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Biopolymers for Military Use: Opportunities and Environment Implications – A Review

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All of us are responsible for the protection of our environment.

1. Introduction

When reading this title, everyone tends to wonder why is there need to talk about biopolymers in the defense field. Isn't the same subject as for the civil field? Or, are we really debating about bio-polymers?

Allow me to recall two of the most known and used definitions of biopolymers:

- chemicals that preserve their efficacy while maintaining low toxicity;
- bricks of human organs or bones reconstruction.

But aren't they also important puzzle pieces when considering the environment?

In this regard, another definition should be added: biopolymers are substances produced without toxic byproducts; they are biodegradable or, at least, biocompatible, having a minimal impact on the environment.

The governments finance military forces, whose duties are the preparation and conduction of different operations, in order to defend people and land. While maintaining continuous improvement of infrastructure and equipment, military forces must assume a growing significance to environmental compliance and restoration efficiency.

Military purposes include utilization of explosive devices and protection equipment. We may number here also biopolymers used as drug delivery matrices. Or as matrices for drug entrapment, being known that every organic molecule has a particular structure that may imprint in a biopolymer matrix.

It is known that the material and its use are inseparable, and that not every material is suitable for any kind of application. Some of them perform successfully under static conditions, but fail or perform undesirably during real situations. Therefore, they must be evaluated together.

In this context, the obtaining and use of environment-friendly compositions, or biopolymers, in order to minimize the risks of potential accidents, while improving the performances, is mandatory.

2. State-of-the-art

Different environments imply different threats. Regarding the military, the hazards have always existed, either at the work place or in the theatres of operation, conducting to health

threat to personnel. Even from its early history, military medicine focused on the reduction or, more, on the elimination of injuries caused by nourishment, drinks, wastes, insects, climate, equipment worn, etc. (Fig. 1). Though, it was demonstrated recently that risks from occupational and environmental exposures to toxic chemicals, hazardous materials, and common military chemical compounds, should decrease.

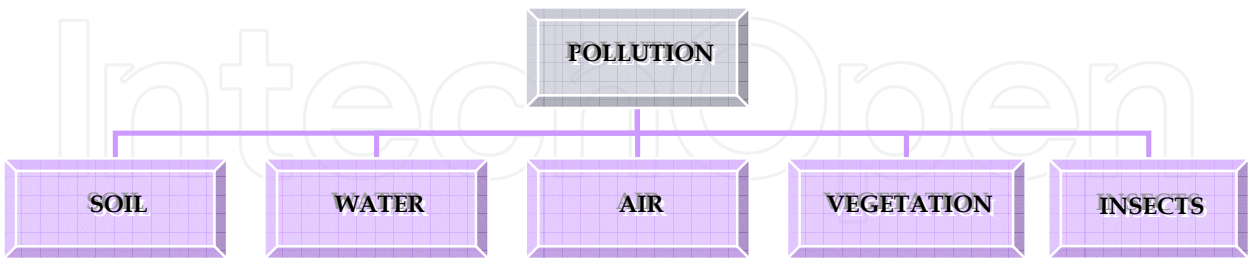


Fig. 1. Indirect influence of natural factors on the humans’ health

In order to accomplish their missions, the staff has to be well trained and healthy. Therefore, occupational and environmental health hazards must be identified and their effects on the health diminished.

Still wondering why biopolymers in military field, then? Due to the actual legislation and concerns, the armies must consider the modification of ammunition compositions, in order to decrease or to eliminate the toxicity ratio to human health and to the environment.

The fields taken into consideration in the present paper are exposed in Fig. 2.

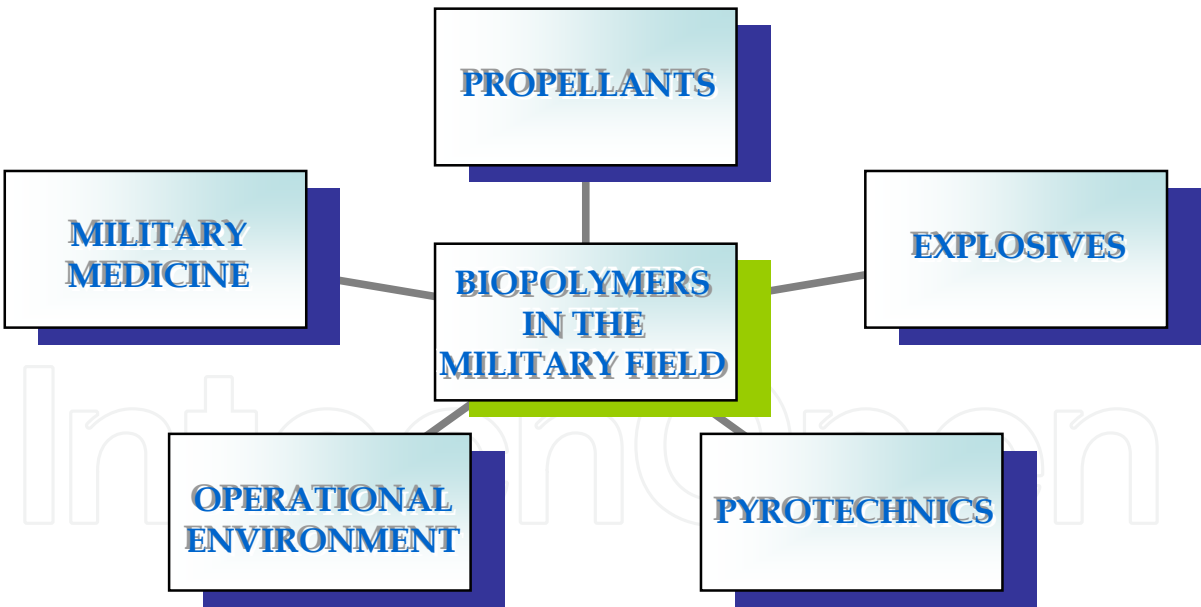


Fig. 2. Fields of use of biopolymers in the army

Firing and munitions testing inevitably conduct to the dispersion of energetic materials and solid by-products in the environment, where energetic materials represent the generic name for any propellant, explosive and pyrotechnics used in weapons or munitions.

Consequently, soil or groundwater contamination by energetic materials, either at the production sites or in military training or testing area occurs. These energetic materials imply a particular environmental concern due to their different chemical, physical and

toxicological properties. Further, every national army has to implement environmental-friendly activities, ensuring that no adverse effect upon the surrounding environment is performed.

All aspects of the life cycle of munitions imply an impact on the environment or human health. Munitions production and firing, demolition procedures and destruction of outdated ammunition conduct to dispersion of energetic compounds into the environment.

Environmental protection should, therefore, be considered versus its effect on the natural environment. Moreover, it is of a great importance to understand the linkages between the effect on the environment and the impact in relation with staff safety, force protection, and force health protection.

Considering the environmental effects of training, operations, and logistics activities, the environmental damage and costs would decrease. A continuous protection of the environment involves availability of the land to conduct real training operations, without encountering environmental issues.

Environmental protection should be recognized in material acquisition procedures, training, and facilities operations. In brief, it should become an institutional and personal ethic, and military staff should become aware that pollution prevention is a proactive measure rather than just a mere compliance or reaction to laws and regulations.

Moreover, the need for strong environment legislation, especially within the context of military units' closure and demilitarization, conducts to important technical studies on the environment impact of munitions and composition modification.

3. Green military chemistry

The concept of Green Chemistry is not new, dating back in the 60's, but only refined and implemented in the 90's, focusing on minimization of the environmental impact of manufacturing processes through the management of energy, wastes, and products.

Its 12 principles, as described by Anastas and Warner (1998), are as follows:

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material feedstock should be renewable rather than depleting whenever technically and economically practical.
8. Unnecessary derivatization (blocking group, protection/de-protection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

11. Analytical methodologies need to be further developed to allow real-time in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

These principles present a multidimensional matrix to guide the design of individual components of any manufacturing process. Life-cycle analysis provides a means to measure how well the principles are being employed, and economics determines whether the process can be commercialized (Slater et al., 2003).

Therefore, these disciplines provide a means to design, monitor, assess, and improve the sustainability of biopolymer production.

4. Propellants

Propellants are designed to produce high temperatures and pressures in a closed chamber for the acceleration of projectiles, rockets, or missiles through the intermediary of the resulting propulsive force. Generally, important burning rates and high temperatures are prerequisites for a propellant (Singh et al., 2006).

In function of their composition, there are two major categories of solid propellants: homogeneous (single-, double-, and triple-base propellants) and heterogeneous propellants (composite and granulated propellants).

Single-base propellants use nitrocellulose (NC) as the main constituent (NC content: 85–96%). Other constituents are chemical stabilizers, such as diphenyl amine and inert or energetic plasticizers, such as dibutyl phthalate, dibutyl sebacate, camphor, or an isomeric mixture of 2,4-dinitrotoluene and 2,6-dinitrotoluene, respectively. In addition to the improvement of the mechanical properties of the propellant, inert plasticizers as well as flame suppressors (such as potassium sulfate or nitrate) act as retardants and coolants, while energetic plasticizers contribute to the total energy output. Single-base propellants are used for all kinds of ammunition for small arms: cannons, tanks, aircraft, and anti-aircraft weaponry.

Double-base (or “smokeless”) propellants were developed for long distance firing with large caliber cannons needing higher bullet speeds and more energetic propellants. Therefore these propellants use NC and nitroglycerine (NG) or other liquid nitrate esters. Because of problems arising from the high freezing point of pure NG, modern mixtures of NG with glycol nitrates, such as diethylene glycol, trimethylene glycol, or other alcohols are used, or the NG is completely replaced. Smokeless double-base propellants consist in 50–60% NC and 30–49% NG or the alternative nitrates.

Triple-base propellants contain nitroguanidine (NQ) as a third constituent in addition to NC and NG. NQ has a low flame temperature, but high nitrogen content. Thus, a large volume of gas is produced upon ignition of these “cold powders”. Their use prevents damage to the barrel of large-caliber weapons.

Long distance solid-rockets and missiles use heterogeneous propellants. These composite propellants consist in an oxidizer, such as, ammonium perchlorate or ammonium nitrate, and a fuel, such as aluminum. The ignition of such a rocket motor produces a huge cloud of smoke particles and hydrochloric acid.

In general, the aim is to produce a large amount of gaseous combustion products with low molecular mass and high combustion temperature, in order to maximize the specific

impulse. In contrast to solid propellants, which are placed directly in the combustion chamber, liquid propellants are injected from external tank into the chamber at the time of ignition (TM 9-1300-214, 1984).

There are two classes of liquid propellants: monopropellants (liquid propellants consisting in a single substance or a homogeneous mixture of substances, such as 80-99% hydrogen peroxide and hydrazine) and bipropellants: a fuel and an oxidizer injected simultaneously. Examples of such fuels are hydrocarbons, alcohols, amines, or hydrazines, as oxidizers hydrogen peroxide, concentrated nitric acid, or nitrogen dioxide. The two components are stored in separate tanks and their simultaneous injection into the combustion chamber initiates the reaction.

When talking about rockets, the characteristics refer to their performances, reliability and, of course, the costs. In the present, the environment impact is also considered, especially when taking into consideration the rocket propellants.

In solid-propellant rockets, the oxidizer is the ammonium perchlorate (NH_4ClO_4) and the fuel is the aluminum (Al). Consequently to the combustion, hydrogen chloride (HCl) and alumina (Al_2O_3) are generated. HCl is known to have a hazardous influence to the environment, and, although Al_2O_3 is not basically harmful, its release as small particles of aerosol represents a potential toxic effect to the human body.

Compounds such as lead (II) salicylate, stearate or, 2-ethylhexanonate are utilized as burn rate catalysts. Military propellants based on beryllium fuels disperse potent carcinogenic beryllium aerosols and can be regarded as severe sources of pollution, despite of their good performance. In other cases, lead oxides, such as PbO , PbO_2 , and Pb_3O_4 or lead (II) chromate or nitrate are, or have been used, as oxidizers in pyrotechnics, especially in “electric matches” (non-explosive fuses). They are utilized for all kinds of pyrotechnic and technical initiation purposes. Furthermore, these lead oxides are occasionally constituents of crackling fireworks and millisecond-delay blasting caps.

Recently, efforts at making lead-free electric matches have increased, through the utilization of nanoscale thermite materials, so-called metastable intermolecular composites (MIC). Apart from avoiding lead compounds, these MICs are characterized by a decreased sensitivity to friction, impact, and heat, coupled with good performance (high combustion temperature).

In this respect, an important issue arises: is it possible to completely replace the solid-propellants?

Researches were performed in this view, and it was found to be very difficult to achieve. Therefore, the idea of a hybrid propellant for the replacement of the solid rocket propellant was embraced.

The conditions to be achieved for the fuel are: high energetic potential and low impact on the environment. In order to meet these needs, organic polymers containing energetic bonds must be considered, such as the azide polymers: glycidyl azide polymer, allyl azide polymer, etc.

5. Explosives

Explosives are materials that detonate. In explosives, a fast reaction produces a very high pressure shock in the surrounding medium. They may be used independent of, or form a part of, ammunition. For military management purposes, the two are controlled as one category of weapons or armaments.

The variation in the properties of explosives is put to practical use in armaments by an arrangement called an explosive train. An explosive train consists in elements arranged upon their decreasing sensitivity and increasing potency. The first element, the initiator, consists in a small quantity of highly sensitive material. This one consists in a primary explosive and other ingredients.

5.1 Military primary explosives

Primary explosives are easily detonated by heat, spark, impact, or friction. In large quantities these materials are extremely hazardous because of their great sensitivity. The other ingredients in the priming composition increase the sensitivity of the mixture to the desired property, such as percussion or heat.

The second element, the booster, contains a larger quantity of less sensitive but more powerful material called a secondary or high explosive. The booster is used either as an intermediate stage to detonate material that is too insensitive to be detonated by the relatively weak initiator or to ensure complete detonation of the main charge. The main or bursting sensitive material but comprises the bulk of the explosive charge (Meyer et al., 2002; TM 9-1300-214, 1984).

Examples of the most common primary explosives are: lead azide, $\text{Pb}(\text{N}_3)_2$, mercury fulminate, $\text{Hg}(\text{ONC})_2$, diazodinitrophenol (DDNP) (Fig. 3-a), lead styphnate (LSty) (Fig. 3-b), lead mononitroresorcinate (LMNR) (Fig. 3-c), potassium dinitrobenzofuroxane (KDNBF) (Fig. 3-d).

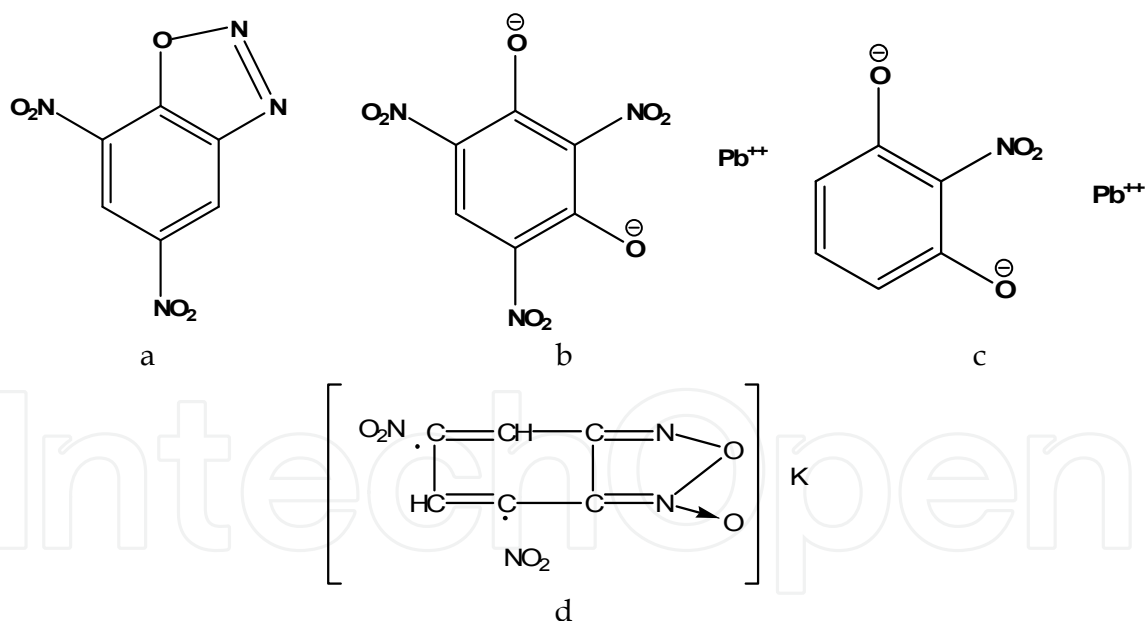


Fig. 3. Structural formulas for: a - DDNP; b - LSty; c - LMNR; d - KDNBF.

5.2 High explosives

Secondary explosives differ from primary explosives in several major characteristics. Small, unconfined charges (one to two grams) of secondary explosives, even though ignited, do not transfer easily from a burning or deflagration reaction to a detonation. Except in the case of dust clouds, ignition by electrostatic spark is difficult. The shock required for ignition is greater for a secondary explosive than for a primary explosive. In some cases, two other

elements, a delay and a relay, may be added to the explosive train between the initiator and booster. The delay is calibrated to prevent detonation of the booster for a specified length of time. A delay is considered a pyrotechnic device. A relay may be required to strengthen the relatively weak output of the delay to detonate the booster.

Aliphatic nitrate esters are compounds prepared by O-type nitration in which a nitro group is attached to an oxygen atom of the compound being nitrated. Some of them are: 1,2,4-butanetriol trinitrate (BTN) (Fig. 4-a); diethyleneglycol dinitrate (DEGN) (Fig. 4-b); nitrocellulose (NC); nitroglycerin (NG); nitroguanidine (NQ); nitrostarch (NS); triethylene glycoldinitrate (TEGN) (Fig. 4-c); pentaerythritol tetranitrate (PETN) (Fig. 4-d); 1,1,1-trimethylolethane trinitrate (TMETN) (Fig. 4-e); cyclotetramethylenetetranitramine (HMX) (Fig. 4-f); cyclotetramethylenetetranitramine (HMX) (Fig. 4-g); cyclotetramethylenetetranitramine (HMX) (Fig. 4-h); cyclotetramethylenetetranitramine (HMX) (Fig. 4-i); cyclotetramethylenetetranitramine (HMX) (Fig. 4-j).

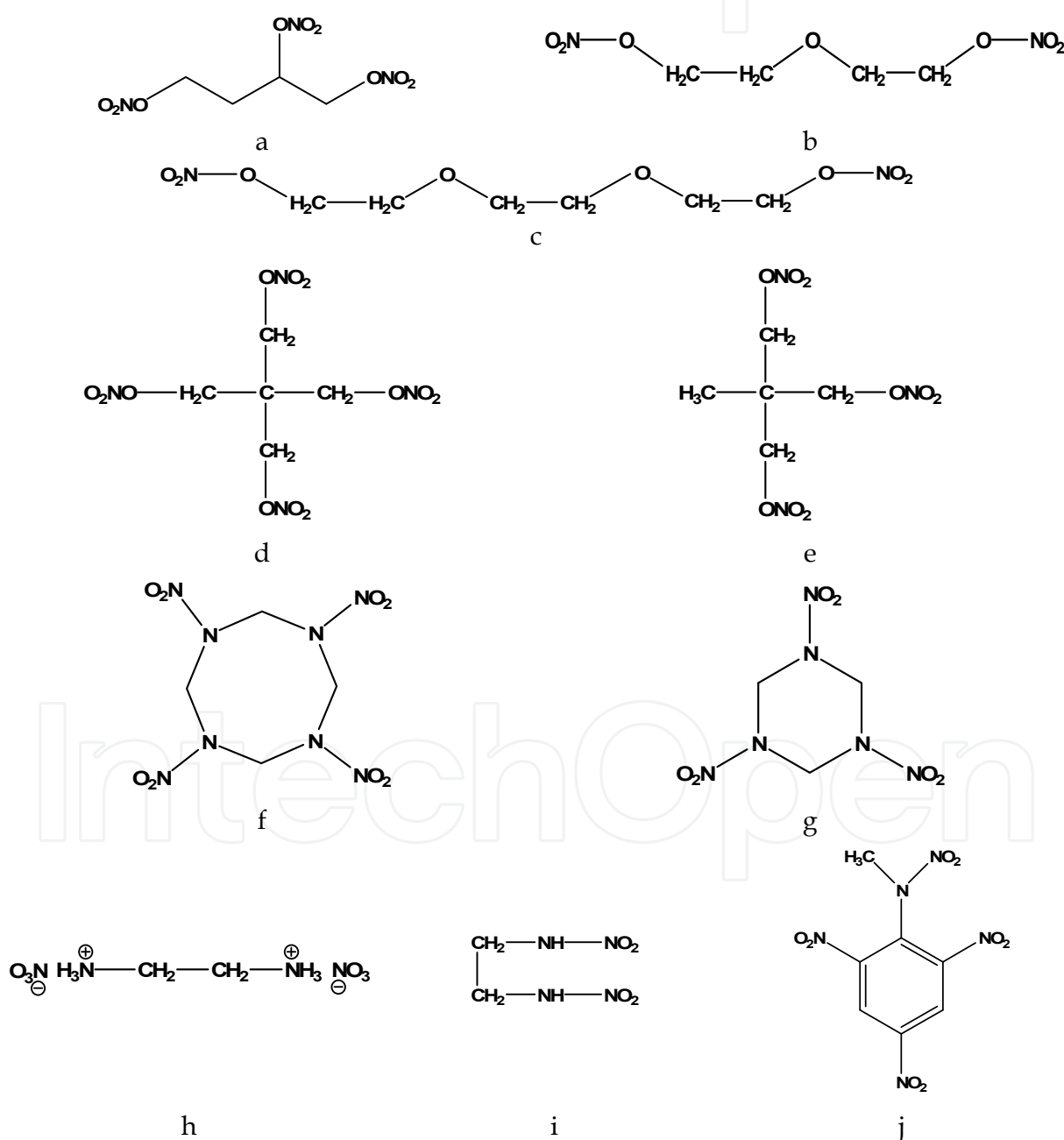


Fig. 4. Structural formulas of high explosives - aliphatic nitrate esters

(Fig. 4-f); cyclotrimethylenetrinitramine (RDX) (Fig. 4-g); ethylenediamine dinitrate (EDDN) (Fig. 4-h); ethylenedinitramine (Haleite) (Fig. 4-i); 2,4,6 trinitrophenylmethylnitramine (Tetryl) (Fig. 4-j).

Nitroaromatics are compounds prepared by C-type nitration in which a nitrogroup is attached to a carbon atom of the compound being nitrated.

In fig. 5 there are given structural formulas of the most known such explosives: ammonium picrate (Fig. 5-a); 1,3-diamino-2,4,6-trinitrobenzene (DATB) (Fig. 5-b); 2,2',4,4',6,6'-hexanitroazobenzene (HNAB) (Fig. 5-c); hexanitrostilbene (HNS) (Fig. 5-d); 1,3,5 triamino-2,4,6 trinitrobenzene (TATB) (Fig. 5-e); 2,4,6 trinitrotoluene (TNT) (Fig. 5-f).

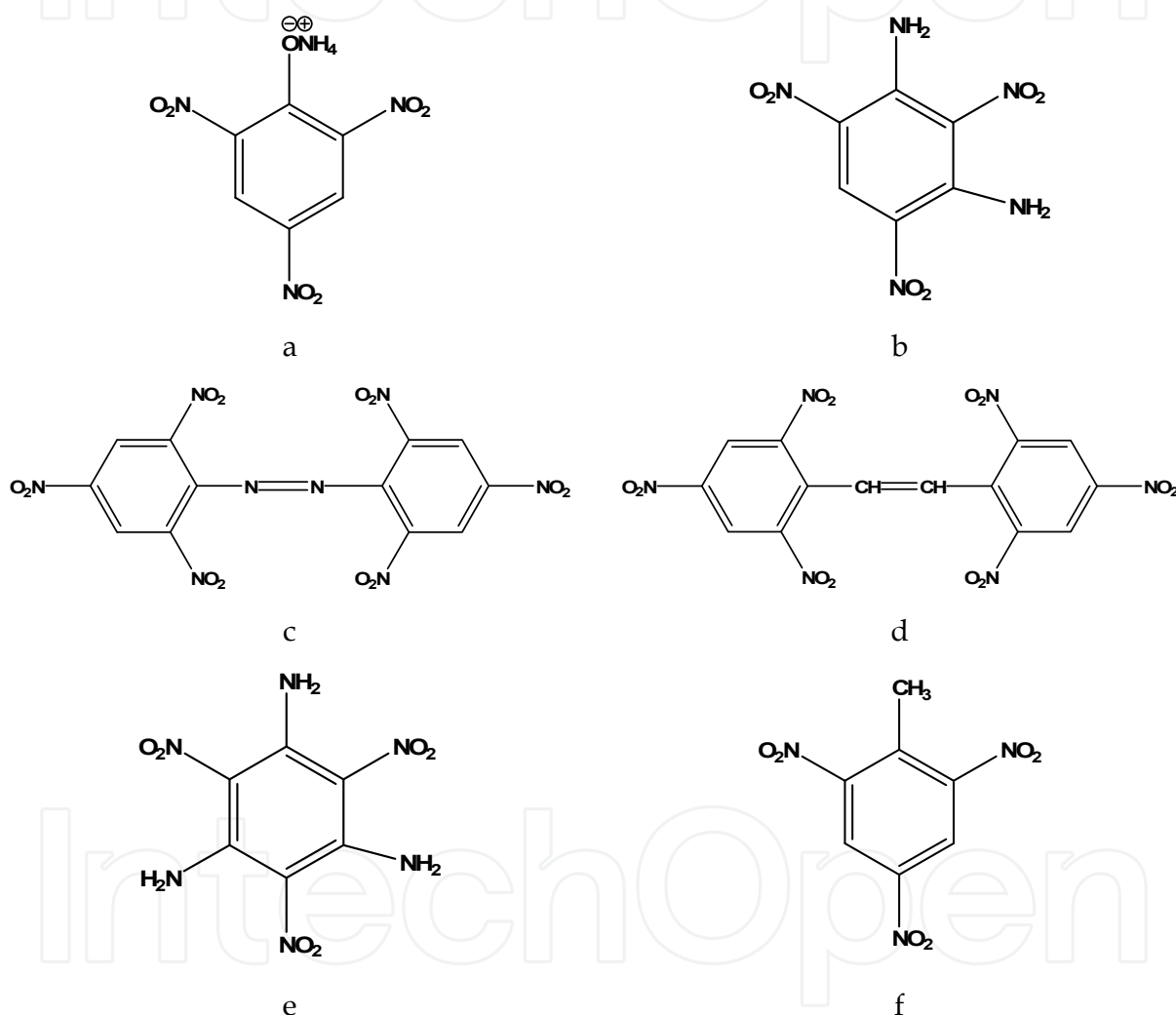


Fig. 5. Structural formulas of high explosives - nitroaromatics

Compositions are explosives in which two or more explosive compounds are mixed to produce an explosive with more suitable characteristics for a particular application. There are:

- binary mixtures, such as amatols - binary mixtures of ammonium nitrate and TNT; ednatols - mixtures of haleite and TNT; octols - mixtures of HMX and TNT; pentolites - castable explosive mixtures of PETN and TNT; tetrytols - mixtures of TNT and tetryl.
- ternary mixtures: amatex (RDX, TNT and ammonium nitrate); ammonals (ammonium nitrate and powdered aluminum incorporated with high explosives such as TNT, DNT,

- and RDX); minols are mixtures of TNT, ammonium nitrate, and aluminum; torpex (RDX, TNT, aluminum powder, and wax).
- quaternary mixtures: depth bomb explosive (DBX) consisting in TNT, RDX, ammonium nitrate, and aluminum.
 - Plastic Bonded Explosives (PBX) contain a large percentage of basic explosives such as RDX, HMX, HNS, or PETN in intimate mixture with a polymeric binder such as polyester, polyurethane, nylon, polystyrene, various types of rubbers, nitrocellulose, or teflon. In some instances a plasticizer such as dioctylphthalate (DOP), DPA, or butyldinitrophenylamine (BDNPA) is included in the ingredients as well as a fuel such as powdered aluminum or iron (Meyer et al., 2002; TM 9-1300-214, 1984).

6. Pyrotechnics

The massive use of polymer materials in the field is driven by their remarkable combination of properties, low weight and ease of processing.

Flame and incendiary compositions represent the oldest chemical weapons, dating back to the caveman's use of flames and burning coals to discourage animals and enemies. While screening smoke was employed in early conflicts, the results of isolated incidents were always uncertain to justify the adoption of smoke as a warfare agent. Dense smoke clouds generated by the black powder became of a great importance. The clouds obscured the field of vision, interfering with aiming and firing, and hampered the movement of troops. More recently, these characteristics have been exploited tactically by the planned employment of screening smoke munitions.

Meanwhile, the development of flame retardant materials requires scientific expertise in the field (Laoutid et al., 2009). Due to their chemical structure, mainly consisting in carbon and hydrogen, polymers used are highly flammable, often being accompanied by the production of corrosive or toxic gases and smoke during combustion. Consequently, improving the fire retardant behavior of polymers is a major challenge for extending their use to most applications (Pal & Macskasy, 1991). Safety requirements are currently becoming more and more drastic in terms of polymers' reaction to fire and their fire resistance performances, while various flame retardant additives, such as halogenated additives, are being phased out for their proven or suspected adverse effects on the environment. The combined challenge thus consists in developing effective and environmentally friendly flame retardant systems for polymer materials (Troitzsch, 2004; Woycheshin & Sobolev 1975).

Also, fireworks, though spectacular and entertaining, are a source of concern because of environmental pollution. A firework disperses the pollutants over a large area. In other cases, such as handheld military flares, however, inhalation of toxic combustion products exhibits a severe health threat.

The substances released upon pyrotechnics decomposition are harmful to the environment. This problem was identified decades ago; however, efforts in this regard are rather recent.

The development of green pyrotechnics is under considerable cost pressure, since it is difficult for new products to compete with the low cost of traditional formulations. Green pyrotechnics therefore need governmental or other external support to succeed (Steinhauser & Klapotke, 2008).

All pyrotechnic compositions contain at least an oxidizer and a fuel. Additional ingredients include binding agents, retardants, waterproofing agents, smoke dyes or color intensifiers.

- a. Oxidizers are substances in which an oxidizing agent is liberated at the high temperatures of the chemical reaction involved. Two oxidizing agents and a fluorine-containing compound are currently used in pyrotechnic compositions. Oxygen is provided by different nitrates: of barium, strontium, sodium, and potassium, perchlorates: of ammonium, potassium, or peroxides: of barium, strontium, and lead. Use of a specific oxidant is determined by the desired burning rate, luminosity, and color. Fluorine is usually provided by polytetrafluoroethylene or chlorotrifluoroethylene.
- b. Fuels include finely powdered aluminum, magnesium, metal hydrides, red phosphorus, sulfur, charcoal, boron, silicon, etc. The most frequently used are powdered aluminum and magnesium. Additional materials such as binding agents, waterproofing agents, and color intensifiers also act as fuels.
- c. Binding agents make the oxidizer and the fuel adhere when compressed into pyrotechnic mixtures. They also prevent segregation and ensure a more uniformly blended composition. Binders also help to obtain maximum density and increased burning efficiency. Non-energetic binders can either be water-soluble (dextrin, polyvinyl alcohol, or arabic rubber) or organic-solvents-based (vinyl alcohol acetate resin, polymethyl methacrylate, or other organic polymers), or solvent-free materials, such as some epoxy binders or Laminac (an unsaturated polyester with styrene cross-links), which binds upon addition of a catalyst.
- d. Retardants are used to reduce the burning rate of the fuel-oxidizing agent mixture, with a minimum effect on the color intensity of the composition. Some retardants act only as inert diluents, while others take part in the combustion reaction at a much slower rate than the metallic fuels. Calcium carbonate, sodium oxalate, strontium resinate, titanium dioxide, polyvinyl chloride, ethyl cellulose, paraffin, linseed oil, castor oil, asphaltum, and sulfur are the most important retardants used. Certain of these serve other purposes as well. For example, sodium oxalate and polyvinyl chloride act also as color intensifiers, titanium dioxide is a source of incandescent solid particles in the flame produced by the composition, and the waxes and oils act as fuels, binding agents, and waterproofing agents, as well as retardants.
- e. Waterproofing agents are applied as a coating on metallic fuels, such as a coating of dried linseed oil on magnesium, or as an ingredient uniformly distributed throughout the rest of the composition. In some cases, the metallic fuel is given a coating by treatment with a solution of acidic or acidified potassium dichromate. Waxes, metal resins, and natural and synthetic resins are used for distribution throughout the composition. Many of these serve also as binding agents.
- f. Color intensifiers are chlorinated organic compounds, such as hexachloroethane (C_2Cl_6), hexachlorobenzene (C_6Cl_6), polyvinyl chloride, and dechlorane ($C_{10}Cl_{12}$). Since they are less reactive than metallic fuels, color intensifiers act to some extent as combustion retardants. Following their physical characteristics, certain intensifiers, such as polyvinyl chloride, can serve also as binding agents.
- g. Smoke dyes are azo and anthraquinone dyes. These dyes provide the color in smokes used for signaling, marking, and spotting.

In the respect of environment protection, green pyrotechnics should primarily avoid perchlorates and heavy metals, taking into account that, for example, the contribution of fireworks to the total annual emission and deposition of lead was estimated to be almost 0.8%.

Chromium was found in scalp hair of factory workers and was identified as the cause of headaches and dizziness. The toxicity of chromium is very much dependent on the oxidation state of the ion, Cr(VI) compounds being the most toxic and carcinogenic compounds (in contrast to metallic chromium, Cr(II), and Cr(III) compounds). For unknown reasons, the chromate cations play an important role in their toxicity.

Although strontium compounds are generally not very toxic, strontium chromate is one of the most potent animal carcinogens ever identified.

Traces of heavy metals (As, Cd, Hg) are found in fireworks as a consequence of contaminated raw materials, but they do not contribute significantly to the total emission and deposition of these elements within the area (TM 9-1300-214, 1984).

Pyrotechnic mixtures are not limited to those using oxygen as the oxidizing species. In terms of green chemistry, compositions based on metals and halogenated organic compounds or polymers, such as magnesium-teflon-Viton or MTV and Al-Teflon/Viton mixtures or similar compositions, are superior to other pyrotechnics because of the poor solubility in water and resulting low bioavailability of both the components and the combustion products (MgF_2 , AlF_3). The environmental compatibility of the Berger mixture using zinc or zinc oxide and hexachloroethane, however, is poor. These mixtures cause the formation of zinc chloride (more bioavailable, though sensitive to hydrolysis) and several organic chlorides.

Derivatives of these compositions have also to be investigated for the achievement of environment protection targets.

7. Operational environment. Disposal, destruction and demilitarization

7.1 Staff protection equipment

Operational shields with overhead and frontal protection are designed for the staff protection. Employees must wear protection equipment when explosive materials are destroyed by detonation or when explosive materials which may detonate are being burned. Also, the wearing of protective equipment is required during exposure or threat of exposure to chemical, biological, radiological or nuclear agents, or unknown agent or agents, when the route of exposure may be inferred from the presence of contaminant on the clothing and skin of victims, while enabling these people to accomplish their assigned missions.

Military protection equipment refers to (EMS; Iacobidze et al., 2003; SLAC, 2009; Wiener, 1996):

- protection respiratory devices: rubbery masks for the protection of the respiratory tract, eyes, and mucous membranes, providing protection against vapors involved in chemical warfare and against biological warfare particles;
- garment ensembles, giving protection against chemical and biological warfare agents and radioactive alpha and beta particles;
- wraps, chemical- and biological-protective for casualties in contaminated environments in which personnel are unable to wear battledress overgarments, the top of the garment having a charcoal lining similar to the BDO, while the bottom being constructed of impermeable rubber;
- individual ballistic protection equipment, against different fragments, splinters and small caliber projectiles, against shock waves from different explosive devices, shells and projectiles; fire-resistant garment;

- gloves, consisting in protective outer glove pairs made out of butyl rubber and an inner glove for absorption of perspiration;
- safety glasses, with permanently attached side shields, required whenever there is a potential for projectile objects in the work area;
- safety goggles and face shields, required when handling any chemical or process that can create fine dust, fumes, mists, and sprays;
- footwear covers, butyl rubber or vinyl overboots for the protection of the combat boots against all agents.

The materials used for those equipments are:

- natural fibers and fabrics, consisting in bulk fibers, yarns, or woven cloth manufactured from plants, such as cotton, wool, linen (flax), sisal, jute, hemp, or silk;
- synthetic materials, consisting in bulk fibers, yarns, woven cloth or other textile products manufactured from polymer-based materials, such as polyethylene, polypropylene, polyamide (nylon), polyester, polyurethane, aramid, or other thermoplastics (butyl and halobutyl rubbers); for example, bullet-proof vests are made of ultra-high molecular weight polyethylene (UHMWPE), with Dyneema and Spectra trade marks of polyethylene-based fibres; shields are made of polycarbonate or polymethyl methacrylate;
- aramid fibers and aramid fabrics consisting in bulk, chopped fibers, continuous strands or woven cloth forms of aromatic polyamide thermoplastic for reinforcing polymer matrix composites and other applications. Nomex, Kevlar, Twaron and Tyvek are trade marks for the most known and used para-aramid synthetic fibers as safety materials, Nomex presenting also a very important flame-resistant potential.

All the materials used are both protective and human-compatible (tested against human skin, eyes, hair), they are practical to wear, light, flexible and cover the vulnerable areas for their particular application.

7.2 Materials disposal

Military polymers and materials cannot be safely disposed by simply dissolving in solution and eliminating, due to the fact that they are water-insoluble, they conduct to toxic by-products, and are hazardous to the environment. Therefore, disposal would consist in burning, detonation, or chemical decomposition.

Destruction methods depend on the quantity and nature of materials to be destroyed, the facilities available, and the land topography. Destruction of explosive materials will be accomplished by burning or detonation. The only exception is made in the case of small quantities of explosives, which can be destroyed by chemical means (TM 9-1300-214, 1984).

It is absolutely prohibited to bury energetic materials in the ground or to dump them in waste places, rivers, or sea. Site selection, physical security, personnel training, emergency equipment, and procedures are governed by environmental regulations, particularly applicable hazardous waste regulations, and by the safety considerations which follow.

Open burning and open detonation operations will be conducted in accordance with applicable air, hazardous waste, and other environmental allowances (Fig. 6). The site selected for the destruction of explosives and other energetic materials shall be located at the maximum practicable distance from buildings or public roads, in order to avoid dispersion of fragments and debris. In all disposal and destruction activities, the quantity of explosives to be safely destroyed at one time shall be determined carefully by starting with a limited

quantity and then gradually increasing that quantity until the optimum amount consistent with safe and efficient operation is determined.

During disposal and destruction operations, the possibility that the mass detonates must be considered and protective measures for the staff and the endowments should be taken. The number of people in the area exposed to the hazard must be kept to a minimum, and the personnel engaged in burning explosives should be provided with flame resistant clothing.

7.3 Demilitarization

The problem of what to do with outdated ammunition to prevent both pollution and hazardous situations from occurring is an enormous one which dates back more than a century. At first glance, two answers become apparent: complete disposal or partial disposal with some recycling. The various chemical constituents of the warhead, propellant, or pyrotechnic are not only explosively hazardous, but are frequently toxic. Disposal by dumping into the oceans, incineration, or detonation have been shown to be not only dangerous but an addition to world pollution and as such, a persistent universal health hazard. Further, the problem of pollution from all military and non military sources became so acute that both state and private facilities are set up to handle pollution abatement and waste recycling. To this end, efforts are developed for safe, efficient, and non-polluting methods of disposal or recycling of outdated ammunition, in particular, their energetic material content.



Fig. 6. Burning of pyrotechnical compositions in the field

Certain energetic materials such as relatively stable high explosives and pyrotechnics can be easily reclaimed and reloaded, but solid propellants, with a limited storage life, require significant degrees of processing before they can be recycled or converted to other products. In many instances, energetic material component recovery was not economically feasible. Energy conservation requirements strongly favor the recycling of energetic materials over pollution-free disposal (or the wasting) of these materials (TM 9-1300-214, 1984).

Preliminary removal of the high explosive charge from a mine, projectile, or shell usually involves the use of hot water or steam to liquefy the explosive, which is then separated from the water by gravity, or contour drilling followed by high pressure water erosion to remove the high explosive residue.

8. Biopolymers and their use in military medicine

Cellulose is the most abundant and most widely used biopolymer. This and related polymers have been produced in the past century and are used in applications including films and injection-molded products.

Like cellulose, chitin is a natural polysaccharide that is extremely abundant. Highly purified chitin, called chitosan, has a variety of medical and food uses and has an important potential of plastic-use. However, there are currently no commercial plastics processes that use chitin as a raw material.

Starch-based plastics find an increased interest in the polymer markets, as biodegradable materials and resins for injection molding. Starch has also been incorporated with non-biodegradable polymers in an effort to have them partially decompose. In this case, only a small portion of the polymer is actually biodegradable (Slater et al.).

Modern medicine has begun to understand and use the benefits provided by biotechnology in health care and casualty care. Practical knowledge of the causes of human disease, biological targets for new drugs, genetic markers, and sophisticated diagnostic tests would increase the effectiveness of medicine (EMS).

As regarding the highly specialized necessities of military medicine, it may provide unique opportunities to absorb these advances at a rapid rate. The developments significantly enhance the capabilities in war-zone medicine. And an increasing number of new capabilities will emerge for carrying out health operations other than war.

A key contributor to this revolution has become biomaterials, and, in particular, biopolymers.

Medical applications of biopolymers include three directions:

- extracorporeal uses: catheters, tubing, and fluid lines; dialysis membranes/artificial kidneys; ocular devices; and wound dressings and artificial skin;
- permanently implanted devices, such as sensory devices; cardiovascular devices;
- temporary implants, such as degradable sutures, implantable drug delivery systems, scaffolds for cell or tissue transplants, temporary vascular grafts and arterial stents.

In this context, biopolymers represent for military medicine an important field of continuous research, in order to improve the characteristics required for the personnel in the theatre.

9. Conclusion

As environmental concerns and the availability of finite resources become increasingly important, the defense industry must begin to focus on the next generation of raw materials

and manufacturing technologies. Manufacturing based on the use of renewable resources as primary feedstocks will increasingly be required to achieve economic and environmental sustainability.

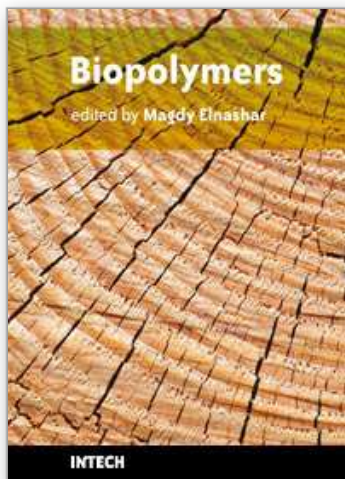
To have a safe, effective, and efficient program of ammunition recycling, ammunition that can be readily recycled must be available. To this end, a new concept in ammunition design has to be conceived. Biopolymers represent a potential alternative to old energetic materials. Therefore, ammunition items (explosives, propellants, and pyrotechnics) will be designed and fabricated so that to be easily and safely recycled.

Meanwhile, each one of us should be aware that terrorists do not care about environment, laws and regulations and the national armies have to be prepared to face properly any kind of attack, using specific protection equipment and endowment, continuously improved.

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Biopolymers are polymers produced by living organisms. Cellulose, starch, chitin, proteins, peptides, DNA and RNA are all examples of biopolymers. This book comprehensively reviews and compiles information on biopolymers in 30 chapters. The book covers occurrence, synthesis, isolation and production, properties and applications, modification, and the relevant analysis methods to reveal the structures and properties of some biopolymers. This book will hopefully be of help to many scientists, physicians, pharmacists, engineers and other experts in a variety of disciplines, both academic and industrial. It may not only support research and development, but be suitable for teaching as well.

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