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Storage of Explosive Materials and Their Physico-Chemical Tests After Many Years of Storage

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Abstract
This article presents a brief historical overview of the components of the munitions testing system containing various types of explosives, their specific characteristics, and describes basic concepts related to explosives. The aim of the article was to assess the basic principles of explosives storage and safe handling during laboratory testing. Standardized methods for the physicochemical properties of explosives contained in munitions are reviewed, along with an explanation of the nature of individual tests. Furthermore, the need to use multiple testing methods or examine multiple parameters for each type of explosive is emphasized in order to obtain the most detailed information about their properties, thereby providing a reliable diagnostic assessment and determining the service life of a given explosive submitted for testing.

Keywords: explosives, specificity, concepts, storage, research methods.

INTRODUCTION

Elements of the munitions testing system, after years of use, were introduced in the 1960s. The rapid development of research techniques, computerisation, and statistical models enabled the development of increasingly effective models for conducting munitions testing, recording them, and processing results. The introduction of standards for munitions testing systematised a number of research problems and algorithms for their evaluation, and the created database of research results conducted over many years is a rich source of knowledge about the processes occurring in individual warfare agents during long-term operation and storage. Analysis of this data enables the selection of parameters that have the greatest impact on the safety and reliability of munitions, and therefore allows for more effective research. The detailed "Instruction on the Quality and Safety

Control of Munitions" (Logis. 3/2010 Ministry of National Defence & Inspectorate for Armed Forces Support) introduced as part of the quality supervision system of munitions in the Polish Armed Forces regulates the functioning of this system and specifies the competences of logistic bodies, research units, military laboratories, certification bodies, operators (military units, material depots and institutions), and manufacturers of munitions. Munitions used by the army are classified as munitions whose uncontrolled operation, in addition to endangering human life, can also lead to significant material losses in the area of their operation. The main factor that has a fundamental impact on the safe operation of munitions is their technical condition. In peacetime, ammunition consumption is relatively low compared to its necessary reserves. Therefore, continuous supervision of munitions used by the Polish Armed Forces is a very important issue. Munitions that have reached the end of their guaranteed technical shelf life (GUP) specified by the manufacturer are subject to periodic inspections, and Technical usability period (opt) assigned by an authorised unit [Agata Kamieńska-Duda 2020, p. 11]. Munitions, like all technical devices, are subject to natural aging processes, which causes changes that reduce their combat usefulness, as well as the safety of use [Figurski J. & Fonrobert P. & Ignaciuk A. 2013, pp. 87-97]. Therefore, being an important component of the country's defence system, they are subject to detailed and systematic diagnostic supervision, which allows for the estimation of the period of further use or the withdrawal of defective batches of ammunition from the army. This need results from the need to ensure a high level of operational safety and operational reliability of the munitions in the equipment of the Polish Armed Forces. The development of explosives research, regardless of the pace at which it develops, is inextricably linked to the constant need to conduct ongoing physicochemical analyses that clearly determine the usefulness of explosives held by the Ministry of National Defence or other institutions with appropriate permits for trading in explosives for consumption.

1. CONCEPT, HISTORY AND SPECIFICITY OF HIGH-ENERGY EXPLOSIVES

Explosives are individual chemical compounds in a liquid, solid or gaseous state or mixtures of various suitably divided homogeneous chemical compounds, in which, under the influence of an external stimulus, an extremely rapid exothermic chemical change can be initiated, spreading spontaneously in an avalanche-like manner throughout the material. Such a rapid chemical change throughout the material is accompanied by the release of dynamically, huge amounts of gaseous products at very high temperatures and very high pressures. The resulting hot and highly compressed gaseous products, when rapidly expanding, are capable of displacing or destroying the surrounding medium. In the vast majority of currently known explosives, this rapid, explosive chemical change is a normal oxidation reaction; however, unlike the oxidation reaction that occurs during combustion of conventional fuels, this reaction occurs without the participation of oxygen from the air. The components required for this reaction, both flammable and oxidising, are contained within the explosive itself, in close proximity to each other, evenly distributed throughout the mass. This is one of the factors that allows for such a rapid reaction. As can be seen from the above, explosives constitute a very convenient, condensed source of exceptionally powerful energy, and for this reason, they are widely used in both military technology and other sectors of the economy, and especially in the mining industry, in quarries, as well as in the large-scale conduct of various earthworks [Cetner W. P. 1986, p. 1]. The explosives industry is therefore one of those fields of technology that is of great importance both for maintaining constant defence readiness in the country and in the overall system of the national economy. The discoveries and practical use of nuclear energy briefly overshadowed classical explosives and inhibited interest in their development. However, nuclear energy cannot completely replace the use of explosives, neither in military technology nor, especially, their peaceful use in the national economy as a specific energy source of exceptionally high power. This statement becomes even more justified when one considers the wide availability of raw materials for the production of explosives, their convenience of use, and the fact that the use of explosives does not entail the threat of radioactive contamination of the environment. [Cetner W. P. 1986, p. 12]. The most popular explosives, in addition to picric acid, include TNT and cellulose. TNT, first obtained by Wilbrand in 1863, is a slightly weaker explosive compared to picric acid, but with satisfactory explosive properties, it is much safer to use, more convenient to handle, and has a wider raw material base. As a result, TNT remains the most important high-explosive material to this day, used to fill almost all types of high-explosive ammunition, both in its pure state and in mixtures and alloys with other explosives, especially with ammonium nitrate. [Budnikow M., Lewkowicz N., Bystrow I., Sirotinski W., & Szechtier B. 1955, p. 9]. Cellulose, the main component of all plant cells, is the most abundant organic substance in nature. It is found in particularly large quantities in fibrous materials such as flax, hemp, bamboo, grass, and coconut fibres. A year before Sobrera discovered nitroglycerine, the German chemist Shonbein first obtained nitrocellulose by treating cellulose with a mixture of hot sulfuric and nitric acids. He used cotton wool as a source of cellulose. When he discovered that the nitrocellulose he had produced was an explosive, he called it guncotton [Brown G. I., 2001, p. 165].

Basic concepts of explosives are, among others:

- Pyrotechnics – this word comes from the Greek language, meaning fire. It is therefore a term for a branch of chemical technology that involves obtaining pyrotechnic masses and making pyrotechnic products from them used to transmit fire and create optical and acoustic effects. [1000 Words on Chemistry and Chemical Weapons, Ministry of National Defence 1987, p. 6];
- Explosion – a set of phenomena accompanying a very rapid transition of a system from one equilibrium state to another, during which a large amount of energy is released;
- Combustion is a relatively slow process that depends heavily on the external conditions in which it occurs (e.g., pressure). In an enclosed space, combustion can evolve into explosive combustion (so-called deflagration);
- Deflagration – an explosion that occurs at a low speed from a few mm/s to several hundred m/s;
- Detonation – this is a type of explosion in which the speed of propagation of the shock wave is the highest possible under the given conditions (it reaches several thousand m/s), so it is an ideal explosion because all the energy that can be used during the explosion is actually used;
- Brittleness is the ability of a detonating explosive to destroy (crumble) the structure of a medium in its immediate vicinity. The cause of brittleness is a shock wave with very high pressure at the front. Brittleness is related to the detonation velocity of the explosive; the higher the detonation velocity, the greater the brittleness. This parameter is determined using the HESSA test. This test involves deforming a lead cylinder as a result of detonating 50 g of the tested material on it. The crushing value H is a measure of the brittleness of a given material. [MON, 1987, p. 7];
- Critical diameter – the smallest diameter of a cylindrical explosive charge within which stable detonation propagation is possible. Critical diameter is a characteristic of every explosive. The smallest critical diameters are achieved by primary explosives, e.g., lead azide crystals with a diameter of 0.05 mm. High-explosives are characterised by a critical diameter ranging from several to several dozen mm;
- The detonation temperature is the temperature to which an explosive must be heated to induce an explosive transformation. Heating the material to the detonation temperature results in rapid decomposition, accompanied by the appearance of a flame and a sound effect – an explosion. The detonation temperature is not the decomposition temperature, because noticeable decomposition occurs at a much lower temperature;

- Durability – this is the ability of an explosive to retain its physical, chemical, and explosive properties over an extended period of time. Durability is an important property that determines its ability to be stored (stored) without the risk of ignition or explosion. Smokeless powders, due to the nitrocellulose they contain, have the lowest durability; they decompose quite easily. To slow down the decomposition rate, i.e., increase durability, several percent by mass of slightly alkaline compounds, so-called stabilisers (urea derivatives, diphenylamine), are added to the powders. These compounds bind the acidic decomposition products of nitrocellulose and its impurities. Durability is negatively affected by an increase in temperature, the presence of moisture, and acidic substances. Explosives from the nitro compound group are characterised by the highest durability. For example, TNT can be stored without the risk of explosion for up to several decades [1000 Words on Chemistry and Chemical Weapons, Ministry of National Defence 1987, pp. 8-9];
- Sensitivity – explosives are substances with a large amount of accumulated energy in a relatively small volume. For this reason, they are considered chemically unstable systems, but they have a certain resistance to external influences, meaning that to initiate an explosive reaction, the material must be supplied with a sufficient amount of energy from an external source. The sensitivity of explosives is the ability to decompose as a result of an external impulse. [Borkowski J. & Fonrobetr P. & Stępień L. 3013, p. 79]

2. SPECIFICITY AND TYPES OF HIGH-ENERGY EXPLOSIVES

Explosives are divided into the following types based on their use:

- ***Initiating explosives*** These are materials that undergo an explosive transformation from a relatively low-energy stimulus. They are therefore very sensitive to mechanical, thermal, and explosive stimuli (flame, spark, impact, or friction). A characteristic property of these substances is the very short transition time to the stationary transformation process (burning or detonation) from the moment the stimulus is activated. Initiating materials constitute a group of explosives with special properties. They differ from other explosives in that they require a small initial impulse and the explosion pressure increase is instantaneous. Due to their lower detonation velocity, these materials are weaker than high-explosive materials, which, given their unequivocally high sensitivity, prevents them from being used as standalone explosive charges. However, they are an essential component of any charge. Without an initiating charge, no detonator could be constructed. [1000 Words on Chemistry and Chemical Weapons, Ministry of National Defence 1987, pp. 12, 14];

- ***Crumbling Explosives*** These materials are significantly less sensitive than primary materials, and are therefore much safer. The basic type of explosive transformation in these materials is detonation, which can only be triggered by a large stimulus, such as a detonating cap. These materials constitute the essential part of the explosive charge and perform a designated "work." High-explosives used in military technology are characterised by the highest brittleness; high-explosives used in mining are significantly cheaper but are characterised by lower brittleness. These materials can have a loose, plastic, or semi-liquid consistency, and can be cast or pressed. [Pankowski Z. 2011, p. 18] The basic concepts characterising the group of high-explosives include the ability to perform work; the concept of "ability" is fundamental. They are determined experimentally for comparison, with the oldest and best-known high-explosives, picric acid and TNT, used as reference materials. The destructive action of an explosive is proportional to the amount of energy released by the explosive, i.e. the force and potential and the ability to perform work. Practically, the capacity for a demolition effect is defined by the volume of the crater created by the explosion of 1 kg of material. A crushing effect is the ability of an explosive material to destroy obstacles with which the material is in direct contact, such as projectile shells (bombs, grenades), concrete structures (bunkers, fortifications), metal structures, etc. It depends primarily on the explosion pressure and detonation velocity. In a remote explosion, the shock wave near the explosion centre exceeds the detonation velocity in speed, and the explosion products are at the wave's head. The last basic concept characterising the group of crushing explosives is cumulative action. [Heger L. 1979, pp. 49, 50-52, 55];
- ***Throwing Explosives*** They are used to impart significant velocity to a projectile or rocket without destroying it. The basic type of transformation here is combustion. These materials are divided into powders, which can be mechanical mixtures (black powder), or physically homogeneous substances (smokeless powder). Rocket propellants, which are usually classified according to their state of matter into liquids and solids. Solid rocket propellants can be smokeless powders or pyrotechnic mixtures consisting of an oxidiser and fuel. Explosives that, due to the nature of the explosion, can be used to propel (launch) projectiles, mines, etc., are called propellants. In addition to the normal properties characteristic of every explosive, these materials possess unique characteristics. Since achieving theoretical conditions is impossible in practice, propellants are required to undergo at least part of the projectile's path through the barrel under increasing pressure. This can be partially achieved by using a material whose explosive

reaction is not a very rapid detonation but rather a slower combustion, called deflagration. Gun powders are typical propellants. The burning process of gunpowder essentially consists of two phenomena: ignition and combustion. By ignition, we mean the spread of the reaction across the material's surface, while combustion is the penetration of the reaction into the powder grain. It is characteristic that the deeper the material's surface, the slower the ignition rate. This phenomenon is important in regulating the ignition speed of the gunpowder charge. [1000 Words on Chemistry and Chemical Weapons, Ministry of National Defence 1987, pp. 12, 51];

- ***Pyrotechnics Masses (Mixtures)*** are mechanical mixtures of an oxidiser (usually chlorates, perchlorates, nitrates, some metal oxides and peroxides and others), fuel (aluminium, magnesium, sulphur, resins, oils and others are most often used as combustible materials), and additives responsible for the flame colouring effect, phlegmatisers that reduce the sensitivity to external stimuli. They are characterised by significantly weaker explosive properties than high-explosives. [Szlachta M. & Seń A. & Czerwińska M. 2020, p. 43]. Based on their effects, pyrotechnic masses are divided into illuminating, signalling, tracer, smoke-screen, and incendiary. The basis of the reaction of each of these masses is combustion. Depending on the purpose, its main effect will be light, or a coloured flame, or heat, or finally smoke. [1000 Words on Chemistry and Chemical Weapons, MON 1987, p. 62];
- ***Explosive Mixtures*** The characteristics of various explosives reveal their advantages and disadvantages, depending on their intended use. In practical use, it turns out, for example, that a given material is too strong or too weak, too sensitive, or too insensitive. To obtain a material with the best properties, explosive mixtures are currently used. By selecting different components in varying amounts, the explosive power, sensitivity, and other properties of the mixture can be freely adjusted. Furthermore, to increase the explosive energy in materials with a negative oxygen balance, an oxidiser is added to the mixtures. The most commonly used solid oxidisers are ammonium nitrate and potassium chlorate. Liquid oxygen or liquid nitrogen dioxide are used as liquid oxidisers. Economic considerations also support the use of mixtures, as inferior and cheaper materials can be used in mixtures, whose negative characteristics can be reduced by the appropriate addition of a higher component. This allows for the conservation of materials based on expensive raw materials or materials that require costly production methods. The use of mixtures also compensates for shortages of certain materials, such as TNT, especially in wartime. Explosive mixtures are divided into gaseous explosive mixtures, explosive aerosols, liquid explosive mixtures, solid explosive mixtures, suspension explosive mixtures,

and emulsion explosive mixtures. [1000 Words on Chemistry and Chemical Weapons, Ministry of National Defence 1987, pp. 12, 51];

- ***Explosive Compounds*** are relatively unstable chemical compounds that, under the influence of external stimuli, are capable of rapid, self-repeating chemical changes that release significant amounts of energy and thermodynamically stable gaseous products. [1000 Words on Chemistry and Chemical Weapons, Ministry of National Defence 1987, pp. 25-27].

3. BASIC RULES FOR STORING AND HANDLING EXPLOSIVES

3.1 Basic Rules for Storing Explosives

An indispensable logistical element of the functioning of military units are military depots and military economic units (*Pl.: WOG*), whose competences and rules for storing and recording combat assets are regulated by the instruction on the management of combat assets in the Armed Forces of the Republic of Poland DU-4.21.4 part 1. It is permitted to store high explosives, ammunition and battlefield simulation equipment as well as explosive objects and hazardous materials, which are specified in the so-called Warehouse Qualification Card. Munitions should be stored in sealed and closed boxes, stacked by assortment, prepared for quick loading (palletised), in accordance with the rules for shared storage. An exception to this rule is the preparation of supplies for military units according to complex requirements. Munitions may be stored unpalletised, but always securely packed in transport crates. All other guidelines regarding the sizes of crates, pallets, and stack heights are described in the aforementioned instructions. It is prohibited to store or transport ammunition and its components in inappropriate or completely unmarked, loose, and unprotected environments, where they are at risk of rubbing against each other, or pose another visible safety hazard. The parameter to be considered when storing munitions is the shock wave pressure that can be caused by an explosion of a given quantity of material contained within them. This value is calculated taking into account the quantity of munitions of a given type, stored using the templates provided in the regulation in question. [Kamieńska-Duda A. 2020, p. 111].

3.2 Rules for Handling Explosives

The properties of explosives, which, even if they are sufficiently durable under certain conditions, are capable of undergoing a violent transformation under the influence of an external stimulus, constitute the fundamental reason for the need to take special precautions when working with them.

It is recommended to use wooden boxes specifically designed for this purpose when transporting explosives. In buildings, materials should be transported in their original packaging or in small, covered cardboard boxes. When working with explosives directly at the workstation, only the minimum quantity necessary for a single test is permitted. No high-explosive materials may be present at the workstation along with the initiating ones. After testing, the remaining explosive material should be closed and the workplace thoroughly cleaned of any remaining material. In many cases, when testing materials, it is necessary to crush them, sieve out the appropriate fraction, or dry them. When performing such operations, it should be remembered that all explosive materials can be divided into three groups in terms of their sensitivity to mechanical stimuli. The first group consists of low-sensitivity explosives (e.g., TNT), the next group consists of high-sensitivity high-explosives (e.g., tetryl, pentrite, hexogen, etc.), and the last group consists of these include primary explosives (e.g., lead azide, mercury fulminate, etc.). Materials in the first group can be ground in a porcelain mortar and in a ball mill. Grinding in a ball mill can be performed using porcelain balls, as well as copper or beryllium bronze balls. Materials in the second group (tetryl, pentrite, hexogen, etc.) must not be ground in ball mills. These materials have an increased sensitivity to mechanical stimuli and therefore grinding them in a ball mill may lead to explosion. In those cases where it is necessary to have explosives with a specific fineness, it is recommended to obtain this fineness by special crystallisation methods (crystallisation conditions, precipitation from solvent, etc.). Materials of the third group (priming explosives), as already mentioned, are particularly sensitive to all types of mechanical stimuli, therefore, special care must always be taken when handling them.

Do not grind the crystals of primary explosives. Dryers intended for drying explosives should be located in a special, isolated room, and each dryer should also be enclosed by a protective screen. Explosives to be dried should be placed in the dryer in cardboard boxes or specially designed glass containers. Drying primary and high explosives should be performed in separate dryers, specifically designed for each type of explosive. Drying high explosives together with initiating substances is strictly prohibited. After drying, the dryers should be thoroughly cleaned of any remnants and traces of explosives. Weighing of high-explosive and propellant explosives is performed on laboratory scales equipped with electrostatic frames in specially designed containers. Explosives, such as many other organic substances, become electrified when poured in a loose (crystalline) state, and there is a risk of electrostatic charge accumulation. This risk is particularly acute when pouring dry explosives heated to elevated temperatures, especially those that are already highly sensitive under normal conditions. Therefore, when drying explosives, it is important to remember that they should only be poured into appropriate containers after they have cooled to room temperature. Glass containers, although not recommended for storing explosives, are often used in laboratory practice for this purpose. When drying a washed glass vessel in a stream of heated air from a blower, an electrostatic charge also accumulates on the vessel's surface. Therefore, explosives, especially those with increased sensitivity to electric sparks, should not be poured into vessels freshly dried in this way. When working with explosives, it is also important to remember that a person can unknowingly pose a certain danger directly due to the possibility of electrostatic charge. A person can become charged to a very high voltage, reaching several kilovolts, and the spark energy upon discharge can reach up to 0.02 J. Therefore, before starting work with explosives with increased sensitivity to electric sparks, especially those with initiating properties, one should eliminate any electrostatic charge by touching a well-constructed grounding system with one's hand. Furthermore, floors in laboratory rooms should have electrostatic properties [Cetner W. P. 1986, pp. 17-25].

4. TYPES OF EXPLOSIVES TESTING

Munitions used by the Polish Armed Forces and other uniformed services are subject to periodic testing to determine the prognosis for their continued use after the end of their technical useful life (GOPT). This is the manufacturer's warranty period for a given product, which for conventional munitions is typically 10 years. [Figurski J. & Fonrobert P. & Ignaciuk A. & Pakuła A. 2013, pp. 17-28]. Physicochemical testing is one component of the entire process to which individual munitions are subjected. Based on the obtained test results, the condition of explosives, which are an indispensable element of individual products used by the army, police, and other uniformed services, can be determined. Appropriate documents are used to meet the qualification requirements for explosives used by the military: laws, regulations, decisions of the Ministry of National Defence, and international NATO standardisation agreements; STANAG and Allied Ordnance Publication AOP. These documents clarify regulations regarding munitions management, but also contain important, detailed information regarding testing, storage, and transportation of materials throughout the ammunition life cycle. One of the main documents specifying physicochemical testing methods for a given type of explosive, which allows for the assessment of new explosives and the technical condition of both explosives and warheads, is STANAG 4170. The technical condition of munitions depends on the conditions in which they are stored. Analyses of the obtained test results have shown that ammunition loses its useful potential most quickly when stored on transport vehicles (combat vehicles) and operated during allied missions. The main factors that influence the rate and course of the aging process of munitions are temperature and humidity. Excessive humidity in the storage area causes corrosion of the metal surfaces of munitions (causing deterioration of the ammunition quality) and promotes the growth of mould and fungi on cotton bags with propellant explosives or on cardboard packaging and elements (e.g. wads, discs, etc.). On the other hand, too high a temperature accelerates the chemical processes occurring in the explosives, which consequently reduces their chemical durability and changes the technical parameters of the explosives. The physicochemical tests to which individual types of explosives are subjected are destructive tests, characteristic for a given group of explosives.

4.1 Aging

To determine a new technical shelf life for a warhead, the explosives contained therein should be subjected to accelerated aging to perform comparative tests before and after the accelerated aging. The accelerated aging process can be performed using two methods: a variable-temperature cycle [PN-V-04002-8 1996] or in accordance with AOP-48 Explosives, Nitrocellulose-based propellants, stability test procedures and requirements using stabiliser depletion. Accelerated aging using a variable-temperature cycle applies to pyrotechnic articles and pyrotechnic mixtures, including heterogeneous propellants. It consists in multi-cycle cooling of the product at a temperature of -50°C for 6 hours, then seasoning at room temperature for 18 hours, and then heating at a temperature of +50°C for 6 hours (which constitutes one aging cycle). [Miszczak M. & Gryka S. 2005, pp. 215-220] In accordance with the AOP-48 agreement, it is possible to carry out a single-temperature or multi-temperature aging procedure for propellant explosives.

Single-temperature aging is used for explosives consisting of known and generally used ingredients and stabilisers. Multi-temperature accelerated aging is used for propellant explosives containing newly developed stabilisers. The multi-temperature aging process involves subjecting a sample of explosives to aging for at least four different durations, with each aging time at minimum four different temperatures. [Szlachta M. & Seń A. & Czerwińska M. 2020, pp. 49,50].

4.2 Chemical Durability Tests

The term "chemical stability" refers to the ability of explosives to maintain their physical and chemical properties unchanged over time. Explosives, especially smokeless powders, contained in warfare agents decompose over time, which can ultimately lead to ignition or explosion. During the initial stages of storage, decomposition of explosives proceeds very slowly. To obtain information on the progress of the decomposition reaction, it is artificially accelerated. Chemical tests are conducted using the following methods:

- **Chemical durability tests – Bergman-Junk method** It is used to test smokeless powders and solid dual-base rocket propellants, burning shells, and nitrocellulose. It involves heating samples of propellant explosives in glass test tubes, in a heating block maintaining a constant, required temperature. For single-base powders, combustible shells, and nitrocellulose, this temperature is +132°C, while for double-base powders and double-base rocket propellants, this temperature is +120°C. Heating the samples decomposes them and releases nitrogen oxides. The value measured by the Bergman-Junk method is the volume of nitrogen oxides generated, which is determined by titration with sodium thiosulfate solution in the presence of starch and potassium iodide and iodate.
- **Chemical stability tests - liquid chromatography** According to the standardisation documents AOP-48 and STANAG 4620; 2007 Explosives, Nitrocellulose-based Propellants, Stability Test Procedures and Requirements Using Stabiliser Depletion – Implementation of AOP-48 is performed by measuring changes occurring in samples at elevated temperatures. The test measure determines the loss and amount of effective stabiliser after artificial aging of explosives at a specified temperature and duration, corresponding to 10 years of natural aging under storage conditions at ambient temperature (25°C). The test is designed to verify that the amount of stabiliser in the finished product does not fall below a safe level after 10 years of storage. AOP-48 allows for the determination of stabiliser content in propellant samples using any validated analytical method. However, this document recommends the use of high-performance liquid chromatography or another method that provides equivalent accuracy and is capable of distinguishing between the designated stabilisers, their decomposition products, and other components. Based on the analyses performed, chromatograms are obtained containing curves in the form of peaks that correspond to the appropriate stabilisers;
- **Durability tests – vacuum stability** test It is a method widely used to determine the chemical stability, chemical compatibility (reactivity), kinetics, and storage of high-energy materials such as single- and double-base powders, solid rocket

propellants, and pyrotechnic mixtures. The VST test is conducted in accordance with STANAG 4556; 1999 – Explosives, Vacuum Stability Test. The stability testing device is equipped with pressure sensors mounted to the test samples of explosives. These sensors continuously record, analyse, and archive the obtained data. Appropriate pressure transducers are used to record pressure changes as a function of time at a constant temperature, i.e., during isothermal testing. The VST technique allows for the determination of the volume of decomposition gases (nitrogen oxides, volatile components) released from the samples during heating of test tubes containing a given explosive. The obtained test results allow for the monitoring and safety management of the production, storage, and warehousing processes of munitions.

- **Thermal durability tests** To determine thermal stability, the requirements of the standardised document STANAG 4515 "Explosives, Thermal Analysis Using Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Heat Flow Calorimetry (HFC), and Thermogravimetric Analysis (TGA) should be followed. This standardisation covers thermal analysis of explosives using differential thermal analysis (DTA), differential scanning calorimetry (DSC), heat flow calorimetry (HFC), and thermogravimetric analysis (TGA). Testing using these methods allows for the verification of changes in thermal properties that may affect the stability and, consequently, the safety and use of a given warfare agent;
- **Thermoanalytical methods (dsc, dta, tga)** Basic thermoanalytical techniques for obtaining information about thermal properties, such as DSC, DTA, and TGA, are characterised by the use of very small sample masses (milligram samples). This ensures high safety during the research, as large amounts of energy can be released during sample decomposition, potentially leading to an uncontrolled exothermic reaction. The sample being tested should be representative and prepared (with appropriate sample size) for analysis to ensure good thermal contact between the substance and the vessel surface. The rate of temperature increase during the test is carefully adjusted to the appropriate sample weight to control the reaction and obtain measurable signals. The obtained thermal curves are used to describe changes occurring in the samples as a function of temperature or time within a given temperature program. Transformations occurring in explosives are depicted on thermal curves as peaks (e.g., melting peak, decomposition peak) or as inflections (e.g., glass transition temperature, mass loss). Differential scanning calorimetry (DSC) involves measuring the difference in heat flow between a test sample and a reference sample under thermally controlled conditions. To perform the measurement, two cells are placed in the measuring cell: one containing

the appropriate mass of the explosive, while the other is empty or contains an inert material (e.g., aluminium oxide). The signal obtained from the device is directly proportional to the difference in heat delivered to the two cells. The determined areas under the peaks reflect the transformations occurring in the test sample. These transformations are accompanied by the release or absorption of energy. Thermogravimetric analysis (TGA) involves measuring the mass loss of the test sample as a function of temperature or time. This technique enables the differentiation of phase transitions based on mass loss, which occur as a result of chemical reactions. Only one vessel containing the explosive under test is placed in the device, and the sample mass is measured directly on the pan assembly. Thermoanalytical methods (DSC and TGA) are used to determine parameters of chemical compounds and their mixtures (particularly explosives) such as glass transition temperature, melting point, phase transition temperature, decomposition temperature, and mass loss or gain within a specific temperature range. DSC and TGA analyses are conducted under an inert gas flow (e.g., nitrogen, air), preventing corrosion of the measuring cell or undesirable oxidation. Furthermore, the inert gas used allows for purging the cell of released gases that could affect the course of the changes.

- **Flow calorimetry (hfc)** - It involves conducting tests under isothermal conditions. The flow calorimeter has a series of thermocouples connected to the test sample holder and the reference sample, making it a more precise method than DSC. The test sample should be representative and properly prepared for analysis. Powders of mixed sizes are placed whole in glass vessels, while larger samples should be crushed and mixed to achieve a fraction of 1-2 mm;
- **Caloric value tests** - involves placing a sample of the tested propellant explosive in a calorimetric bomb, which is then placed in a water calorimeter. The sample is burned in a vacuum, resulting in an increase in the system's temperature. The amount of heat released during combustion of the propellant explosive allows for the determination of the heat of combustion. Propellant explosives subjected to calorimetric testing may be in the form of filings, shavings, or pieces no larger than 2 or 4 mm (depending on the sample's calorific value). A direct current source is used to ignite the sample placed in the calorimetric bomb. The BN-66/6093-12 standard provides two methods for determining the heat of combustion, depending on the calorific value of the tested samples. High-calorific propellant explosives, i.e., those with a heat of combustion greater than 850 kcal/kg, are burned in a calorimetric bomb without the addition of reference powder. However, in the case of low-calorie explosive samples, when the combustion heat is less than 850 kcal/kg, combustion takes place with an admixture of reference powder with known physicochemical parameters;

- **Testing sensitivity to mechanical stimuli** Friction sensitivity tests can be performed using two methods. These are described in detail in STANAG 4487 (edition 1) – explosive, friction sensitivity tests, and the PN-EN 13631-3:2006 standard, Explosives – Determination of Friction Sensitivity. For both methods, the test samples should be properly prepared. If the explosive is free-flowing, it should be sieved through a 500 µm sieve, and the fraction that passes through the sieve should be used for testing. For cast or pressed explosives, they should be crushed using suitable non-sparking tools, ground in a brass or agate mortar, and then sieved through a 500 µm sieve. Explosives in the form of solid charges (plastic material, powder charges, etc.) should be cut into a disc or crushed to obtain flakes. However, in the case of determining the friction sensitivity of a material moistened for transport, first weigh approximately 5 g of the material, place the tested material in a weighing vessel in a thermostatic chamber at 60°C, and dry the sample until a constant mass is obtained. Both methods of determining the friction sensitivity of an explosive material are carried out using a friction apparatus (Peters' device) by placing the tested explosive material (volume of approximately 10 mm3) on a porcelain plate in such a place that the porcelain punch, when lowered with the arm, touches the sample. A specified weight should be suspended from one of the arm's notches. After the device is activated, the punch rubs against the plate surface. An explosive transformation is considered to have occurred when the tester observes the appearance of effects such as flame, smoke, a burning smell, a crackling sound, a weak or strong explosion (it is possible for these effects to occur together). According to the PN-EN 13631-3 standard, if at least one of the effects is observed, the load should be reduced in accordance with the device's nameplate until the load at which an explosive transformation is not achieved in six tests.

  The test allows for the determination of:
  - upper sensitivity limit – the lowest punch pressure at which an explosive transformation was obtained each time in 6 tests;
  - upper limit of insensitivity – the highest punch pressure at which no explosive transformation was obtained in 6 tests;
  - lower sensitivity limit – the lowest punch pressure at which at least one explosive transformation was achieved in 6 tests. Friction sensitivity testing is performed by performing 25-30 tests. After obtaining the test results, they are grouped into a test table and failure, and the 50% point is determined. The 50% point means the determination of the degree of sensitivity when 50% of positive reactions (explosive transformations) of the tested sample occur;

- **Impact sensitivity marking** - can be performed using two methods, which are described in detail in STANAG 4489: explosive, impact sensitivity tests and the PN-EN 13631-4: 2004 standard, explosives for civil uses. High explosives - Part 4: Determination of impact sensitivity. For both methods, samples are subjected to appropriate treatment before testing. Loose explosives should be sieved through a 0.5 mm sieve, and the fraction passing through the sieve should be used for testing. Explosives - cast or pressed - should be crushed using appropriate non-sparking tools and then sieved through a 1.0 and 0.5 mm sieve. Explosives in the form of charges intended for testing, discs with a diameter of 4 mm and a height of approximately 3 mm should be cut out. When determining impact sensitivity, a sample of the explosive is placed in a striking device (pile driver), while a 1, 2, 5, or 10 kg hammer is mounted between the pile driver guides at the appropriate height, depending on the expected upper sensitivity limit of the explosive (checking the literature). An explosive transformation is considered to have occurred when flame, smoke, a crack, or a weak or strong explosion is observed. To ensure that a transformation has occurred, the appearance of the contacting roller surfaces should be checked. When determining impact sensitivity in accordance with the PN-EN 13631-4 standard, the test is performed six times at a given load and hammer height. This allows you to determine:
  - upper sensitivity limit – the lowest height of the hammer drop when an explosive transformation occurred each time in 6 consecutive tests;
  - upper limit of insensitivity – the highest height of the hammer position at which no explosive transformation was observed in 6 consecutive tests;
  - lower sensitivity limit – the lowest height of the hammer drop at which no explosive transformation occurred in 6 consecutive tests.

  To determine impact sensitivity according to STANAG 4489, 10 initial test runs are performed to establish a starting point for the tests. The starting point for the test runs should be the load value based on literature data that gives half the positive results in previous tests or from data for materials with similar mechanical sensitivity. If all positive or all negative results are obtained,
  During the preliminary tests, the tests should be repeated, reducing or increasing the height of the hammer suspension accordingly. If increasing the height of the hammer gives the same results, it should be replaced with a hammer with a greater mass. The starting point for the actual tests should be the average value of the obtained preliminary tests. Determination of impact sensitivity according to from STANAG 4489 involves carrying out 30 tests, after which the 50% point, interval value, standard deviation, standard deviation/interval should be determined. The 50% point (H50) is the height of the hammer drop

at which 50% of positive reactions (explosive transformations) of the tested sample occurred;

- **Testing additional parameters** This test determines moisture content, constancy, and density. These tests can be performed for all explosives: high-explosives, propellants, and pyrotechnic mixtures. Moisture content is determined by heating a given type of explosive at a specified temperature for a specified period of time, in accordance with the BN-66/6091-21 standard. The constancy test for explosives is conducted in two stages and involves heating samples at 75°C for 48 hours. The first stage aims to determine the thermal stability or instability of the explosive mass. If, during the thermal heating of the explosive sample, it changes colour, burns, and/or explodes, the tested explosive mass is considered thermally unstable. If the tested sample does not undergo any of the above changes within 48 hours, the percentage mass loss is determined in accordance with the PN-EN 13631-2:2003 standard. Density determination of all types of explosives is performed in accordance with document AOP-4682:2018 – Energetic Materials. Test Methods for Ingredients, using a gas (helium) pyrometer. The device operates by using gas to precisely determine the sample volume. The volume of an explosive sample is the portion of a previously calibrated measuring chamber that is not occupied by gas. Measurements are conducted in a helium atmosphere under isothermal conditions. Helium, a noble gas, does not interact with other substances at ambient temperature and does not adsorb at elevated temperatures. A vessel filled with explosives to two-thirds its volume is flushed with pure helium, which fills the material's pores much faster and more accurately than a liquid (as occurs during hydrostatic density determination).
- **Ballistic properties tests (manometric bomb)** - A manometric bomb is used to determine the ballistic properties of propellant explosives, among other things. It allows for the study of phenomena accompanying the combustion of gunpowder in a constant volume. By performing tests using a manometric bomb, we can determine the dependence of the pressure of gaseous products resulting from the combustion of the propellant on time. Based on these tests, we can determine the maximum pressure of the gaseous products and the vigour of the propellant explosives. The NATO standardisation document STANAG 4115 (2nd edition), Definition and Determination of Ballistic Properties of Gun Propellants, describes the use of a manometric bomb to determine the ballistic properties of propellant explosives necessary for internal ballistics calculations and specifies the conditions for comparative testing between individual research institutions. According to this document, we can directly determine the rate of pressure increase and the vigour of propellant explosives.

Due to thermal losses and thermal expansion of the manometric bomb, the co-volume and powder force cannot be used for ballistic modelling; however, they are applicable for indirect calculations of burning rates. Furthermore, the above document specifies the parameters that must be met by the measuring equipment. The most important element of the test system is the pressure sensor, necessary to record the pressure increase in the bomb during combustion of the propellant. According to STANAG 4115 requirements, this sensor must be a piezoelectric sensor with a minimum frequency of 25 kHz. The obtained ballistic parameter results are compared with the data contained in the technical documentation for the given product, and based on this, the feasibility of further use of the tested munitions can be determined.

- **Destructive testing** After completing the physicochemical tests of the munitions components and the explosives contained within them, all residues are transferred to destructive testing, which is the final stage of the entire testing cycle. Depending on the type of explosive, this stage can be carried out by combustion or destruction using a stimulating explosive charge. The basic method of destructive testing of various types of munitions residues is their destruction using an explosive charge. Explosives of normal potency are typically used. When conducting destructive testing, attention should be paid to the safety of those directly involved in the work, as well as bystanders living in areas adjacent to the designated work areas. When planning the destruction of munitions residues after testing, the weight of the explosive should be precisely determined to ensure that the permissible detonation quantity in a given area is not exceeded. [Szlachta M. & Seń A. & Czerwińska M. 2020, p. 54-68].

CONCLUSION

Knowledge of basic concepts, the specific nature of explosives, and the basic principles of handling them ensure maximum safety for laboratory workers conducting tests. Physicochemical properties are an extremely important step in the diagnostic testing process for both new and long-term stored explosives, as they allow for the assessment of the current and accelerated aging technical condition of explosives and the presentation of long-term forecasts for their future performance. Detailed tests of thermal properties, chemical durability, sensitivity to mechanical stimuli ensure safety during storage, transport, and handling of a given munitions agent, as well as its operational reliability during use. Scientific and technical units and research institutes are important elements in the fields of science and engineering, but in the case of munitions diagnostics, a comprehensive assessment is necessary. As a result of acquired experience, its principles and procedures have been gradually improved to provide the broadest possible picture of the condition of munitions used by the Polish Armed Forces and other uniformed services based on test results. The development of a diagnostic system enabling the issuance of an opinion on the forecasting of the shelf life of explosives enables the monitoring of their qualitative condition.

BIBLIOGRAPHY

[1] AOP-48 Explosives, Nitrocellulose based propellants, stability test procedures and requirements using stabiliser depletion.

[2] AOP-4682. (2018) 2018 – Energetic materials. Tests methods for ingredients.

[3] BN-66/6091-21. Explosives. Determination of water content; PN-C-86002; 1961 Black powders. Determination of moisture, hygroscopicity and chemical composition.

[4] BN-66/6093-12- Smokeless powders. Designation of combustion heat.

[5] Borkowski J., & Fonrobert P., & Stępień L. (2013) Elements of quality, construction and design and properties of explosives of warfare agents, PTU issue 125 WITU.

[6] Budnikow M., & Lewkowicz N., & Bystrow I., & Sirotinski W., & Szechtier B. (1955) Explosives and Elaboration, Ministry of National Defence.

[7] Brown G. (2001) A History of Explosives. Books and Knowledge.

[8] Cetner W. P. (1986) Chemistry and Technology of Explosives – Preparation of Explosives and Intermediate Products. Military University of Technology.

[9] DU-4. 21. 4 part 1. (ref. Uzbra. 2646/2014). Instruction on the management of combat assets in the Armed Forces of the Republic of Poland.

[10] Figurski J., & Fonrobert P., & Ignaciuk A. (2013) International regulations on reporting of accidents involving munitions, Problemy Techniki Uzbrojenia R.42, no. 4.

[11] Heger L. (1979) Encyclopedia of Explosives, Warsaw University of Technology.

[12] Kamieńska-Duda A. (2020) Supervision over the operation of combat assets in the context of the security of the functioning of military units of the Armed Forces of the Republic of Poland.

[13] Miszczak M., & Gryka S. (2005) Analysis of NATO and Polish standardization documentation in the scope of testing the physicochemical stability of solid heterogeneous rocket propellants, "Problemy Techniki Uzbrojenia no. 3(96).

[14] PN-EN 13631-2. (2003). Explosives for civil uses. High explosives. Part 2: Determination of thermal stability of explosives; PN-EN 268: (1993) – Propelling explosives for commercial ammunition. Requirements and test methods.

[15] PN-EN 13631-3. (2006). Explosives – Determination of friction sensitivity.

[16] PN-EN 13631-4. (2004). Explosives for civil uses. High-explosives, part 4.

[17] PN-V-04002-8. (1996) Pyrotechnic mixtures and pyrotechnic articles. Physical and chemical stability. Testing of resistance to long-term storage using variable temperature cycles.

[18] Pankowski Z. (2011) Incendiary materials used in ignition systems of modern artillery ammunition, PTU issue 120, WITU Publishing House.

[19] Collective work. (1987) 1000 words about chemistry and chemical weapons, Ministry of National Defence

[20] Stanag 4115 (II edition), denifition and determination of ballistic properties of gun propellants.

[21] Stanag 4170 Principles and methodology for the qualification of explosive materials for military use.

[22] Stanag 4487 (edition 1) – explosive, friction sensitivity tests.

[23] Stanag 4489 explosive, impact sensitivity tests.

[24] Stanag 4515 Explosives, Thermal analysis using differential thermal analysis (dta), differential scanning calorimetry (dsc), heat flow calorimetry (hfc), and thermogravimetric analysis (tga).

[25] [Stanag 4556 (1999) - Explosives, Vacuum stability test.

[26] Stanag 4620 (2007) - Explosives, Nitrocellulose based propellants, stability test procedures and requirements using stabilizer depletion – implementation of AOP-48

[27] Szlachta M., & Seń A., & Czerwińska M. (2020) Warfare materials and agents. Research and development on safety.

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