HIGH-ENERGETIC MATERIALS IN DEFENCE INDUSTRY

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Abstract
High-energetic materials involve operations with special equipment. An application of new non-traditional materials – composites and nano-materials makes this field highly up-to-date and from a research point of view it is needed to pay attention to it. The paper presents current characteristics of such materials, their classification and supposed trends of their development. Research in the field of high- energetic materials makes a mutual progress conditional on mechanical and electrical engineering, which includes special equipment. The paper also deals with issue of mutual interaction of weapon and ammunition systems containing energetic materials. Work with high-energetic materials is not only a part of work for defence industry as well as a part of work in crisis management, mining, building and other parts of the life of a society.

Keywords: High-energetic materials, explosives, special equipment, nano-materials, composites, crisis management.

1 Introduction

The explosives form a significant part of many kinds of ammunition. The explosives are substances able to produce an explosive transformation (fulminating compounds, traskaviny, high explosives -trhaviny, propellants, streliviny, pyrotechnical composites) [1].

Therefore the ammunition includes projectiles of various kinds, effective heads of rocket systems, hand grenades, bombs, engineering mines, and in accordance with their assignement, they contain explosives or determine their composition [2].

2 High-energetic materials

High-energetic materials are substances able to develop a extremely rapid exothermic reaction associated with development of a huge volume of gases having high temperature [1].

A reaction is launched through an initiation by a mechanical, thermic (thermal) electric incentive or by a blasting wave. Composite explosives may contain substances of an explosive nature (explosives), auxiliary substances adjusting needed features of a composite explosive, as well as substances, that are not explosive. A part of a composite explosive is a substance of a non-explosive nature, as a rule a suitable fuel and an oxidizer, providing a chemical reaction with an oxygen needed for burning, as an amount of an oxygen delivered from an ambient atmosphere is not sufficient for combustion of the compound in a sufficient short time period[3], [4].

The explosives are classified among fuels and sometimes they are designated as energetic materials. The term of an energetic material is a wider and it includes for example components of liquid rocket fuels as well.

By a practical application the high-energetic materials are divided into:

a) **Fulminating compositions** – are easily inflammable explosives, which usually serve to an initiation of high explosives or propellants. They are featured in a transition from an explosive burning into a detonation. They are present at a practical application only in a non-significant amount, e.g. a fulminating composition in a blasting cap - or in an ignition cap e.t.c. The most common types of fulminating compositions are various azides of heavy metals as lead, silver or quicksilver or other substances. Mercuric fulminate is widespread (a popular fulminating quicksilver).
b) **High explosives** – are explosives, which are relatively sparsely sensitive to external influences and on contrary when initiated they can detonate with a high detonation speed. As a rule they are applied at

blasting operations in mines, quarries, in tunnel excavations, demolitions and in charges of military ammunition. The most widely applied fulminating compositions include pentrite, hexogen, TNT and their compounds, then dynamites and a large amount of industrial explosives having different composition. A lot of compound explosives, military ones, but first of all industrial ones, use ammonium nitrate as their basic element. A typical explosive transformation of high explosives is a detonation. In a poor initiation or in a flame ignition many high explosives do not detonate, but they get into an explosive combustion (in an enclosed space), or it burns down as a normal organic combustible (in an open air). The transition of an high explosive from detonation into explosive burning is highly undesirable phenomenon, as a destruction usually occurs, but in a lesser extent than it was planned.

c) **Propellants** – are used as a propellant charge for cartridge cases of fire arms for military, sport and hunting purposes. They are aiming to provide a projectile with the highest mechanical acceleration, also to force a projectile out from a weapon barrel tube with the highest or required velocity through a controlled development of huge amount of hot gases. A black gun-powder and propellants based on nitrocellulose (projectile cotton wool) is an example. Propellants include also rigid fuels. A typical transformation of explosives is an explosive combustion. Velocity of combustion in a propellant varies and it depends on pressure and temperature, at which an explosive combustion takes place. Velocity of explosive combustion increases with an increasing pressure and temperature. In an extreme case, the explosive combustion of the propellant gets down to a detonation –however such behaviour is extremely unwanted, as it results in an accident (it means fragmentation, destruction) of the weapon or a rocket engine. Propellants can be brought directly to a detonation through a sufficiently strong impulse and then they behave as high explosives.

d) **Pyrotechnical composites** – are mixtures of flammables, oxidizers and other auxilliary substances, creating respective pyrotechnical effect. They can be also illuminating and signal compounds, tracer compounds, ignition compounds, flashing compounds, acoustic compounds (whistling sound) and many others. A typical explosive transformation is almost wholly explosive combustion. Sometimes pyrotechnical composites are not included in explosives.

The explosives are classified in high explosives and fulminating compositions due to their practical purpose, but also by their features – a typical high explosive can not be easily activated by a simple impulse; the fulminating compositions in amounts, that are used, are extremely dangerous. While a production capability of a line producing tritole can reach tens of tonnes, a daily capacity of a line producing fulminating compounds represents only tens of kilograms of a fulminating quicksilver or units of kilograms of lead azide or other fulminating compounds [5], [6].

The propellants are divided by their specification in :

- Black gun- powders and pyrotechnical compounds, assigned mainly for ammunition laboration, i.e. activators, tracers;
- Smokeless powders and combustible pastes are assigned mainly for barrel tube weapons;
- Rigid fuels, mainly assigned for rockets

The smokeless powders are divided by their typical elements into:

- Single-compound (nitrocelullose) smokeless powders, a main component is nitrocelullose („nc‟)
- Double-compound (nitroglycerine) smokeless powders, main components are nitrocelullose, plastified with nitroesters (nitroglycerine „ng‟) and (dietylenglycol-dinitrate „dg‟)
- Three-compound nitramine smokeless powders, containing in addition to nitroglycerine and dietylenglycoldinitrate as well crystalline nitramines (hexogen-RDX)
- Three-compound nitroguanidine („nq‟) smokeless powders (for example for 155 mm ammunition)
- Special types of smokeless powders, assigned for laboration of igniters (designation BENITE, or CBI- porous nitrocelullose powder)
- Combustible bodies used as a propellant charge for large caliber munition)
- Spheric powders with a low content of nitrocelullose (about 10%) produced with a special technology [7].

3 Powder charge

Powder charge is made up from powder grains of various shapes (balls, straps, slices etc.). Powder grains are made of powder paste, which is mostly of diglycol, nitroglycerine or nitrocelullose [7].

Fig. 1 Black gun-powder [7]

Black powder usually means a compound of potassium nitrate, sulphur and charcoal. Smokeless powders, nitrocellulose ones, but also nitroglycerine ones, contain some inert substances, that generate smoke as well when fired, that might reveal a firing position during the day. Smokeless powder can be also a mechanical mixture of ammonium saltpeter and charcoal.

From the end of the XVIII century it has been produced having almost the same composition, namely:

75% - potassium nitrate (KNO_3);
15% - charcoal (C);
10% - sulphur (S) [7] .

First, these three compounds are ground, then are mechanically mixed so that they form a homogeneous mixture, that is called black gun-powder after having been pressed in a shape of pressed grains. Composition is changed depending on the application of the powder in practice.

There are powders, where dinitroglycol or nitrotoluene is used during their production instead of nitroglycerine and therefore these powders can not be classified into no class, therefore they form a separate group.

The most typical feature of the powder is a nature of its combustion process and conditions, at which this powder burns down depending on a powder geometry. All powders form mechanical compounds, that do not burn fully regularly and when the powders with a low mass burn down, they are not subject to any combustion rule. All powders of colloid nature (i.e. gelatinate), based on pyroxyline (nitrocellulose) burn regularly, by a combustion rule in parallel layers (geometrical rule). In case, we will consider physical –and- chemical properties of the powder as dividing criteria, the powders can be classified in two main groups:

1. powders – mechanical compounds;
2. powders – colloid compounds (gelatinate).

Mechanical compounds fall then in:

1. Black powders, composed of potassium nitrate, sulphur and charcoal, containing about 75% potassium nitrate , 10% sulphur and 15% charcoal. So the powders prismatic, coarse-grained, artillery ones, rifle, hunting, blasting and timing ones.

2. Ammonia-potassium nitrate powders, containing about 90% of ammonia-potassium nitrate and 10% of charcoal.
3. Other kinds of powders , that are similar to a black gun-powder by their composition, are called powder of colloid type based on nitrocellulose and based on nitroglycerine. Those based on nitrocellulose are gained through gelatinization of a nitrocellulose by means of volatile solution, the others are obtained through gelatinization of a nitrocellulose by means of nitroglycerine. In accordance with a kind of a solution used in a preparation of the powder, they are divided in:

1. Powders with a volatile solvent;
2. Powders with a little volatile solvent;
3. Powders with a non-volatile solvent.

Powders with a volatile solvent contain nitrocellulose and rests of alcohol-and-ether compound, which was a solvent itself, in addition to difenilamine and centralite, being stabilizers, plus admixtures, for example to damp a flame and others. By a purpose and a way of application these powders are classified in:

1. Rifle powders;
2. Artillery powders;
3. Powders for special purposes (burning quickly, flameless, powders with an increased performance etc.).

Powders with a little volatile solvent are divided by their composition in ballistites and cordites. These powders contain nitrocellulose, nitro-glycerine, and centralite, acetone, moisture (humidity), vaseline and other admixtures. Difference between ballistites and cordites is in a fact, that ballistites contain no volatile solvents and nitrocellulose with a mean content of nitrogen is used for their production. Cordites contain rests of volatile solvents and nitrocellulose with a high content of nitrogen (piroxiline) is used for their production. This group of powder includes powders with a dinitroglycol solvent.

Powders with non-volatile solvent are relatively new and meanwhile they are rarely used in practice. These powders contain nitrocellulose (pyroxiline), rigid solvent (trotyl, dinitrotoulene, and dinitroanisol), a stabilizer, some humidity and eventually a small rate of additions (max 2%).

3.1 Smokeless powder

Smokeless powders are explosives, creating hot fumes delivering a movement through their defined explosive combustions to a projectile in a barrel tube when fired. The required inner ballistic features of a smokeless powder are determined by its chemical composition, by features of an applied nitrocellulose, by a way of processing, by a shape and size of a grain, or by geometrical parameters of a grain.

Smokeless powder is used as a driving charge for all kinds of cartridges for barrel-tube arms, from cartridge cases of small shooting arms, through cartridges of medium calibres assigned for canons, up to cartridges for large-caliber howitzers and howitzer systems.

Smokeless powders are compounds based on nitrocellulose, where additional substances are admixed to polymer matrices so that they adjust resulting features, or substances improving the way of their processing. The features of an applied nitrocellulose make a radical effect on mechanical as well as ballistic features of a resulting smokeless powder. Important features of a nitrocellulose are mainly content of nitrogen, and molecular mass of this polymere. Nitroglycerine, diethylenglycoldinitrate, diethanolnitramine dinitrate, pure 2,4-dinitrotoluen, a technical dinitrotoluen (compound of 2,4- and 2,6- isomers), or a so-called liquid trotyl (compound of dinitrotoluen and trinitrotoluen isomers) are used as explosive gelatinators of a nitrocellulose, softening a nitrocellulose matrix and adjusting its explosion heat. Also non-explosive gelatinators (dibutylftalate, or Centralite I) are used for softening the nitrocellulose matrix. Some crystalline explosive fillers (e.g. nitroguanidine, reducing a powder errosiveness) can be added into a softened nitrocellulose matrix. Some organic stabilizers(difenylamine, Centralite I a Centralite II) are added into a compound aiming to stabilize a smokeless powder, chemically binding nitrogen dioxide on themselves, having been generated through a decay of nitrocellulose and other contained organid nitrates. Substances as Centralite I, technical dinitrotoluen, dibutylphtalate, or camphor are used in smokeless powders aiming to slow down a combustion, mainly on surface layers of the powder (a function of surface flegmatizers). Some organic substances based on waxes, vaselines or a transformer oil are added into a powder to improve a compressibility. Anorganic substances play a role of combustion catalyzers in smokeless powders (oxide and lead carbonate, calcium carbonate, tin dioxide), stabilizers (magnesium oxide, calcium carbonate), flame damper (potassium sulphate), substances increasing a grain porosity (natrium sulphate, potassium nitrate), substances improving a powder compressibility (zincous sulphate) and substances improving working properties and a specific mass of the powder (graphite).

Smokeless powders are produced in form of grains of various shapes – slices, rollers, roundels, balls, rings, tubes with one or more (max. seven) lengthwise orifices etc.

Designation of smokeless powders of a Czech production, having been commissioned within the Army of the Czech Republic, as well as in the Armed Forces of the Slovak Republic includes information about a chemical composition of the powder, its geometric shape, dimensions, some features or admixtures, a manufacturer, series, and a year of production.

Smokeless powders are classified by their chemical composition in single-compound nitrocellulose powders having been with no content of explosive softeners using volatile solvents, designated with an abbreviation (Nc). Double-compound nitro-glycerine powders containing nitro-glycerine, designated with an abbreviation (Ng). Double-compound diglycol powders containing diethylenglycoldinitrate, designated with an abbreviation (Dg) and a triple-compound gudole ones containing nitro guanidine, designated with an abbreviation (Gu, or NQ).

The designation following an abbreviation of a chemical composition states a shape of a smokeless powder grain, which is really a little bit smaller, as volatile substances of a solvent release from powder resulting from storage. If the powder has a special designation (e.g. Nc dp C1, Ng sp sample 43), its dimensions and other data are not provided.

Other data include powder designation following its characteristic size, as numerical or written data indicating its features (eg. Explosion heat, or some additives). In case that some powder is produced by license documentation sometimes there is a designation of original powder in brackets (so called equivalent).

The last data in a powder designation is a manufacturer designation and designation of a production series. Manufacturer designation is stated by a code, consisting of three letter designation, or a mark (eg. S&B). Powder series is designated with a serial number, which is the last two figures of the production year.

Homogenized powders are designated with a serial number of a homogenized series, described with Roman numerals and slashed following a year of homogenization. This designation is written or following a designation of an original series, or it is stated separately. Homogenized powder can be designated with a serial number of a homogenized series with Arab numerals and slashed with two numerals of the year of homogenization – it is additional option for designation. Such designation was done for smokeless powders having been homogenized in a laboration works, in such a case, it consists of three numerals always starting with a digit 5. Designation R (retour) after a serial number means, that some part or amount was used from a previous production (series) or from remade older series of the powder [8], [9].

For example a designation Nc tp 3x1,25 / 3,5-F1 WXH 501/80 means a nitrocellulose tube-shape powder with a matrix dimension: 3,0 mm (a grain diameter), 1,25 mm (thickness of a grain wall), 3,5 mm (grain length), surface flegmatized (with camphor- terpenoid), manufacturer WXH, series 501, year of homogenization 1980, allows determining basic parameters without material sheets.

Smokeless powders and a homogenous TPH of a Czech production can be designated also with commercial designation of the manufacturer (Explosia Pardubice-Semtín a.s.), with a starting letter S (a single-compound, nitrocellulose), or with a D letter (double-compound, nitro-glycerine or diglycole or multi-compound ones) and a serial number with three-digit designation (in an older version), or put to five-letter designation (in a newer version), i.e. a serial number (e.g. S 020). The mentioned three-numeral does not express a particular value of features of a smokeless powder, however as a rule the velocity of powder combustion decreases with an increasing number (it is only an orientation aid). The last two digits in a five-digit code (e.g. 02 in a designation D 100-02) represents a modification of a powder mass (e.g. D 100), assigned for a particular customer or an application[8], [9].

The smokeless powders together with homogenous rigid fuels are the least stable military explosives; such instability is caused by a chemical decay (denitriding) of a nitrocellulose and liquid nitroesthers (nitroglycerine, diethylenglycoldinitrate). Whereby nitrogen dioxide is released (dioxide nitrogen and nitrate) and heat, such chemical decomposition takes place at a significant velocity at a normal temperature and therefore if a contact with a nitrocellulose is not prevented through a rising dioxide nitrogen, so a nitrocellulose decay takes place. That is why smokeless powder contains organic stabilizers (diphenylamine, Centralite I, or Centralite II), binding dioxide nitrogen on itself and in such a way it prevents their contacting with nitrocellulose (my research relates with this problem, through which I want to demonstrate a decrease of stabilisers in a long-term storage, through an artificial ageing, as in our ammunition dumps there is ammunition, which is older than 15 years, even older than 20 years). From original stabilisers some nitroso- and nitro- derivates come into being (e.g. N-nitrosodiphenylamine, 2-nitrodiphenylamine, 4-nitrodiphenylamine, 2,4-dinitrodiphenylamine up to hexanitrodiphenylamine rise from diphenylamine). If stabilization efficiency of stabilisers is exhausted then a smokeless powder becomes instable and its auto-ignition may occur.

Decay process of a powder is backed up with:

1. humidity;
2. solar radiation;
3. substances of acid or alkaline nature.

Ageing process also reduces a molecular mass of a nitrocellulose and a content of nitrogen in it that is directly reflected in mechanical features of smokeless powders. (decrease of a tensile strength, trend to a fragmentation due to ignition pressure), even an inner ballistic capacity decreases (i.e. irregular burning, pressure pulses, an intense increase of pressure during combustion of powder when fired), that may result in affecting an outer ballistics of a projectile, or up to a degradation of a weapon during firing, or shots. The inner ballistic features of smokeless powder are significantly effected by a physical instability becoming evident e.g. through a decreasing content of volatile solvents in nitrocellulose powders, through an absorption or releasing humidity, or even a migration of gelatinizators of crystalline elements on a surface of a grain itself or into a powder wrap page (e.g. a paper cartridge case) etc. The migration of nitro-glycerine itself to the grain surface reduces a powder handling safety. A specific characteristics for an advanced decay of a powder is an occurrence of stains, bubble and cracks on a surface of the grains, the powder adheres and changes its shape and becomes tender and falls apart. The last stage of powder decay is releasing of brown smokes of dioxide nitrogen [8], [9].

In explosive testing it is needed to pay attention to a stability of smokeless powders, as their instability can result in extreme cases in an accident of a degradation of weapon systems and explosion in ammunition dumps.

Rise of instability can be detected for smokeless powders through determining their content of volatile substances and their humidity, by a visual control, by determining a content of stabilisers and other extractable elements of the powder through HPLC (High Pressure Liquid Chromatography), determining a period, when an auto-catalytic decay had started, through determining a volume of released decayed gases and through determining inner ballistic features of the powder. Selected parameters need to be monitored also after an artificial ageing process.

4 Conclusion

High-energetic materials are substances, which pertain to an area of ammunition application by their nature. It is necessary to obtain knowledge relating their parameters in their practical application to get their better characteristics and understanding. For that reason, the studies, or issues need to be completed and respective consequences to be drawn. The knowledge should be involved in various regulations and technical procedures and standards in production, storage and servicing of special assignment products, for example in ammunition production.

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