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Impact of TNT Storage Time on Its Physicochemical and Explosives Properties

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Abstract. The Polish Armed Forces have very sizable stocks of explosive ordnance, of which some have exceeded the allowable service life. From the point of view of ageing and acceptable ways of disposal, some high explosives cannot be used if they have been stored for years. That is why studies are performed on the safety of utilizing such kinds of explosive ordnance. During the storage period, high explosives' physical and chemical parameters deteriorate. For example, the sensitivity of such materials increases, resulting in them becoming dangerous. Therefore, diagnostic tests to determine the quality of high explosives for further use (extending the exploitation period or referral for disposal) are conducted. The main goal of this work was to compare how the effect of the ageing process impacts the physical and chemical properties of high explosives and those containing 2,4,6-trinitrotoluene in particular. Many factors effectuate the quality of the stored high explosives, e.g. acidity, melting point, decomposition temperature, friction- and impact sensitivity. The authors investigated high explosives from selected mines produced in different periods and compared these results with those obtained from testing mines of previous years.

Introduction

Considering that Poland has significant stocks of explosive ordnance with some exceeding allowable service life, monitoring the impact of storage time on the physical and chemical properties of 2,4,6-trinitrotoluene (TNT) is a pertinent issue.

TNT's popularity stems from its low melting point (i.e., 80.65°C) and the process occurring with no decomposition. This makes TNT readily cast. TNT is used as an admixture with many other high explosives, mainly due to the low melting point. Comparative studies with other explosives, such as penthrite (PENT), Royal Demolition explosive (RDX) or octogen (HMX), corroborated that TNT is highly stable and has a low sensitivity impact. Studies also reported it being distilled under vacuum (10 – 20 mm) at 210 – 212°C without decomposing. The first significant drawback of the TNT lies in the high environmental impact of the required production process, which caused it no longer be produced in Canada and the USA. Furthermore, the United States record a surplus of this explosive, and research and production are focused on even more powerful compositions. [1]

In Poland, the TNT is still the primary explosive used for explosive ordnance. This is attributable to, first of all, its properties, as it is a durable material, resistant to ageing processes and can retain its performance parameters for an extended time.

From the point of view of ageing and acceptable ways of disposal, some types of high explosives cannot be used if they had been stored for years. That is why safety studies of explosive ordnance determining their safe use are carried out. During the storage period, physical and

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chemical parameters of high explosives deteriorate, for example, the sensitivity of such materials rises, resulting in them becoming dangerous.

Moreover, it needs to be remembered that TNT is highly susceptible to photodecomposition [2,3], it reacts easily in an alkaline environment [4], but even though materials that could replace TNT have been sought for over a century, it is still the most commonly used component in the production of high explosives [5] and for almost a hundred years – as a high explosive component of explosive ordnance.

The authors conducted diagnostic tests to determine the quality of high explosives for further use (extending their exploitation time or referring them for disposal) which were enacted under the explosive ordnance quality control and safety system. To evaluate the quality of explosive materials, the authors focused on acidity, melting point, decomposition temperature, friction- and impact sensitivity.

The main goal of the project was to compare, how the effect of the ageing process influences the physical and chemical properties of high explosives, as there are many factors reflecting the quality of the stored high explosives, e.g., acidity, their melting point, decomposition temperature, friction- and impact sensitivity. The same parameters are considered when developing new explosives, especially explosive mixtures, to determine the potential reactions between the components of the mixture and its stability (which is important during long time storage in various conditions). Analysis of high explosives from selected mines from different manufacturing years was performed and the comparison of the results with those obtained in previous years was conducted by the authors.

Experimental Part

To evaluate the quality of explosives, acidity, melting point, decomposition temperature, friction and impact sensitivity testing was performed. The investigation was done according to the following STANAG military standards: "Specification for TNT for deliveries from one NATO nation to another" (STANAG 4025), "Explosive, friction sensitivity tests" (STANAG 4487) and "Explosives, impact sensitivity tests" (STANAG 4489).

Friction sensitivity tests were performed using a friction tester, whereas impact sensitivity tests were carried conducted using a BAM Fallhammer (BFH 10) and thermal analysis involved the use of a TGA/SDTA apparatus.

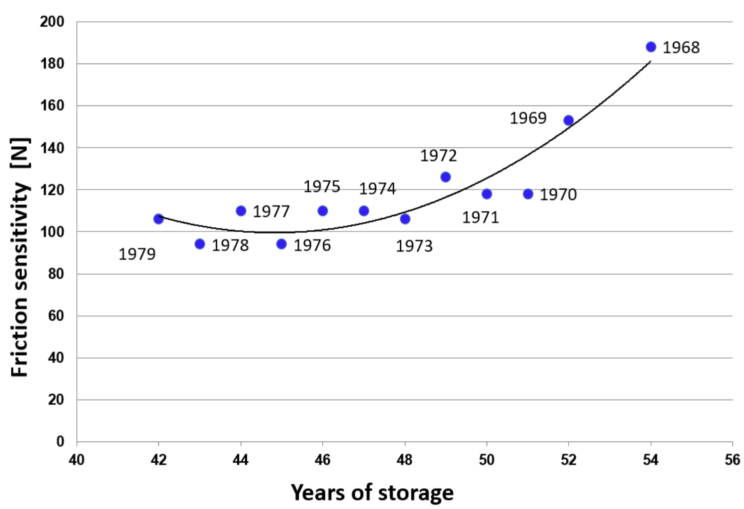

Fig. 1. *Friction sensitivity as the function of the years of storage, indicating the TNT ageing process*

Acidity testing consists in determining the content of free acids in samples of an explosive by dissolving the tested sample in acetone, adding H_2O and titrating Na_2CO_3 against a mixed indicator. Selected results for TNT friction sensitivity, impact sensitivity and melting temperature as dependent on the storage period are presented in Figs. 1-3.

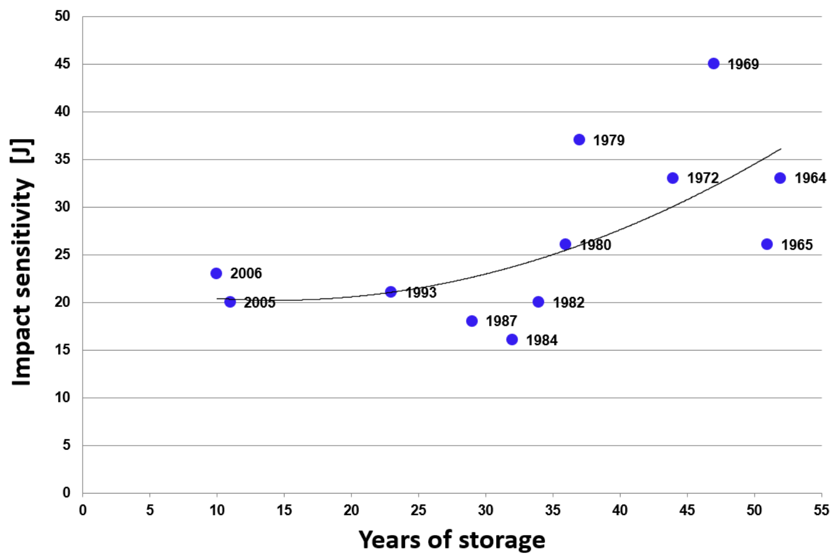

Fig. 2. Impact sensitivity as the function of the years of storage, indicating the TNT ageing process

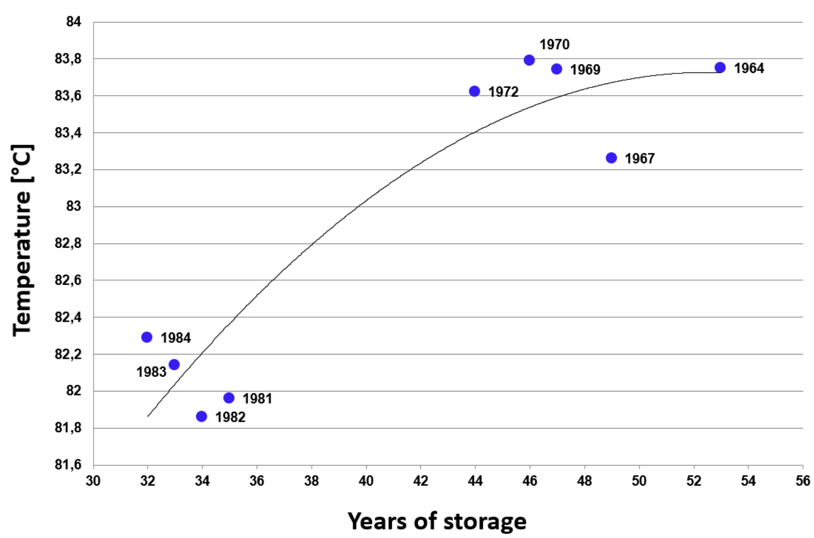

Fig. 3. Melting point as the function of the years of storage, indicating the TNT aging process

The chemical and physical parameters of TNT samples display a difference in stability over time between samples from the 1960s-70s and after the 1980s. The diagrams illustrate changes in the quality of the examined TNT samples as dependent on the storage time and they reveal that the quality parameters are superior for older samples. It seems that the difference between the parameters of the samples from the 1960s and early1970s (visible in Fig. 1 - 3) and the values for the samples from the 1980s and 1990s could be a result of the strategy adopted by the Army at that time. Materials from the earlier periods seem to be more resistant to ageing due to the superior assembly process. These materials were manufactured in a more precise way and with prolonged periods of use and storage in mind. As far as the samples produced after the 1980s, they could be affected by the lower quality of the manufacturing, which translates to lower resistance and increased sensitivity to external stimuli (friction impact and temperature).

Fig. 4 illustrates the condition of TNT as sampled from the mines from the 1960s-70s, and Fig. 5 presents trinitrotoluene which was produced recently.

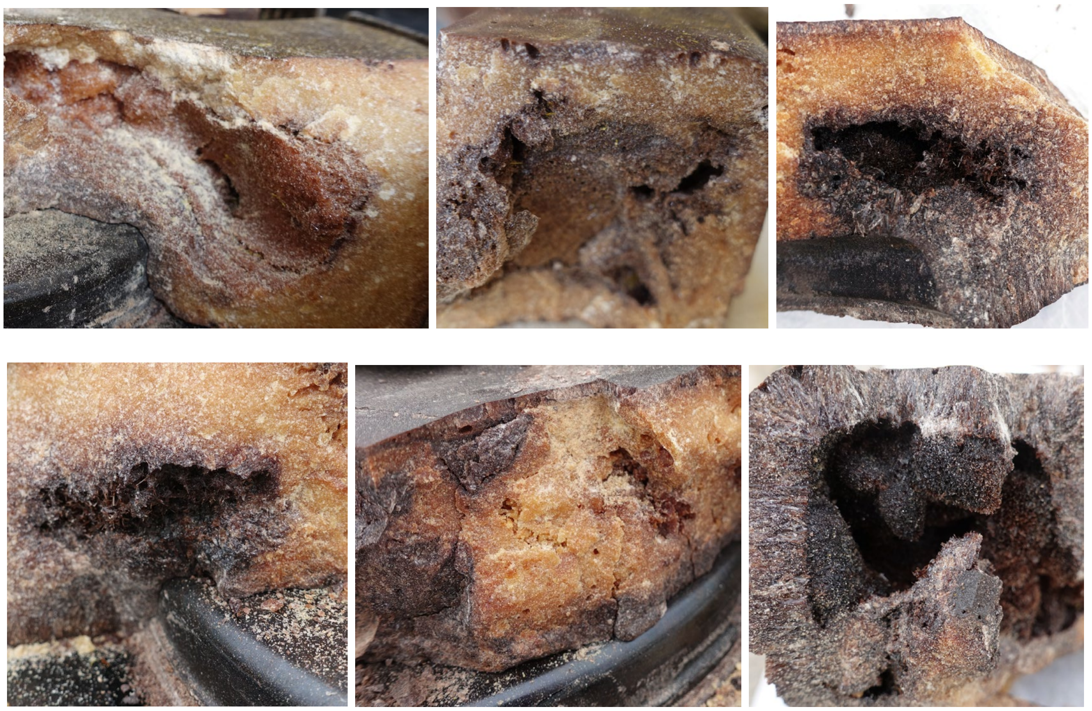

Fig. 4. *TNT fragment sampled from the mines from the 1960s-70s*

Fig. 5. *TNT from a recent batch*

As a result of the tests of the physicochemical and explosive properties of TNT taken from the mines from the 1960s and 1970s, the authors found that advanced ageing processes of the explosive led to changes in its physicochemical and explosive parameters, which translates into the safety of the product use. TNT recrystallized, it is heterogeneous, contaminated, cracked with local shrinkage in the volume of the mine.

Moreover, the tests of older materials, in comparison with those of "freshly-produced TNT" revealed that their parameters differ notably (Table 1). Low melting points indicate the use of low-quality TNT for elaboration in the case of the former. The external appearance of the tested samples, presented in Figs. 4-5, indicates a lack of homogeneity of the explosive (TNT).

Discolorations, contraction cavities, recrystallized material and its impurities indicate that advanced ageing processes occurred within the material, and point to inferior quality of the explosive itself and the filling process.

Due to the low thermal conductivity of TNT, heat exchange is hindered, and thus the crystallization process is slow. As a result, an undesirable casting is obtained in the form of low-density coarse-crystalline material. Crystallization carried out improperly may result in the so-called contraction cavities. The formation of TNT cracks may have resulted from the improperly carried out crystallization process, yielding an overly dense casting. These are the defects that arise at the stage of explosive's production already.

In order to determine the suitability of explosive ordnance for further storage, a number of additional tests, such as acidity is being conducted.

Table 1. *Deterioration of TNT parameters indicated based on acidity testing*

TNT year of production	Impact sensitivity	Friction sensitivity	Melting point	Acidity
2019	>50 J	> 356 N	80.2°C	0.005 max. % [6]
1965	88 J	154 N	77.7°C	>0.005
1969	31 J	208 N	77.9°C	>0.005

Summary

Following a long-term (e.g., a few decades) storage was noticed that high explosives are capable of maintaining their physical and chemical properties at an acceptable level. This means that the parameters of the explosives depend mainly on the filling (production) quality, and secondly on the storage conditions.

The explosive stored in the warehouses of the Polish Armed Forces were manufactured 20 to 60 years ago. Furthermore, for the explosive to be suitable for filling, it should meet certain standards at the initial stage of production. For TNT, these are:

– The melting point of 80°C minimum (TNT with a melting point below 80°C was classified into a lower purity category, or even as a TNT waste TNT, when it fell below 76°C;
– Friction sensitivity >360 N;
– Impact sensitivity >50 J;
– Acidity: 0.005 % max [6,7].

The analysis of TNT test results has not yielded a definitive answer, as to the potential response of TNT to the conditions of even more extended storage.

The parameters characterizing the response of explosives and enabling the estimation of further storage period include friction- and impact sensitivity and thermal stability, as well as acidity testing.

Visual assessment of the quality of explosives at the sampling stage (homogeneity of the material, no cracks, crystals) provides the answer to the question, whether verification of all the assumed parameters will be possible. The most common parameter, which lies outside the assumed parameters, is acidity.

Additionally, both the friction- and impact sensitivity of the lower-quality material with which the mine was filled in possible to determine, in the case of a large number of contraction cavities, and high discoloration. These parameters are quite high (e.g., impact sensitivity > 100 J), the melting point is low (< 78.0°C), while the acidity cannot be determined. However, the majority of the explosives filling the mines from the 1980s, 1990s, or at the beginning of the 21st century investigated by the authors reveal stable properties, as their parameters are characteristic for the commonly used TNT, and such mines can be successfully stored in warehouses for many years. In case of the explosive from the 1960s and 1970s it is the quality of the final product (the type of mine casing and its airtightness), the quality of the filling process and the storage conditions (stable temperature) which guarantees that the acceptable parameters for the explosive itself will be maintained.

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