chemical compositions, characteristics and practical applications is given. The classification of propellants, the function of stabilizers and the modification of the ballistic properties are discussed.

Keywords: Composite · Double base · Propellant · Single base · Stabilizer

1. Introduction

The names ‘Gun Powders’, ‘Powders’, and ‘Propellants’ are related to solid materials primarily used to accelerate projectiles from guns of all sizes and for propelling rockets and missiles. These materials must be of high energy content and must have defined burning characteristics. The energy must be delivered in a very short period of time. Most initial development in the field of propellant has been activated by military and space exploration needs.

Gunpowder, a mixture of salpeter, charcoal, and sulfur, also known as ‘black powder’, was first used as a propellant in mortars and guns. This old type of propulsion source had serious disadvantages. It was rather unpredictable in use, it developed extremely dirty gases and residues and caused considerable fouling of gun barrels. The emitted amount of smoke and muzzle-flash immediately disclosed the position of the gun to the enemy.

The discovery of gelatinized nitrocellulose (NC) in France led towards the generation of smokeless powders. These can be divided into two classes: Single Base (SB)

and Double Base (DB) propellants. The main ingredient of *SB propellants* is basically nitrocellulose, which has been made colloidal by the action of solvent. *DB propellants*, contain nitroglycerine (NGL) or other nitroglycol compounds and NC. In addition, DB propellants with picrite or nitro-guanidine added to the formulation are considered as a separate class and are called Triple Base (TB) propellants.

A third type, the *composite propellants*, is a more recent development compared with the two others. This is based on an oxidizing solid, commonly a perchlorate, together with an organic binder, which acts as fuel and gives also adequate mechanical strength to the resulting propellant. The excellent mechanical properties allow propellant grains to be manufactured in dimensions larger than with SB or DB. This and the high-energy content of composite propellants make them favorable for use in medium and large size solid rocket motors.

2. Single Base Propellant

2.1. Nitrocellulose

The main compound of SB propellant is nitrocellulose (**1**, NC), or more exactly the nitrates of cellulose, present in the composition from 85 up to about 96%. This energetic compound was discovered in 1846 by Dr. Friedrich Schönbein [1]. In 1868, Abel and later several other authors of various nationalities [2][3] found ways to stabilize NC. The rest of the composition consists of plasticizers. They exist *e.g.* in an inert form like dibutyl phthalate (**2**), dibutyl sebacate (**3**), dibutyl adipate (**4**), and camphor or as energetic ones like the isomeric mixture of 2,4-dinitrotoluene (**5**) and 2,6-dinitrotoluene (**6**) (Fig. 1). The role of the plasticizers is to act as surface moderants and at the same time as coolants. The principle of a surface moderant is to retard the initial burning rate, the initial gas generation rate, and the initial flame temperature. Typical

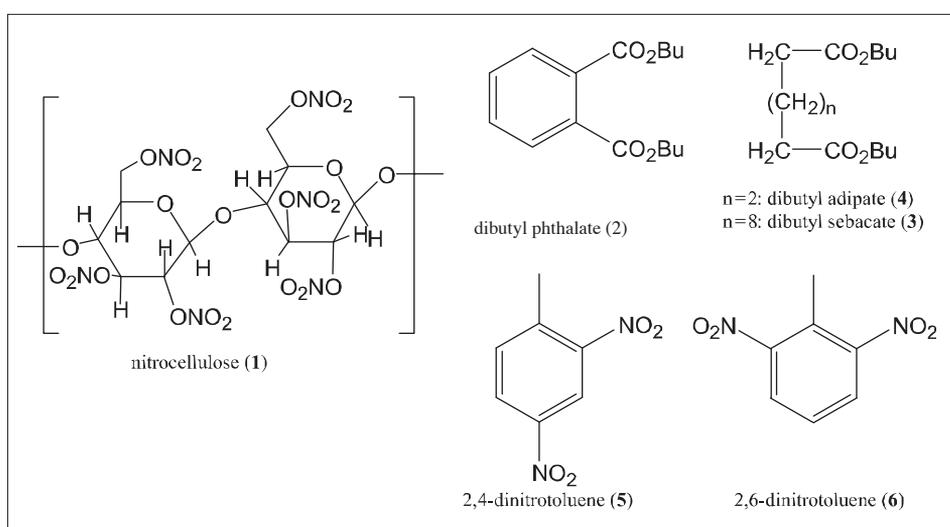


Fig. 1. Chemical structure of nitrocellulose and the most commonly used inert and energetic plasticizers

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concentrations of plasticizers are between 1 and 10%.

2.1.1. Nitration of Cellulose

The mechanism of the nitration reaction of cellulose is complex and has only been elucidated a century after its invention and a long time after its industrial production was established. Originally the production of nitrocellulose was very simple, but became more scientific with the gradual advance in basic knowledge.

Chemically, cellulose contains three alcohol groups per unit, one primary and two secondary. Theoretically, it is therefore possible to obtain the mononitrate (6.76% nitrogen content), the dinitrate (11.12% nitrogen content), and the trinitrate (14.14% nitrogen content). The true nitrogen content results from the statistical distribution of the NO_2 groups on the different glucose units [4]. It is most probable that the primary hydroxyl groups are nitrated in preference to the secondary groups and the latter are denitrated more easily. This has been demonstrated by using ^{15}N nitric acid [5]. The nitration of cellulose is a reversible esterification under equilibrium control. However, as a result of the diffusion phenomena of the reactants in the fiber, this reversibility is particularly slow and thus practically very limited. The extent of denitration in diluted acid or in pure water is insignificant, which means that NC can be transported in aqueous solution without appreciable risk of denitration. Treating NC with boiling pure water for 100 h reduces the nitrogen content by 1% only [6]. The nitration reaction is highly exothermic with an enthalpy per mol of HNO_3 of $\Delta H = -8373$ kJ/mol. Increasing the temperature of nitration does not really modify the amount of nitrogen at equilibrium but only slightly accelerates the reaction.

Due to the complexity of the nitration reaction of cellulose, different methods, acids and mixtures of acids, were tested: pure nitric acid, sulfonitric mixtures, acetonitric mixtures, and also phosphonitric mixtures. All these techniques allow specific reaction profiles of nitration to be established and it is now possible to produce nitrocellulose in a suitable way [6].

2.1.2. Stabilization of Nitrocellulose

One of the most important problems in nitrocellulose technology concerns the purification process which is responsible for increasing the stability of the product as far as possible. Numerous catastrophic explosions took place due to insufficient purification of the product. Abel discovered in 1865 that the amount of acid retained in the NC fibers was responsible for the lack of stability [7]. It was experimentally demonstrated that the resistance of nitrocellulose to temperature elevation was dependent on

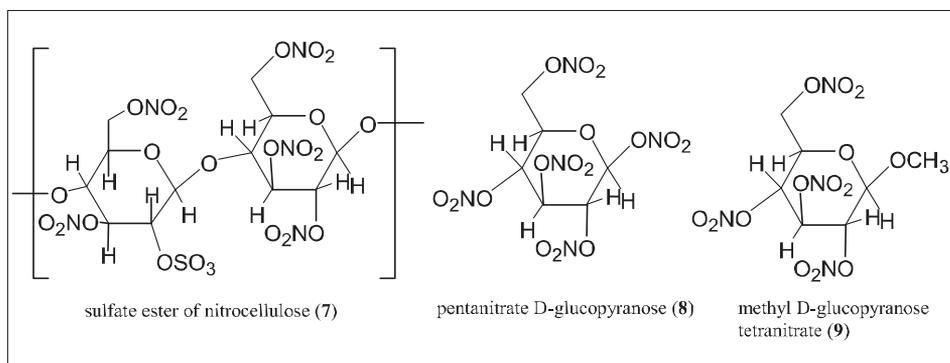


Fig. 2. Chemical structure of sulfate ester of nitrocellulose and of the glucopyranose derivatives originating from hydrolysis of NC

the composition of the nitration acid mixture consisting of sulfuric acid, nitric acid, and water. The formation of sulfuric acid esters (7) was assumed to be responsible for the low stability of the nitrocellulose.

Sulfuric acid, as occlusions or esters, is not the only reason for the instability of nitrocellulose. Celluloses always contain some hydro- or oxycelluloses. The hemiacetal function, present at the end of the chain, is easily esterified and the resulting esters are very unstable. This is the case for the pentanitrate of D-glucopyranose (8), illustrated in Fig. 2, which is very unstable, whereas the methyl D-glucopyranose tetranitrate (9) is stable [8]. To increase the stability these esters have to be broken down and removed.

In practice, the NC is boiled in water to remove the acid occlusions or to break the esters down. During this process, the nitrogen content of nitrocellulose decreases simultaneously with the degree of polymerization. The hydrolysis of the nitrate groups of the polymer occurs simultaneously with the radical cleavage of the acetal bonds of the cellulose [6].

2.1.3. Chemical Properties

Nitrocellulose (NC) has the chemical properties of a nitrate ester, complicated to

varying degrees by (a) the presence of residual hydroxyl groups, (b) the fibrous structure often inhibiting the penetration of chemical reagents, as in the case of cellulose, and (c) the crystalline microstructure which also introduces some chemical accessibility.

Nitrocellulose is insoluble in water, which allows its preparation, stabilization, and transport by quenching, using the appropriate quantity of water. The solubility of NC in organic solvents is essentially a function of the nitrogen content and to a small extent to the degree of polymerization. In case of a polymer like nitrocellulose, the notion of solubility is more qualitative than quantitative. In general, NC is soluble in all proportions, but increasing the quantity dissolved increases the viscosity. In fact, the limit of solubility is often a limit of viscosity. Table 1 illustrates the solubility of NC according to [9] as a function of the nitrogen content.

Whereas there are many bacteria capable of destroying cellulose by degradation and absorption at the sugar stage, no microorganism seems to thrive on NC, even when incompletely nitrated. An American military study [10] discovered that *Aspergillus fumigatus* can use the nitrogen of moist NC, not by direct attack, but by ac-

Table 1. Solubility of nitrocellulose according to [9]

Nitrogen content [%]	Acetone	Ethyl acetate	Ethanol	Diethyl ether
14.14	soluble	soluble	insoluble	insoluble
13.00	soluble	soluble	insoluble	insoluble
12.75	soluble	soluble	increased solubility	insoluble
12.00	soluble	soluble	increased solubility	increased solubility
11.00	soluble	soluble	increased solubility	partially soluble
10.00	soluble	soluble	decreased solubility	decreased solubility
9.00	decreased solubility	decreased solubility	insoluble	insoluble
8.00	hardly soluble	hardly soluble	insoluble	insoluble

celerating its hydrolysis and recovering the resulting nitrogen. Because NC is non-toxic, it is often used in food packaging.

Nitrate esters have poor resistance to acid and are more stable in basic medium. In the case of nitrocellulose, the polymeric structure must also be taken into account; these exhibit the following properties [6]:

- The action of concentrated or very slightly diluted acids or bases usually leads to denitration of the polymer, often leading to destruction of the product.
- Concentrated cold sulfuric acid dissolves nitrocellulose and hydrolyses the NO_2 groups liberating nitric acid.
- Concentrated bases like sodium hydroxide, potassium hydroxide or ammonia have strong saponification action accompanied by more or less rapid destruction of the polymeric bonds.
- Relatively weak and diluted bases, like sodium carbonate solution, are fairly compatible with nitrocellulose (allowing an alkaline digestion treatment to be used for stabilization).
- However the nitrocellulose should not be treated with medium to concentrated solutions of sodium carbonate, because a saponification of the product may occur, even when cold.
- Other products denitrate nitrocellulose easily, e.g. aqueous solutions of alkaline hydrosulfites.

2.1.4. Explosive Properties

The energetic performances of NC are given by the nitrogen content. The higher the nitrogen content, the higher the heat of explosion. More nitrogen is present in the molecule and more oxygen can be used to oxidize the reducing agents (carbon and hydrogen). This leads to a better oxygen balance in the molecule. The heat of explosion and other explosive properties according to [11][12] are shown in Table 2.

For military purposes, the propellants with the highest nitrogen content are used because the highest performances are requested. Therefore two main products are employed:

- Grade A 'pyrocellulose': nitrogen content between 12.3 and 12.8%
- Grade B 'guncotton': nitrogen content higher than 13.35%.

2.2. Application of Single Base Propellants

The disadvantages of black powder – unreliability in use, smoke together with acidic residues and therefore corrosion of the gun barrels together with the low energy content – demanded 'better' powder. This was established with the discovery of gelatinized NC and the thereafter developed Single Base (SB) propellant. No smoke, little muzzle flash, more energy, reliability in use, long

Table 2. Heat of explosion and other explosive properties according to [11][12]

Nitrogen content [%]	13.5	13.3	12.5	12.5	Observations
Heat of combustion (constant volume) [J/g]	9475	–	10069	10660	CO_2 and H_2O liquid
Heat of formation [J/g]					Determined from elements at standard state
– constant volume	2386	2482	2641	2901	
– constant pressure	2294	2206	2549	2805	
Heat of explosion [J/g]					Measured in a calorimetric bomb
	4601	4053	3559	–	(H_2O vapor)
	–	4409	–	–	(H_2O liquid)
Detonation velocity [m/s]	7300 (d=1.2)	–	2630 (d=0.3)	–	d: density for the measurement
Specific gas volume by detonation [l/kg]	920	841	880	–	
Shock sensitivity [J]	–	3	1.2	–	Julius Peters impact machine, Bruceton method
Friction sensitivity [N]	no reaction (353)	no reaction (353)	10% (353)	–	Julius Peters friction machine, Bruceton method

storage life – SB propellants show all these positive characteristics.

Used in rifles and guns during the medieval times, SB propellants are still found today in the same types of weapons, of course, tailored to the new requirements.

In nearly all calibers of handgun, rifle, machine gun, aircraft- and antiaircraft gun, cannons and howitzers, SB propellant grains or sticks of any geometric shape can be found. In bigger caliber cannons and howitzers, like those illustrated in Fig. 3, SB propellant grains or sticks can be part of the whole charge.

The following list shows different geometries of SB propellant and their main application:

- Ball powders can be found in ammunition for pistols, rifles and machine guns;

ammunition for rifles can also contain cylindrical grains or short tubes.

- Flake powders are restricted to ammunition for antitank guns and mortars.
- For aircraft- and antiaircraft guns, grains in the geometry of short tubes or hollow cylinders are used.
- In modern aircraft- and antiaircraft guns the use of the more progressive burning 7-perforated grains is normal.
- Tank guns use the even faster burning 19-perforated grains.
- Long stripe- and cross-stick propellants are found in ammunition for cannons and howitzers.

The use of SB propellant in caseless ammunition for small caliber guns, NC with low nitrogen content in combustible cartridge cases and in combustible containers



Fig. 3. Firing of SB ammunition with large caliber cannon. One can see the muzzle flash but not the smoke.

for modular-charges for big caliber guns must also be mentioned.

3. Double Base Propellant

Due to the demand of the military for long distance shooting and therefore more velocity of the bullets and more energy in the propellant, the search for new energetic materials continued. With the addition of nitroglycerine (NG), or other 'nitroglycols', as energetic plasticizers to nitrocellulose (NC), these goals could be met. Due to the solventless production technology for the Double Base (DB) propellants, bigger size propellant grains with large wall thickness (web) and big blocks of propellant with different and complicated geometries became possible.

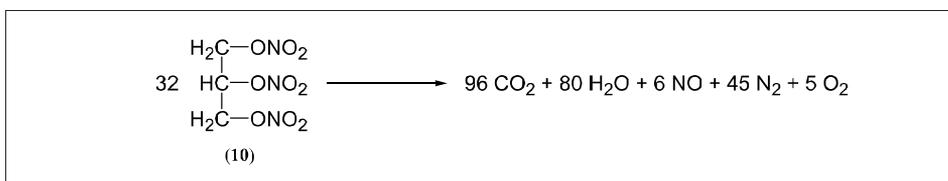
3.1. Nitroglycerine

Nitroglycerine (**10**, NG), strictly glycerol trinitrate, is one of the most commonly used explosives. It is the main component of high explosives such as dynamite as well as an ingredient of most mining explosives and it is an essential ingredient of smokeless, so-called double base propellants.

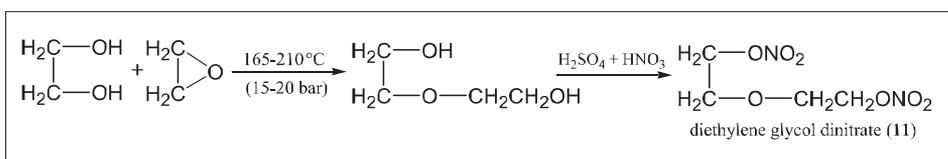
NG is prepared by nitration of glycerin. In the process, glycerin is slowly tipped into a mixture of concentrated nitric and sulfuric acids. The solution is slowly and carefully mixed and the temperature must never exceed 30°C. When the reaction is finished, the mixture is poured into a large amount of water where the NG settles to the ground. The separated NG is washed with water and sodium carbonate until it becomes neutral.

3.1.1. Chemical Properties

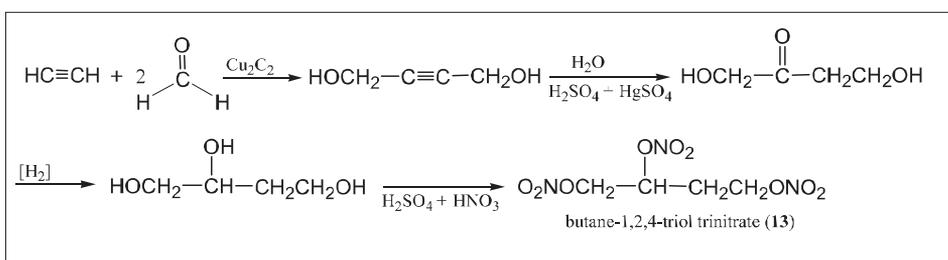
There are two modifications of NG, differing in freezing point and crystalline forms. With respect to crystal structure the modification melting at the lower temperature represents a labile form, which can be transformed spontaneously into the higher melting and stable modification of NG. The melting point and the freezing point, respectively, is about 2 °C for the labile form and 13 °C for the stable form [13]. With such a low freezing temperature, it is not convenient to work with pure NG. By adding other explosive compounds, it is possible to obtain mixtures with a higher freezing temperature. In respect to obtaining mixtures with higher freezing points the capacity to dissolve other nitro compounds in NG was investigated [14]. NG is able to dissolve NC containing a relatively low percentage of nitrogen, as collodion cotton ('pyrocellulose'). Dissolving of NC at room temperature takes a very long time, whereas at 60–65 °C it is completed in 15–20 min. The consistency of the solution obtained depends on the concentration of



Scheme 1. Chemical equation describing the explosive decomposition of nitroglycerine



Scheme 2. The commercial synthesis of diethylene glycol dinitrate (**11**) consists of the conversion of glycol and ethylene oxide into diethylene glycol, following by a nitration process



Scheme 3. Semi-commercial scale synthesis of butane-1,2,4-triol trinitrate (**13**)

NC in the NG and on the viscosity of the NC. For practical reasons, *e.g.* in the manufacture of blasting gelatin, pyrocellulose that gives high viscosity solutions of jelly consistency should be used, even if they contain only a small quantity of NC. This principle applies also for the elaboration of double base propellant formulations. Typically, double base propellants contain 50–60% nitrocellulose and 30–49% nitroglycerine.

3.1.2. Explosive Properties

The explosive decomposition of NG is generally expressed in Scheme 1. The heat of explosion for this reaction is about 6100 J/g. This figure is 1.5 times higher than that of NC. This gain of energy is positive and fulfills the military demand for increased bullet velocity and prolonged range of shooting. The high shock sensitivity of NG and the high flame temperature, which favors gun barrel erosion, was reason to evaluate and introduce other nitroglycols.

3.2. Other Plasticizers Used in Double Base Propellants

Another nitroglycol introduced into double base propellant formulations is diethylene glycol dinitrate (**11**). The commercial synthesis of this compound, illustrated in Scheme 2, consists of the conversion of glycol and ethylene oxide into diethylene

glycol [15]. The nitration reaction is then performed using a mixture of nitric acid with oleum. The compound obtained, diethylene glycol dinitrate (**11**), is much less sensitive to shock than NG and its heat of explosion amounts to only 4480 J/g. Advantage is taken of this low heat of explosion in the manufacture of flashless and non-erosive low calorific smokeless DB propellants. By using a triglycol like triethylene glycol dinitrate (**12**), it is possible to obtain a compound that is insensitive to shock and delivers an even lower heat of explosion (3140 J/g) [6].

Another compound, a polyhydroxylic alcohol ester called 'nitrobutanetriol', is a good solvent for pyrocellulose. It is less volatile than NG and is a chemically stable compound. Its explosive strength is not much inferior to that of NG and its heat of explosion of about 6000 J/g is quite similar to that of NG [15].

Butane-1,2,4-triol trinitrate (**13**) was produced in Germany during World War II on a semi-commercial scale according to the sequence of chemical changes outlined in the Scheme 3 [16].

To further lower the flame temperature and the stress in the loading chamber and barrel during the ballistic cycle, a certain percentage of nitroguanidine (**14**) is added to DB formulations. The resulting propellant is called Triple Base [17] (Fig. 4).

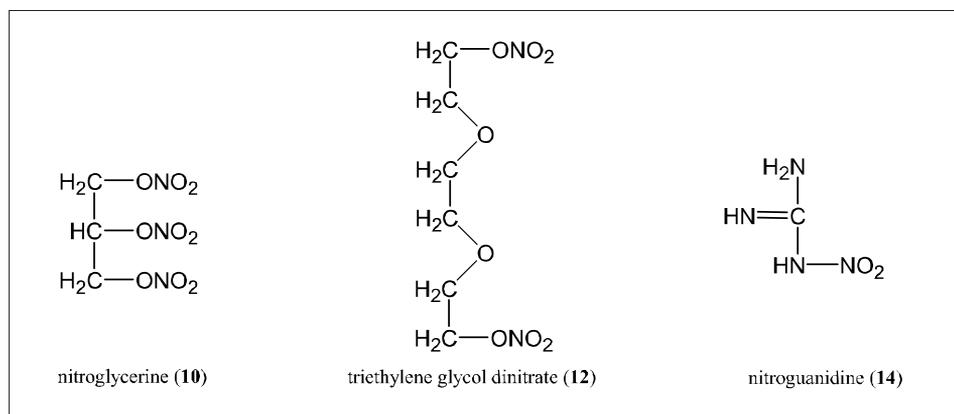


Fig. 4. Chemical structure of nitroglycerine and other common nitroglycols, used as substitutes



Fig. 5. Anti-aircraft missile Rapier. Its launch and flight motor consist both of double-base propellant.

3.3. Application of Double Base Propellants

Large caliber cannons and howitzers use DB (or Triple Base) propellant in the shape of tubes or slotted tubes.

Flake powders are found in ammunition for pistols and grenade launchers.

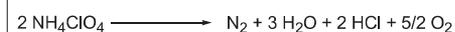
Rockets and missiles: the antitank missile Dragon has rolled up DB propellant sheets in its numerous small motors. The ejection of the missile from the launcher is done by a charge of short tubes of DB propellant. The launch motor of the antitank missile TOW is constructed of big size tubes. The launch motor of the Russian antitank missile RPG-7 consists of DB sticks and the flight motor of a hollow DB cylinder. To produce bigger DB rocket motors, the casting technology is used. An example of this propellant type is the anti-aircraft missile Rapier with its launch and flight phase propellant cast into the same motor, illustrated in Fig. 5.

4. Composite Propellant

The size, dimension, and geometry of propellant grains based on SB and DB propellant is limited. For rockets or missiles with a longer range as guns or long-range missiles, other types of propellants were required. During World War II, the development of the composite propellants began. In the beginning, ingredients used were tar or rubber and an oxidizer. Today, a curable polymeric binder is loaded with an oxygen-rich, crystalline solid (mostly perchlorates), and a metal (mainly aluminum). After mixing, the highly viscous mass is cast into big and complicated molds. After curing either a case-bonded or free-standing solid rocket motor is obtained. Under a case-bonded motor one understands that case and cast-cured motor are one unit, whereas a free-standing motor is a propellant block which is later applied into a case.

4.1. The Oxidizers

The two main oxidizing compounds used in composite propellant manufacture are ammonium perchlorate (AP) and ammonium nitrate (AN). The most frequently used is AP. The explosive salt of perchloric acid is considerably more interesting than the explosive chlorate, because it is more stable and safer to handle. The explosive decomposition, occurring during the burning process, is described in Scheme 4 [18]. One can see that during the burning process a lot of hydrochloric acid (HCl) is developed. With the moisture in the air, this leads to an intense white smoke, so the trajectory and the starting point of the missile can easily be observed. Adding HCl-suppressant substances, like magnesium-aluminum alloys or sodium nitrate, the formation of this white smoke will be reduced. This problem is very important for tactical missiles, but is less important for space exploration. The heat of explosion of AP is 1115 J/g, which is less than that of NC or NG. Because composite propellant must burn for a relatively long time, the burning rate has to be low and a high heat of explosion is not at the forefront.



Scheme 4. Chemical equation describing the explosive decomposition of ammonium perchlorate

AN on the other hand, does not show the problem of hydrochloric acid production, but its main drawback are the different crystal modifications. A crystal modification change in a rocket motor is fatal. It will influence the physical properties, cracks in the propellant could occur enlarging the burning surface. Under operational conditions the propellant produces more gases than the nozzle can manage and the rocket or missile finally explodes. The use of AN for rocket motor technology also needs the addition of a crystal structure stabilizer, *e.g.* potassium nitrate.

4.2. The Reducing Agents

The first fuels used in composite propellants were tar or rubber. Later, with the evolution of polymer technology, more modern polymeric fuels were introduced like polymethacrylates or polybutadienes. The polymers used in rocket propellant technology are quite similar to those used in high explosives technology (PBX). They will not be described in this paper.

As the polymer is only partly responsible for the reducing part of the redox reaction in the formulation, some metals are added in the composition. The most popular ones are aluminum, zirconium (high density), beryllium (very energetic but tox-



Fig. 6. Firing of Ariane 5 with the huge smoke cloud typical for composite propellant motors

ic), boron, and magnesium. The pyrotechnic properties of these reducing agents are not the purpose of this article.

4.3. Application of Composite Propellants

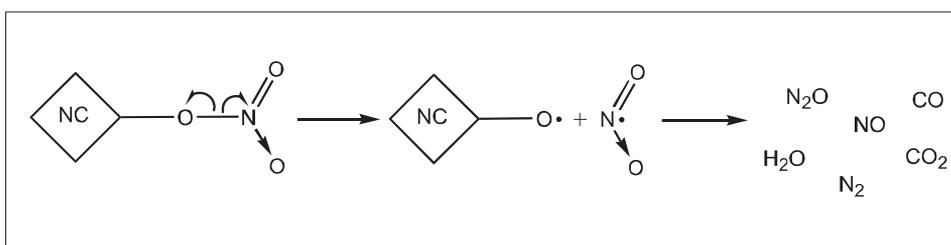
Most of today's air-to-air missiles (Sidewinder, AMRAAM) or ground-to-air (Mistral, Stinger, 9K38 Iгла or SA-18) are propelled by solid rocket motors based on composite propellant.

Very large solid rocket motors are used as boosters for the European Ariane Space Missile (Fig. 6) or the US Space Shuttle. The weight of the composite propellant of a single booster motor for the Space Shuttle is 480 tons!

The only use of composite propellant in guns is restricted to the so-called Base Bleed grains. For extended long range shooting, mostly with 155 mm caliber Howitzers, a composite propellant grain is burned off during the flight of the shell. The emitting gases of the slow burning Base Bleed grain do not deliver thrust, but limit the drag at the end of the projectile. This reduction of drag results in a significantly longer reach of the projectile.

5. Stabilizers of Powders and Propellants

Powders and propellants must contain one or several additives called 'stabilizers', the function of which is to prevent chemical change in the energetic constituents over a reasonable period of time. Any changes could lead to unacceptable variations in the



Scheme 5. The mechanism of the homolytic scission of the nitrate ester of nitrocellulose

mechanical and ballistic properties or increase the risk of auto-ignition during storage.

The problematic nature in NC propellants is the ageing reaction that liberates NO_x into the medium. The primary part of the mechanism of this reaction is the homolytic scission of the nitrate ester of NC, which is illustrated in Scheme 5 [19]. This part of the process is an unimolecular reaction and, according to the kinetic equation of Arrhenius, only the temperature is an influencing factor. The radicals formed during the first step of the reaction exponentially activate the oxidative degradation of NC, which may lead to an auto-catalytic degradation of the propellant. To avoid such an autocatalytic process, stabilizers are introduced in the propellant formulation, to catch the nitrogen-oxides (NO_x) formed during the first part of the degradation reaction. By introducing stabilizers, the first part of the degradation is not influenced but the second part is broken down.

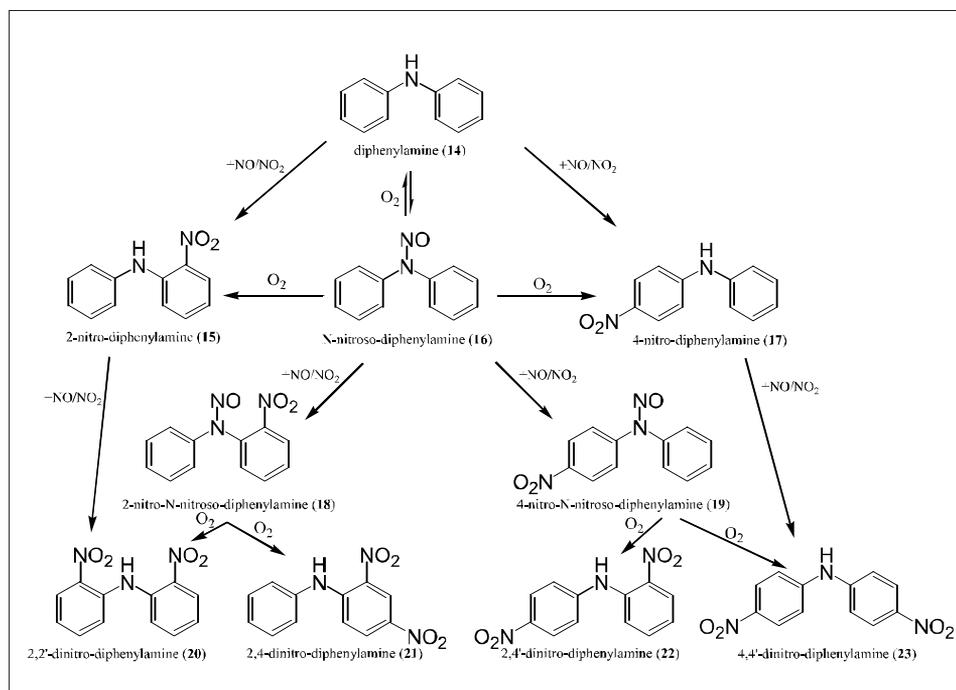
The origin of stabilizers goes back to the invention of powder by Paul Vieille in 1884, who first recommended the use of amyl al-

cohol, but abandoned it after 1905 for diphenylamine (**14**), considered a better stabilizer [20]. It is a colorless crystalline product in which the hydrogen bound to the nitrogen is sufficiently mobile to readily permit substitution reactions, but which also confers a sufficient basicity to promote the hydrolysis of labile nitrate esters like NG. Diphenylamine fixes nitrogen oxides by a series of nitrosation and nitration reactions or transnitrations, which are both sequential and competitive (Scheme 6). A study of the different nitro derivatives of diphenylamine gives precise information about the ageing state of a propellant and of ammunition, respectively. Chemical analysis using HPLC gives a fingerprint of the ageing of the propellant. An example to illustrate the fingerprint of a DB propellant is given in Fig. 7. One can see the main peak of the first degradation product N-nitrosodiphenylamine (**16**), but also the degradation products of the following step: 2-nitro-diphenylamine (**15**) and 4-nitrodiphenylamine (**17**).

According to the work of Marquoyrol [21], if the quantity of diphenylamine introduced into DB propellants reaches or exceeds 3–4%, an incompatibility problem occurs. Since 2-nitrodiphenylamine (**15**) still possesses stabilizing properties and is compatible with NG, it can consequently be used in some double base propellants. The elaboration of more recent stabilizers (Fig. 8) completely compatible with NG and other nitroglycols, allows new DB and triple base propellants to be produced which may be better stabilized and may be stored for a longer period [20]. This also leads to a prolongation of the shelf life of ammunition in a fully safe manner.

6. Combustion Modifying Agents

The velocity of a burning reaction, also called combustion, is given by the steady state of heat production and the efficiency of heat transfer to reach ignition temperature within the material. The combustion of this material is linked to the superficial pyrolysis reaction of the constituents. This re-



Scheme 6. Sequential and competitive degradation mechanism of diphenylamine stabilizer

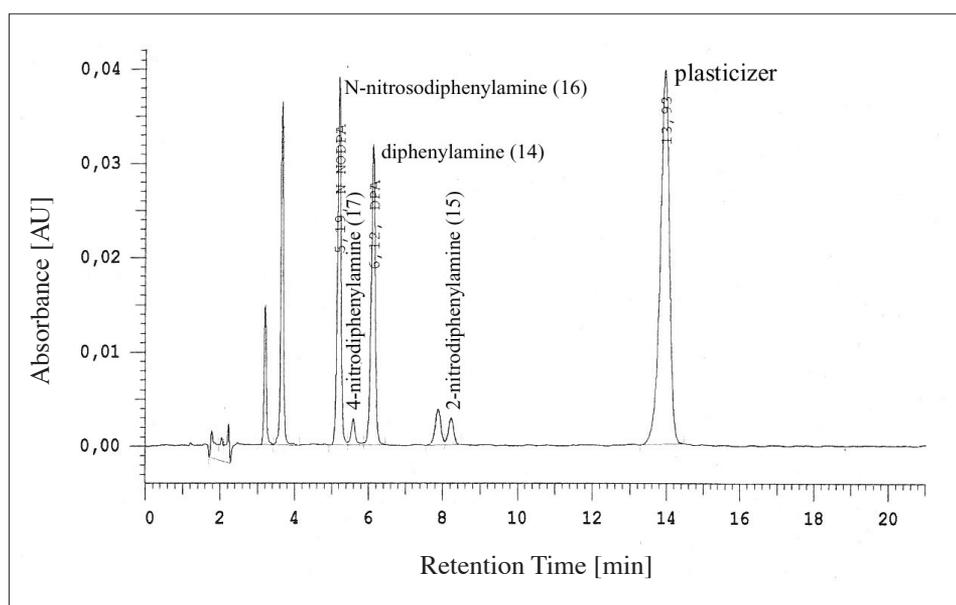


Fig. 7. HPLC chromatogram of a double base propellant, stabilized with diphenylamine. The presence of many degradation products is an indication for a propellant which was manufactured more than 10 years ago.

action produces gases, which react with each other, producing flames with high temperature, not well localized and with a bad reproducibility. This phenomenon has different influences [20], (a) the ballistic stability of the projectile or the rocket is no longer optimal and the performance of the propellant is not constant; (b) the high temperature of the flame favors erosion effects in gun barrels or in rocket motor nozzles; and (c) the muzzle flash, due to the flame, would immediately disclose the position of the gun to the enemy. To avoid such problems, it is possible to act on the pyrolysis reaction or on the flame itself to modify the combustion reaction. Addition of special chemicals will influence the propellant burning rate, impart plateau or mesa burn-

ing characteristics to the propellant at certain pressures, and reduce the sensitivity of the propellant to temperature.

6.1. Burning Accelerators or Regulators

The use of inorganic and metallic salts may enhance the combustion velocity of propellants. For example potassium cryolite, an aluminum fluoride compound (K_3AlF_6), is able to accelerate the burning rate of propellant. Copper chromite ($CuCr_2O_4$), which is used as catalyst for the degradation of perchlorate, also accelerates the burning behavior of propellants. The mechanism of this process is not yet known.

For composite propellants, ferrocene (31) and ferrocene derivatives (Fig. 9), are

known to be efficient burning rate accelerators. It seems that the ferrocene group activates the decomposition of perchloric acid in the first step of the burning reaction. Different ferrocenic compounds have been tested [22] because ferrocene is a solid with a high sublimation tendency. This property leads to a migration of ferrocene to the surface of the propellant. An interesting solution has been found by fixing the ferrocene group to a polymeric chain to avoid this migration phenomenon. The commercial compound Butacene[®] (33) from the French company SME Propulsion, is often used in composite propellants. Catocene (32) is a ferrocene derivative often used in the contemporary propellants. The liquid catalysts have a negative influence on the rheological

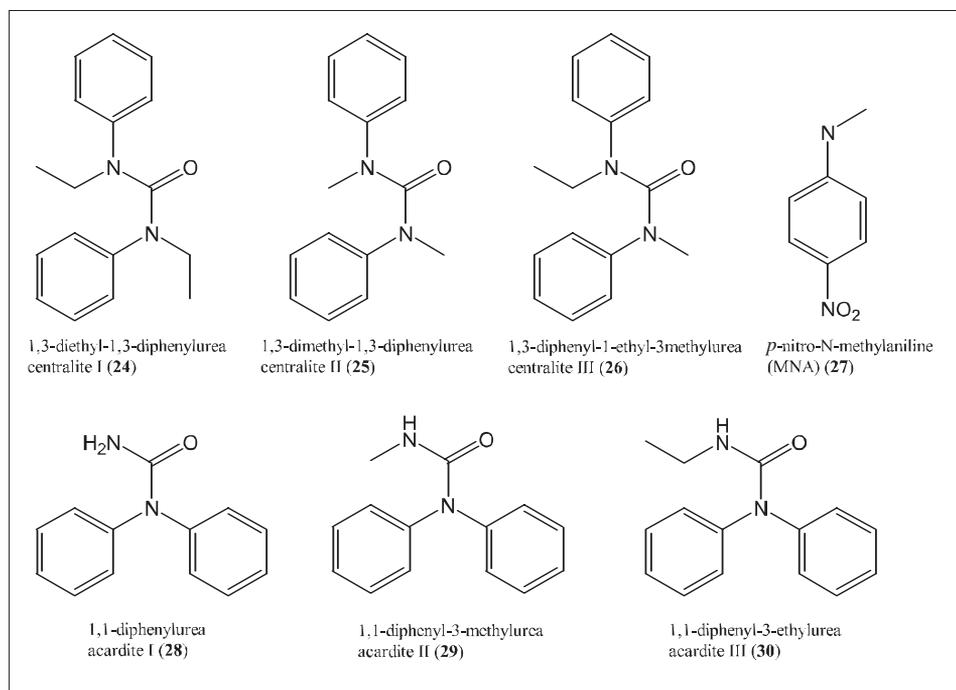


Fig. 8. Chemical structure of the most popular and modern stabilizers

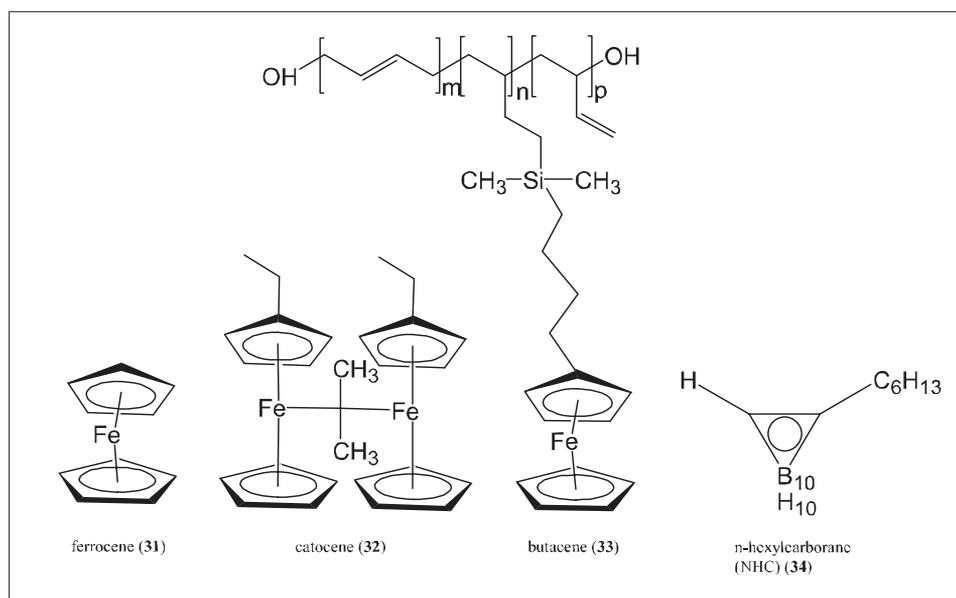


Fig. 9. Burning accelerators or regulators based on ferrocenic or borane compounds

properties of the propellants. To avoid this problem, a new generation of catalyst, based on carborane molecules have been introduced. An example is *n*-hexylcarborane (NHC, **34**) (Fig. 9) [23].

The introduction in the propellant formulation of carbon black, obtained by calcination of hydrocarbons, regulates the burning rate of propellant, leading to a more efficient thermal exchange. Sometimes carbon black may catalyze the decomposition of nitric esters by the influence of free radicals liberated into the microfibers.

6.2. Ballistic Modifying Agents

Ballistic modifying agents are able to modify the general law of combustion

$$v = a + b P^n$$

by introducing a plateau effect or mesa effect. The mechanism of these compounds on the burning process is not well understood. The formation of a large number of free radicals in the burning zone is able to influence the combustion reaction. It is possible that the increase of the pressure at the burning surface is responsible for the observed modifications. The compounds that are used to modify the combustion are combinations of lead and copper salts. The following compounds are usually used for such compositions: lead oxide (Pb_3O_4), copper oxide (CuO), lead stearate (**36**), copper salicylate (**39**), lead or copper oc-

tanoates (**37**), and lead β -resorcylate (**35**) (Fig. 10).

Today, the general use of lead must be avoided. Many research projects are now concentrating on the replacement of lead compounds with a new generation of ballistic modifiers. Nevertheless, in rocket propellants lead and copper compounds have proven to produce better storage stability, ballistic reproducibility, burning behavior, aging characteristics and temperature insensitivity than propellants containing ballistic modifiers free of heavy metal compounds.

6.3. Muzzle-Flash Regulators

The muzzle-flash is due to a post-combustion of gases, carbon monoxide, and hy-

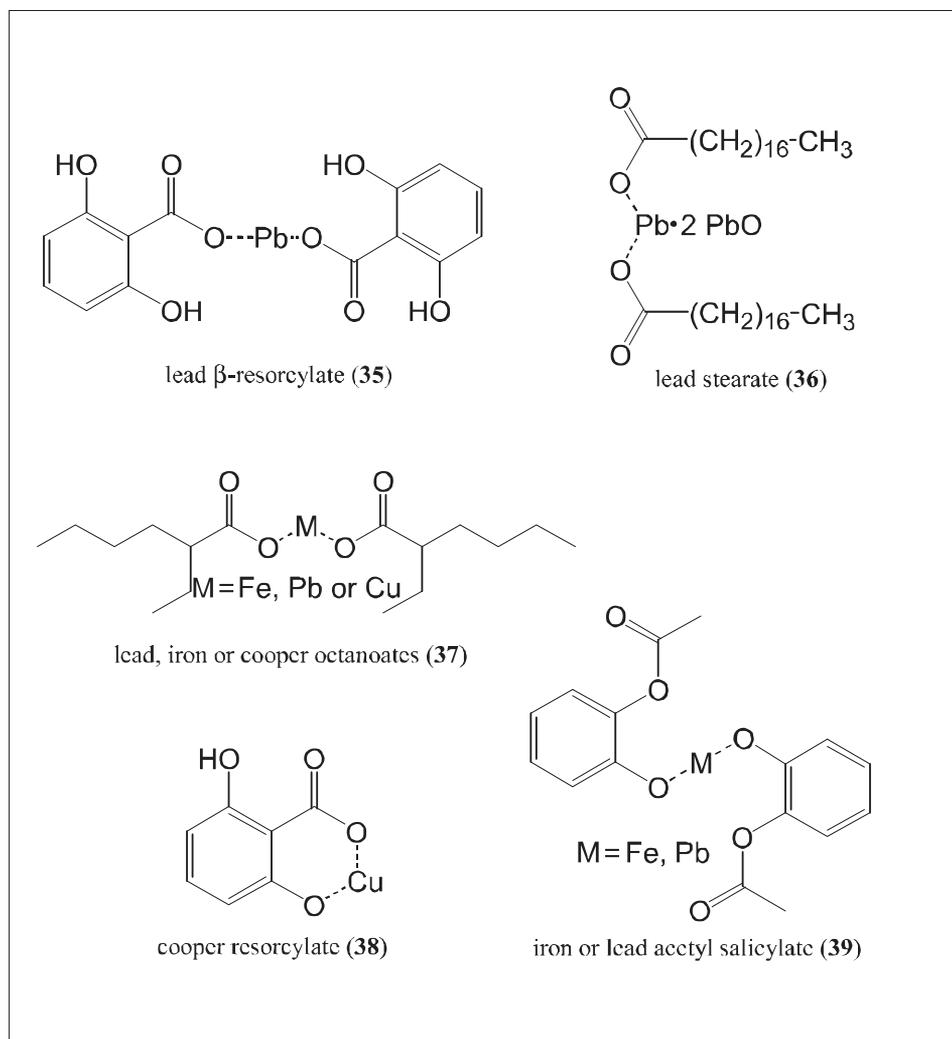


Fig. 10. Chemical structure of the most popular ballistics modifying agents

drogen, resulting from the combustion in the chamber. The incorporation of compounds able to liberate an important quantity of inert gas during the combustion will avoid this post-combustion. The incorporation of nitroguanidine, the principal constituent of triple base propellant, is able to play this important role.

Well-known anticatalysts for the post-combustion phenomenon are potassium salts, particularly potassium sulfate (K_2SO_4). The disadvantage of potassium salts is their high water solubility.

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