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DETERMINATION OF CHEMICAL STABILITY OF GUNPOWDERS BY QUALITATIVE AND QUANTITATIVE METHODS

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ABSTRACT

The results of the testing presented in the study are made on one base 51-year-old gunpowder.

By the quantitative and qualitative methods the content of the remaining stabilizer is determined and by doing this the stability of the treated gunpowder is determined.

In this case the methylviolet method was applied from the qualitative methods in accordance with the treatment of the one base gunpowder at 134,5 °C, and the results were determined by methylviolet indicator. At this temperature the treated gunpowder demonstrated stability during more than 40 minutes.

The method of liquid chromatography was applied from the quantitative methods. By this method, the content of the remaining stabilizer was determined (diphenylamine and its inter-products) in the treated gunpowder. It was proven to be within the limits from 0,54% to 0,67%, depending on extraction time.

According to the SNO 8069/91 standard, the powder is chemically stable and usable at least in the next two years.

Key words: gunpowder, chemical stability, stabilizer

Introduction

Explosive materials are substances which under the impact of an external impulse, have the capacity to decompose quickly during which gases are released, heated to several thousand degrees Celsius and at high pressures [1,2]. In order to facilitate the recognition, examination and use, explosive materials are grouped on various bases, and more precisely: primers, birsant (high explosives), propellant materials (gunpowders) and pyrotechnic composites [2,3].

All these explosive materials are related by two basic properties: sensitivity to external exposure influences, i.e. the capacity of explosive materials to react to external conditions; and the stability of the explosive materials which is expressed in their capability to retain their initial qualities (chemical, mechanical and physical, ballistic and others) within certain limits and in the foreseen period for their use. The surety of the explosive materials is analyzed according to their stability, whether they are incorporated in particular systems or are kept separately.[1][3,6]

The chemical stability of explosive materials implies their capability to remain stable after their insertion into ammunition, at temperatures from –30 to +60 °C, and remain unaltered for a number of years, i. e. not to be subject to the process of chemical decomposition. However, it has been noted, nitrocellulose as a basic component of gunpowder (figure 1), shows signs of thermal degradation, (decompositon). This decomposition of nitrocellulose is a complex process which is thought to be catalized by the byproducts of the decomposion itself, especially by the reactive nitrogen oxides [4].

The process of self-decomposition is exothermic. The rate of decomposition of nitrocellulose at a temperature below 40 °C is within the allowed limits, but the phenomena becomes more complex and may become dangerous because of the possibility for autocatalysis to appear. The reaction begins with the decomposition of the esters into radicals, and then new reactions follow from the radicals which attact the nitroesters which have not decomposed (nitrocellulose), and so on. Then as usual, gases develop (N_2, N_2O, NO, CO, CO_2) , H_2O, aldehydes, acids, and other species which lowers the caloric value of the explosive material, and a degradation of the mechanical properties occurs. The formation of gasses, especially in large cailber ammunition where the conditions for eviction of the gasses is difficult, produces pressure in the mass which may result in the apparition of cracks on the projectile.

The released heat acts catalitically and speeds up the process of self- decomposition. If not evicted from the gunpowder mass, it accumulates in the material and in certain conditions may cause selfignition of the gunpowder. The lowering of the csaloric value of the gunpowder immediately influences the lowering of the balistic qualities. For these reasons during the production process attention is given that these processes be brought under control, and this is partially achieved with the addition of compounds known as stabilizers (for istance diphenylamine and others), which have a task to bind released nitrogen gasses and in that way impede the process of self- decomposition.

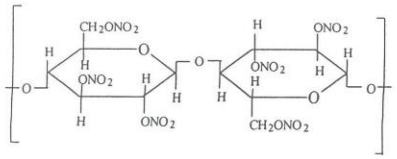

Figure 1. Structural formula of nitrocellulose[8]

With the aim to delay the exothermic process of self-decomposition of the nitrocellulose, during the production process of single base gunpowders[2], compounds are added which are usually named stabilizers. One of the most frequently used stabilizers is diphenylamine, which is present as 1% of the total gunpowder

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[1] Explosive materials are incorporated (installed) in various systems of classical and missile ammunitions, mine and explosive devices and other, which are required to be use efficient even for a 20-30 year period from their production.

[2] Gunpowders which in their composition have a single active component (most frequently nitrocellulose) are termed single base gunpowders.

mass[6,7,8]. Diphenylamine reacts with the byproducts of the decomposition of the nitrocellulose, during which nitrate derivatives of diphenylammiine are formed.

Because the stabilizer as the main acceptor of the nitrogen oxides is closely related with the decomposition of the nitrocellulose, it is thought that the content of the remaining stabilizer is an adequate indicator for determiniing the evolution of the gunpowder. For these reasons monitoring of the content of the stabilizer in the gunpowder is performed depending on the time of storage of the ammunition in which the respective gunpowder had been inserted. When the amount of stabilizer in the gunpowder mass is reduced below 50%, the gunpowder is thought to be chemically unstable and as such, not suitable for further use [6,11].
The mechanism of the diphenlylamine reaction with the products of the denitration of the nitrocellulose occurs by substitution of the hydrogen atoms of diphenylamine with the nitroso-gasses of the nitrocellulose, during which N-nitorsodiphenylamine is formed and then in the subsequent stages of substitution several intermediary products are formed – diphenylamine derivatives (figure 2) [14] which are also thought to have a stabilizing effect.

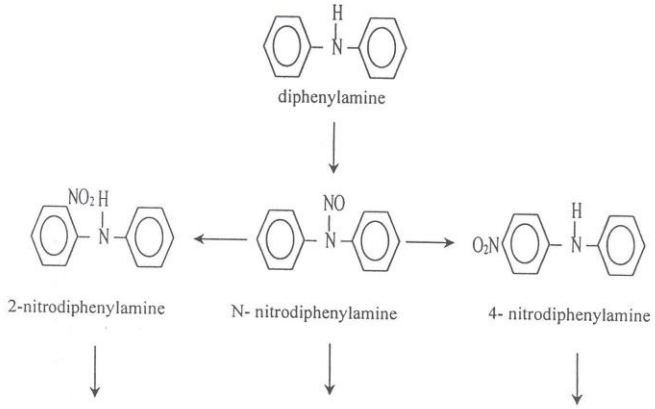

Figure 2. Diphenylamine reaction mechanism

The data from the determination of the total content of stabilizer (diphenylamine and its derivatives) serves to predict the time of safe storage of the gunpowder, which requires the use of exceptionally quick and accurate instruments and methods. Classical methods do not fulfill these criteria, because the examinations take long (several days), and the gunpowder is treated at higher temperatures which results in its accelerated aging and decomposition according to mechanisms which are still not sufficiently clear.

Gas chromatography has been used for a long time as a leading method in the determination of stabilizer content in gunpowders. Although this method is sufficiently quick it still has certain drawbacks which make it unsuitable for this purpose, i.e. the substances that are analyzed before being entered into the gas chromatography column need to be transformed into gas phase, which causes partial or complete decomposition of the thermally unstable compounds [11]. In this manner thermally unstable derivatives of diphenylamine, N-nitrosodiphenylamine, are decomposed which prevents the determination of the actual content of diphenylamine and its derivatives.

More recently, a solution was found with the use of the high-pressure reversible liquid-phase chromatography which enables determination at much lower temperatures.

Experimental

With the use of the classical methylviolet method and the method of liquid chromatography a 51-year-old nitrocellulose gunpowder was assayed.

The work procedure for both methods is standardized with the SNO 8069/91 standard.
The analysis of the examined gunpowder with the methylviolet method is done according to the stated standard which requires a prior preparation of the gunpowder material. The preparation consists of mincing and sifting the gunpowder with the aim of forming gunpowder particles reduced to an appropriate dimension. Five (5) assays were weighed from prepared mass, 2,5 g each. The weighed amount of gunpowder was poured into test tubes for further analysis. A methylviolet indicator strip was vertically

inserted into each test-tube at the height of 25 mm from the gunpowder mass. Then, the test tubes were closed with stoppers and were placed in a thermal block (figure 3), which was pre-heated to a temperature of 407, 5 K (134,5 °C).

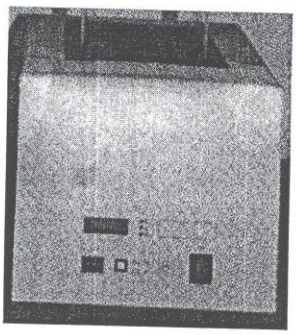

Figure 3. Thermal block used in testing the chemical stabilty of gunpowders with the methylviolet method

After placing the test tubes in the thermal block, time was measured from the beginning of the heating process of the gunpowder until change of color of the methylviolet paper was observed. After 30 minutes of heating, at 5-minute intervals, the test tubes were taken out of the thermal block to determine the color change of the indicator paper and then were immediately placed back.

The time it took for the first assay (of the five analyzed) to change color was taken as a measure of the chemical stability of the gunpowder, but so that the elapsed time between the analysis of the assays was not more than 5 minutes. The time that it takes, from the beginning of the heating process until the complete change of color of the indicator, is used in the evaluation of the chemical stability of the gunpowder. The accuracy of the analysis is verified in such a way so that after the change of the color of the methylviolet paper had occurred , the test tubes are filled with distilled water, and if during this process a faint violet coloration appears at the upper rim of the paper, it is thought that the recorded time is the same as the time needed for the complete discoloration of the paper. If violet color appears on the entire paper, then a complete change of color had not occurred.

For this type of gunpowder a time period of more than 40 minutes is the criterion for its chemical stability. The liquid chromatography analysis was performed with the aid of a Varian liquid chromatograph with a UV detector and a RPC 8 column with dimensions of 4,6 x 250 mm (stationary phase bondesil with particle dimensions of 5 μm).

The gunpowder assays were dissolved (dichloromethane solvent) and left for an appropriate time period in order to extract the stabilizer from the gunpowder. After this, with the aid of a microliter syringe, an assay of 2 μl was taken from the solution for analysis. Standard Merck solvents were used for this purpose.

All measurements were performed at room temperatures, at a wave length of 254 nm. The ratio of the solvents in the liquid phase was 60% acetonitrille and 40% water, with a 1 ml/min flow [9]. Every experiment was repeated several times, with the aim to prove the reproducibility and the accuracy of the results.

The liquid chromatograph experimental results are shown as chromatograms.

Results and discussion

According to the methylviolet method, the analyzed gunpowder showed stability for longer than 40 min. From these data, and in accordance with the standard stated before, the gunpowder at the moment of analysis was chemically stable and can safely be used but there is no possibility to predict its stability for in the following period.

With the aim of making a prediction for the chemical stability of the gunpowder and its usability, tests were done with the quantitative method i.e. determination of diphenylamine content with the aid of the liquid chromatography method.

The results shown in figure 4 and 5 were obtained after the extraction of diphenylamine in duration of 15 hours and 30 hours respectively.

The presence of diphenylamine in the analyzed gunpowder is evident from the chromatograms (figures 4 and 5), (peak 1) which appears at approximately 12 min. Beside diphenylamine, presence of its derivatives is also obvious: 4-diphenylamine (peak 2), N-nitrosodiphenylamine (peak 3), and 2-nitrodiphenylamine (peak 4), formed according to the reaction of diphenylamine with the separated NO and NO_2 gasses, shown in figure 2 .

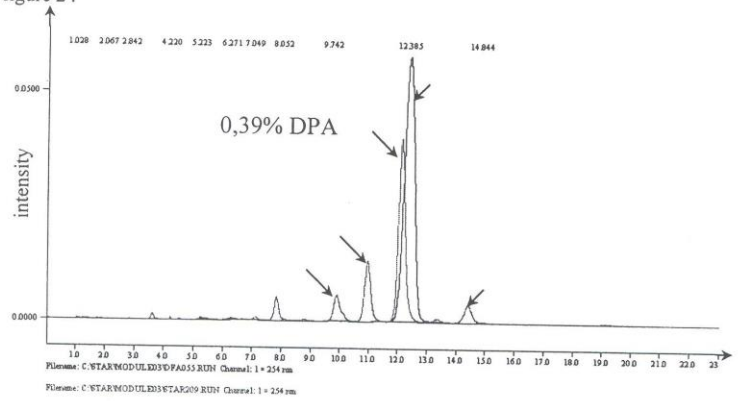

Figure 4. Diphenylamine chromatogramme after a 15 hour extraction

1, 5 DPA - diphenylamine; 2,3 and 4-peaks of DPA derivatives

Quantitatively the presence of diphenylamine and its derivatives is determined from the surface of the peaks, or from their intensity. A reference peak of pure diphenylamine with the concentration of 0,5 % had been obtained for this purpose. (figure 4 and 5, peak 5) It is obvious that the concentration of diphenylamine and its derivatives in the analyzed gunpowder is different depending on the time of extraction. After the extraction, in duration of 15 hours, the entire contents of the remaining stabilizer (diphenylamine and its derivatives) was 0,67 % (figure 4) while after 30 hours of extraction it was 54 %. This is most likely the result of certain reactions that take place between diphenylamine and its derivatives with the solvent where they decompose and result in the formation of other complexes.

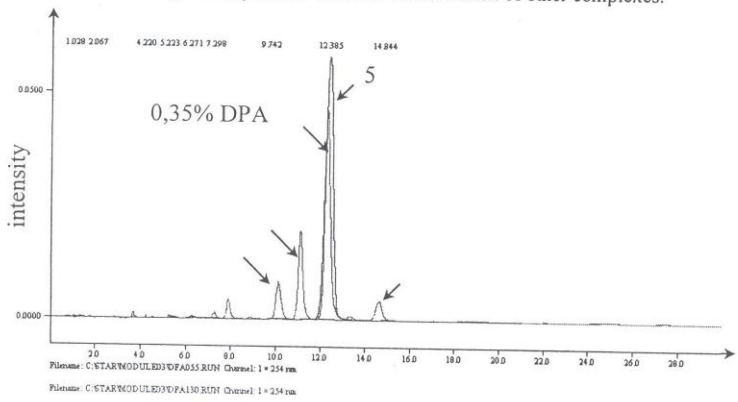

Figure 5. Diphenylamine chromatogramme after a 30 hour extraction

1, 5 DPA - diphenylamine; 2, 3 and 4-peaks of DPA derivatives

Conclusion

Although the results of the methylviolet method are only qualitative, they nevertheless confirm that the derivatives of diphenylamine have a stabilizing effect on the gunpowder material. The quantitative determination in this case shows that the content of the remaining diphenylamine is below 0,5 % which would mean directly that the gunpowder is unstable and as such unusable. However, taking DPA derivatives also into account for the total content of the stabilizer, both methods applied in the examination showed that the gunpowder is stable. This means that the total content of stabilizer in the gunpowder was more than 0,5%. It can therefore be concluded that the examined propellant (gunpowder) at the moment of testing was chemically stable, which means that ammunition equipped with this explosive material can safely be used. It can also be predicted that under ordinary storage conditions the gunpowder should be stable for at least the following 2 years [9].

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Biography

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