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DETERMINATION OF CHEMICAL STABILITY OF GUNPOWDERS BY QUALITATIVE AND QUANTITATIVE METHODS

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Abstract:

This work presents the results from the analyses made on monobasic gunpowder, which consists of two types of stabilizers (diphenylamine and centralit I) with total mass of representation of about 1,3%.
The content of the residual stabilizer of gunpowder treated at different temperature and at different length of time was determined by using two quantitative methods.. By processing and comparing the results gained at raised temperature an attempt was made to foresee the time of stability of the gunpowder in normal conditions of storing.
As quantitative methods in this case The Hansen test and liquid chromatography (HPLC) were applied According to the first method the gunpowder was treated at 110 °C in the period from 0 to 72 h, and the results were validated by using pH - meter.
The second method was used to determine the content of the residual stabilizer at the same gunpowder treated at 110°C as long as the content of the active stabilized does not go below 50% m/m from the starting one.

Keywords: *gunpowder, chemical stability, stabilizer*

1. INTRODUCTION

The compressive explosive materials, which include all types of gunpowder, contain one or more *nitro esters,* dealt in the stability as a science and practice of the chemical mechanical and ballistics evolution of the homogenous gunpowder and propulsives [1, 2].

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 stability is analyzed according to the safety of the explosive materials whether they are incorporated into particular systems or are kept separately [3].

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,the esters especially the nitroesters are not stabile and are subject to spontaniuous self degradation (decomposition).The rate of decomposition incerases by increasing the temperature while the kinetics goes ccording to the known Arneus law.So the nitrocellulose as basic component of the gunpowder shows signs of thermal degradation. 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 most frequent method for stabilization of the nitrocellulose gunpowder is adding of the diphenylamine, which reacts, with the products of the decomposition when nitrated derivates of diphenylamine are created. However the stabilization of the intracellular gunpowder can be performed by adding a mixture of two stabilizers (ex. Diphenylamine and centralit) in certain proportion. The nitro cellular gunpowder used in the ammunition are mostly made with the content of the stabilizer from 1% to 1,5% [4].

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].

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-nitrosodiphenylamine is formed and then in the subsequent stages of substitution several intermediary products are formed – diphenylamine derivatives (fig. 1) [7] which are also thought to have a stabilizing effect.

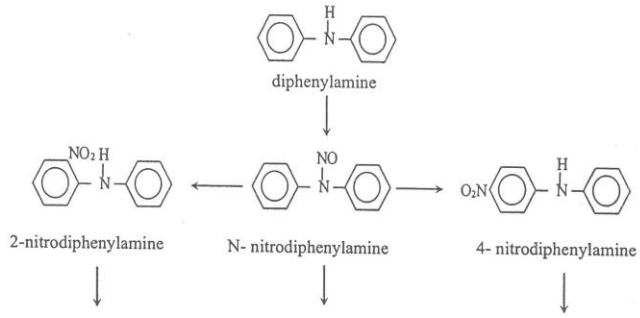

Fig 1. Diphenylamine reaction mechanism

The data from the determination of the total content of stabilizer (diphenylamine, centralit and its derivatives) serve 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 [8]. In this manner thermally unstable derivative of diphenylamine, N-nitrosodiphenylamine, is decomposed to diphenylamine [9] 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.

2. EXPERIMENTAL

In this case a monobasic gunpowder with initial content of the stabilizer of about 1,3% is examined. It is determined that a mixture of diphenylamine and centralit I is used as a stabilizer,in a content of about 0,7% and 0,5%, accordingly. The analyses are made by using the classical Hansen method and the liquid chromatography (HPLC).

Before the beginning of the treatment at the given temperature for extraction of the damp, the gunpowder was treated at 80 °C in a period of four hours. The analyses by the Hansen method are carried out by using a suitable thermo block in which the gunpowder was treated at temperature of 110 °C, and then in the test tube with gunpowder a distilled water with pH 5,5 was added and after the intensive mixing with duration of 3 - 5 minutes the pH of the solution was measured. The analyses with liquid chromatography are carried out by using a liquid chromatograph of the company Varian with UV detector and column RP C8 with dimensions 4,6 x 250 mm (stationed phase Bondesil with seize of the particles of 5 μm).

The procedure of work is standardized with standard [10].

The thermally treated samples of gunpowder are first diluted with a solvent (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 2μl 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. Every experiment was repeated several times, with the aim to prove the reproducibility and the accuracy of the results.

3. RESULTS AND DISCUSSION

According to the Hansen method the gunpowder is considered as chemically stabile if after eight hours of treatment at 110 °C the value of pH doesn't go below 3,30. So, in our case it is a case of a stabile gunpowder because the pH value is bigger than 3,30 and after 72 hours (Table 1). Most probably because of the strong base influence of the diphenylamine, pH of the solution increases from 5,5 to 6,10 at the beginning which brings to gaining nonrealistic results for evaluation of the stability. Also, from these results the mechanism of the reaction and the structure of the real stabilizer can not be determined as well as the future course and speed of the gunpowder degradation can not be predicted too.

The results of the examination of the stability by using the liquid chromatography are shown as chromatograms (fig. 2 and 3).

The presence of diphenylamine in the analyzed gunpowder is evident from the chromatograms and centralit, (peak 1) which appear at approximately 12 min. i.e. 13 minutes. Beside the basic stabilizers diphenylamine and centralit, the presence of thier derivatives is also obvious: 4-nitrodiphenylamine (peak 3), N-nitrosodiphenylamine (peak4), and 2-nitrodiphenylamine (peak 5), formed according to the reaction of diphenylamine with the separated NO and NO_2 gasses, (fig.1) and N-nitroso-N-ethylanilin (peak 6).

Table 1. *Gunpowder treatment at 110 °C*

No.	Time of treatment [h]	pH
1.	2	6,10
2.	4	6,05
3.	6	5,73
4.	8	5,60
5.	10	5,05
6.	12	4,53
7.	24	3,65
8.	48	3,48
9.	72	3,43

Quantitatively the presence of diphenylamine and its derivatives is determined from the surface of the peaks. Reference peaks had been obtained for this purpose. The quantitative analyses show that the content of the total stabilizer in the gunpowder is bigger than 50% m/m after 24 hours treatment at the given temperature (Table 2), while after 48 hours is about 40% m/m. The results on figure 4 show obvious thermal instability of the diphenylamine and centralit derivatives. That instability results into recurrent reaction, especially in the period from 8 to 24 hours.

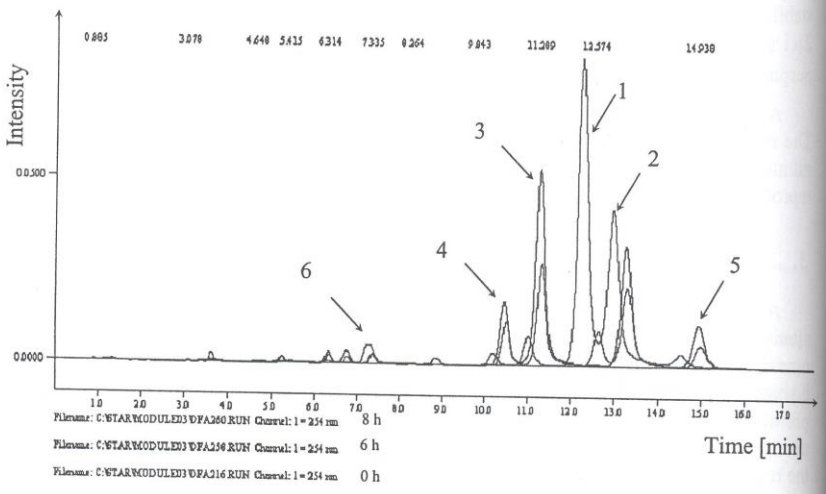

Fig 2. Chromatogram of diphenylamine ,centralit I and their derivatives from 0 to 8 h treatment na 110 °C
1 - DPA (diphenylamine); 2 - centralit I; 3 - N-nitroso-DPA; 4 - 4-nitro-DPA; 5 - 2-nitro-DPA; 6 - N-nitroso-N-ethylanilin

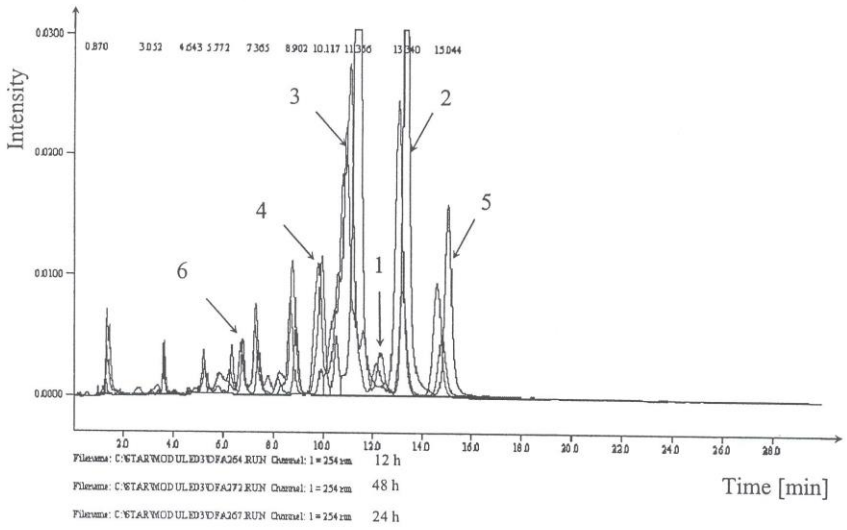

Fig 3. Chromatogram of diphenylamine, centralit I and their derivatives from 10 to 48 hrs treatment at 110 °C
1 - DPA (diphenylamine); 2 - centralit I; 3 - N-nitroso-DPA; 4 - 4-nitro-DPA; 5 - 2-nitro-DPA; 6 - N-nitroso-N-ethylanilin

Table 2. *Content of the stabilizer after treatment of the gunpowder from 0 to 72 hrs at temperature of 110 °C*

Time of treatment [h]	DPA [%m/m]	Centra-lit [%m/m]	N-NDPA [%m/m]	2-NDPA [%m/m]	4-NDPA [%m/m]	2-Ncentr. [%m/m]	Total stabil. [%m/m]
0	0,69	0,52	0,05	0,01	0,02	0,01	**1,30**
2	0,39	0,36	0,13	0,03	0,02	0,01	**0,94**
4	0,33	0,29	0,25	0,05	0,04	0,01	**0,92**
6	0,16	0,28	0,27	0,04	0,05	0,01	**0,81**
8	0,00	0,33	0,40	0,04	0,05	0,01	**0,83**
10	0,00	0,36	0,52	0,05	0,02	0,00	**0,95**
12	0,00	0,40	0,64	0,05	0,01	0,00	**1,10**
24	0,00	0,36	0,55	0,04	0,03	0,02	**1,00**
48	0,05	0,12	0,32	0,02	0,04	0,02	**0,57**
72	0,05	0,02	0,28	0,01	0,05	0,02	**0,43**

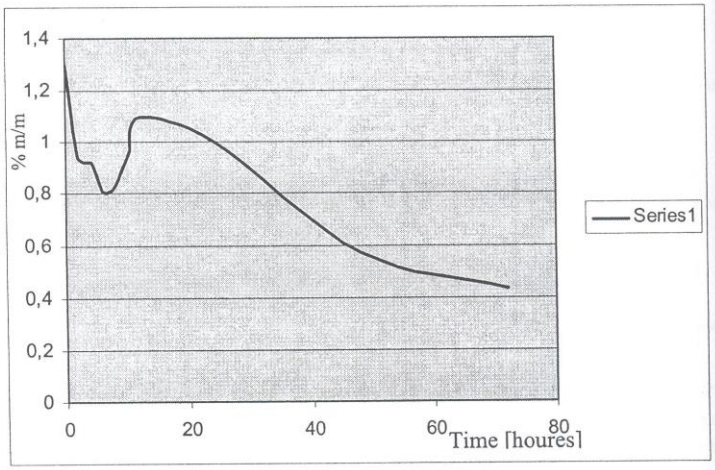

Fig 4. Diagram of the loss of the stabilizer in the gunpowder at treatment of 110 °C

If the gained results for the speed of the loss of the stabilizer in the gunpowder are replaced in the form [1]:

$$D_{50}(20°C) = \frac{d_{50}(T) \cdot \gamma_{10}^{\frac{T-20}{10}}}{365}$$

where:

- $D_{50}(20°C)$ - Time during which the gunpowder spent half of the stabilizer at storage temperature $T = 20$ °C;
- γ_{10} - coefficient (factor of accelerating the degradation reaction for 10 K);
- $d_{50}(T)$ - time during which the gunpowder spend half of the stabilizer at temperature of treatment $T = 110$ °C,

then the following is gained:

$$D_{50}(20°C) = \frac{1,7 \cdot 2,5^{\frac{110-20}{10}}}{365} = 17,8 \text{ years}$$

This would mean that the examined gunpowder will be chemically stabile in the next 18 years. Still, this result should be taken with a dose of reserve, because it doesn't include the effect of the mass and the surrounding of the gunpowder bullets.

4. CONCLUSION

1. The classical methods including the Hansen method do not give a real picture of the condition of the chemical stability of the gunpowder, but only initial conclusion that at the moment of the examination it is stabile or non stabile.
2. Different then the previous method the liquid chromatography enables gaining real data for the condition of the gunpowder and the stabilizer into it. Because of the relatively high temperature of treatment and the instability of the derivatives of the basic stabilizer, certain mistakes are possible but they do not have big influence over the final evaluation of the chemical stability of the gunpowder.
3. The results gained by using the liquid chromatography can be used with a dose of reserve ,to predict the time during which the gunpowder would be stabile.

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