

EXTRACTION OF ECOLOGICALLY DANGEROUS COMPONENTS OF SINGLE-BASE POWDER UNDER THE WATER INFLUENCE

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Purpose. In the presented work authors consider the migratory ability of the chemical stability stabilizer such as diphenylamine and its N-nitroso- and nitroderivatives of single-base gunpowder. **Methodology.** The moisture influence has been investigated in two directions. The first direction is the vaporous moisture influence on chemical stability, which estimated as the composition of the chemical stability stabilizer formed derivatives. The second direction is the influence of the liquid moisture (liquid medium), completely washing the powder elements, on the composition of chemical stability stabilizers of the single-base powder and quantity of eluted stabilizers – first of all such as diphenylamine. **Results.** Authors determine that at the contact of gunpowder and water the elution of diphenylamine and N-nitrosodiphenylamine is observed. **Originality.** The quantity of the eluted components depends on pH of the contacting liquid medium; their maximal quantity is eluted to the acid liquid medium. **Practical value.** Results of this researches will allow to estimate degree of ecological danger of single-base gunpowder at storage in depressurization conditions. *References 10, tables 3, figures 1.*

Key words: diphenylamine, single-base gunpowder, aqueous medium, extraction

ВИДІЛЕННЯ ЕКОЛОГІЧНО НЕБЕЗПЕЧНИХ КОМПОНЕНТІВ ПІРОКСИЛІНОВИХ ПОРОХІВ ПІД ДІЄЮ ВОДИ

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Розглянуто міграційну здатність стабілізатора хімічної стійкості дифеніламіна і його N-нітросо- та нітропохідних піроксилінових порохів. Досліджували вплив вологи по двох напрямках. Перший напрям – вплив пароподібної вологи на хімічну стійкість, про яку судили по складу похідних, що утворилися, зі стабілізатора хімічної стійкості. Другий напрям – вплив рідкої вологи (рідкого середовища), що повністю омиває порохові елементи, на склад стабілізаторів хімічної стійкості піроксилінових порохів і кількість стабілізаторів хімічної стійкості, що вимиваються, – в першу чергу дифеніламіна. Встановлено, що при контакті пороху з водою відбувається вимивання дифеніламіна і N-нітродифеніламіна. Кількість вимитих компонентів залежить від рН контактуючого рідкого середовища; найбільша кількість їх вимивається в кисле рідке середовище.

Ключові слова: дифеніламін, порох піроксиліновий, водне середовище, виділення

PROBLEM STATEMENT. In depressurization conditions of the long stored ammunition when there are external devices (warehouses), interfering a direct hit of water, the powder elements are affected by the environment water vapors.

The amount of moisture getting to gunpowder composition will be defined generally by the relative air humidity and the ability of powder elements to absorb the moisture. Here we speak about absorption of the moisture which is in the vaporous state.

If there are no the devices interfering a direct hit of the moisture, the moisture gets to the powder element in the liquid state. Its quantity getting to gunpowder will be defined by characteristic of the surface and internal structure of the powder elements caused by the existence of open pores.

The moisture influence has been investigated in two directions. The first direction is the vaporous moisture influence on chemical stability, which estimated as the composition of the chemical stability stabilizer formed

derivatives. The second direction is the influence of the liquid moisture (liquid medium), completely washing the powder elements, on the composition of chemical stability stabilizers of the powder element and quantity of eluted chemical stability stabilizers – first of all such as diphenylamine, being ecologically dangerous to the environment [1,2].

It is known that the increased air humidity of environment leads to increase of the gunpowder humidity, which accelerate the processes of hydrolytic degradation [3, 4] having the stronger impact on the chemical stability and the safe storage duration decrease, than the thermal decomposition [5]. Hydrolytic degradation takes place only at joint influence of acids and water. The speed of hydrolysis depends on the concentration of hydroxyl and hydrogen ions, thus the hydroxyl ions are more active. The minimum speed of hydrolysis of the nitrate esters corresponds not to the neutral, but to the acidic medium [6]. It is also known that in presence of large amounts of water there is no gunpowder decomposition acceleration, that's

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why it's possible to store the gunpowder under water for a long time [7].

EXPERIMENTAL PART AND RESULTS OBTAINED. To study the effect of moisture, which was sorption trapped into the powder elements, the gunpowder with small powder elements 2/3 from the lot number 6, having age of 10 years at the time of research, has been examined. Two samples of gunpowder were investigated. One sample with natural humidity of 0.9 % on weight served as an example of comparison. The second sample was prepared by the addition of external water in number of 3.0% from gunpowder mass to the first sample. The samples were placed into the hermetically closed glass bottles into which the necessary amount of water by the volume was entered.

Further the samples were thermostated at the temperature of 368.0 ± 1.0 K for 56 hours. The moisture in the conditions of carrying out experiences was in the vapor phase. After the temperature control the samples, adjoining to the moisture vapors, were exposed to the vacuum drying at the room temperature and the endurance together with comparison samples in the desiccator. Than the content of DPA and its derivatives was defined in the samples. The definition of mass fractions of diphenylamine and its N-nitrozo- and nitroderivatives in the single-base gunpowder was carried out by the standard method of high performance liquid chromatography [8, 9], based on the extraction from gunpowder of diphenylamine and its derivatives and the chromatography of the received extract on the microcolumnar liquid chromatograph Milikhrom-6 with the spektrofotometric detector in UV-area at isocratic elution.

The eluent consisting of methyl alcohol and twice distilled water at a ratio of components 65:35 (by volume) was applied to determine the mass fraction of diphenylamine and its N-nitrozo- and nitroderivatives in single-base gunpowders.

The reference solution, which was prepared in a penicillin bottle, was used for calibration. For this purpose 0.01 g of diphenylamine, 0.002 g of N-nitrosodiphenylamine, 0.001 g of 4-nitrodiphenylamine and 0.001 g 2-nitrodiphenylamine, weighed with accuracy to four decimal, were placed to the bottle. This corresponds to 1.0% of the diphenylamine mass fraction, 0.2% of N-nitrosodiphenylamine mass fraction, 0.1 % mass fractions of 4-nitrodiphenylamine and 2-nitrodiphenylamine, on the powder portion equal to 1,000 g. The internal standard solution (the solution of acetanilide in methanol with a concentration of 1 mg/cm^3) in the amount of 5.0 cm^3 was added to the bottle. Than the intro-

duced components were dissolved with agitation and the eluent in the amount of 5.0 cm^3 was added.

For the analysis, the column with sizes of 2×100 mm filled with the reverse phase sorbent Silasorb C18 with $5 \mu\text{m}$ particle size was used. The components definition was carried out at the detector wavelength of 220 nanometers.

The analysis of solid samples was carried out as follows [10].

About 1.0 g of dried and ground powder, weighed accurately to four decimal places, was placed into the penicillin bottle. The bottle filled with 5.0 cm^3 of 1% by the mass solution of acetanilide in methanol. The contents of the bottle was sealed and left to stand for 30 min with occasional stirring. Further, to the bottle contents was added 5.0 cm^3 of water eluent, which was mixed thoroughly, pressed the residue in the bottle with the glass rod with a flat end. The resulting extract was filtered through the porous glass filter and from the formed filtrate was selected the sample for chromatography.

Preparation of liquid medium tests was carried out as follows. To 20 ml of the liquid medium the internal standard solution (0.1 ml of atsetanilid to 100 ml of dichloromethane) in the amount of 5 ml was added. The contents placed into the hermetically sealed bottle were mixed intensively on the device for stirring during 5.0 hours. The received mixture was allowed to be stratified when upholding, than it was selected with the syringe the methylenchloride layer of the volume $4 \mu\text{l}$ for input into the chromatograph measuring system.

After chromatography using a computer program the primary mathematical data processing, which consists of calculating the peaks area of the analyzed components and internal standard has been performed.

Mass fraction of the analyzed component diphenylamine and its derivatives in the powder (X , in % by mass) was calculated by the formula:

$$X = \frac{X_i \cdot C_{2i} \cdot m}{C_{1i} \cdot m_1}, \quad (1)$$

где X – the component mass fraction in the reference solution, in percent;

C_{1i} – the ratio of the peak area of diphenylamine (and its derivatives) to peak area of internal standard in the reference solution;

C_{2i} – the ratio of the peak area of diphenylamine (and its derivatives) to peak area of internal standard in the sample solution;

m – the calculated mass of gunpowder sample, g;

m_1 – the exact mass of gunpowder sample, g.

Table 1 – Results of HPLC analysis of samples 2/3 lot number 6 (10 years of the storage)

No. of the sample	Name of the sample	Mass fraction, % by mass			
		DPA	N-NO-DPA	4-NO ₂ -DPA	2-NO ₂ -DPA
1	initial	0,60	0,35	0,13	0,11
2	with addition of 3% of the moisture	0,56	0,32	0,10	0,11

The received results are presented in table 1, showing that the depth of single-base gunpowder aging in the conditions of the increased humidity (sample 2) is almost

commensurable with the depth of single-base gunpowder aging in the conditions of natural humidity. The content of DPA in gunpowder, subjected to heat in a moist atmos-

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phere, was 0.56% on weight concerning 0.60% on weight at controlling the temperature in natural atmosphere. The content of N-nitroso-DPA in gunpowder after humid temperature controlling was 0.32% by weight, and in the reference sample was 0.35% by mass.

The analysis of these data specifies that not only process actually of decomposition, but also the process

of "washing-out" of stabilizers influences on the change process of stabilizers content. If there was no process of stabilizers "washing-out", the reduction of DPA fraction in the samples with the increased humidity, would lead to increase the N-nitroso-DPA fraction. In practice, the smaller value of N-nitroso-DPA fraction was received.

Table 2 – The content of DPA in the liquid medium contacted with gunpowder

Sample in	The content of DPA, g	Mass of gunpowder, g	Concentration of DPA·10 ⁶ , g (DPA)
			$\frac{g (gunpowder)}{ml (solution)}$
water	0,00019181	4,7998	2,0
acid	0,00023666	4,244	2,8
alkali	0,000161295	4,5707	1,8
water (particles)	0,000086177	0,719	12,0

At the same time were conducted the researches of the water influence on the condition of the powder elements which were completely shipped in water at temperatures relative to 293.0 ± 1.0 K.

The powder elements samples for research were prepared as follows. From the powder tube 37/1 (external diameter – 12.0 mm, diameter of the channel – 4.5 mm), the fragments about 10.0 ± 1.0 mm long were cut off, the received fragments (3 pcs.) were placed into the thick-walled glasses. Except the powder elements samples of the specified sizes, the small granular sample of this powder tube was also investigated. Further the powder elements were filled in with three types of the liquid water medium: the distilled water, alkalized water (0.01-n NaOH solution), the acidified water (0.01-n HCl solution), and the small granular sample – only with the distilled water. The amount of the filled-in liquid made 20 ml. As models of comparison were used the powder elements, identical time sustained in comparison with the samples which were filled in with the water medium of various pH, and the sample ground to the sizes of the particles (less than 0.1 mm). After the addition of liquids the glasses were hermetically sealed. Time of an exposition of glasses with the contents made 2500 hours (about 104 days). After the specified time the glasses were opened. For the analysis the powder elements were separated from the liquid and dried up at the room temperature to the constant weight for 45 days. The liquid was also selected for the analysis.

The content of chemical stability stabilizers was determined as in the solid phase (powder elements, small

gunpowder particles), so in the liquid phase (the water medium of various pH).

Three analytical samples were selected from each powder element by drilling according to the direction of the central channel of the certain sample part with the drills of diameter 5.7 mm (first sample); 8.0 mm (the second sample). The rest of the element made the third analytical sample.

The analysis of the received results given in table 2 showed that the amount of diphenylamine, which passed during of experience into the liquid medium, depends on pH of the liquid medium and the geometrical sizes of powder elements.

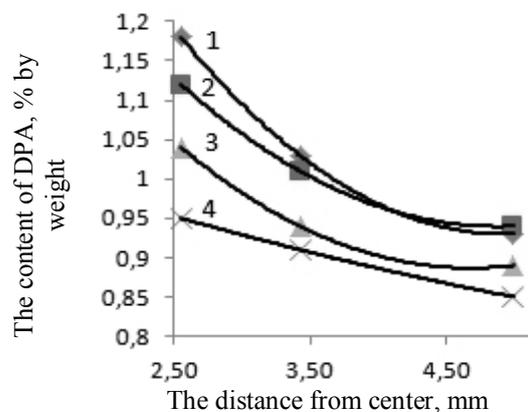


Figure 1 – The content of diphenylamine according to the layers in the samples sustained in: 1 – air; 2 – neutral water; 3 –alkaline water; 4 –acidic water

Table 3 – The average content of components in the samples sustained in various environments

The component	The components content in powder elements after the endurance in water				
	Tube fragment				Small particles in neutral water
	in air	in neutral water	in alkaline water	in acidic water	
DPA	0.98	0.97	0.92	0.88	0.78
N-nitroso-DPA	0.18	0.18	0.17	0.20	0.16
4-nitro-DPA	0.02	0.02	0.02	0.02	0.02
2-nitro-DPA	0.03	0.03	0.03	0.03	0.02

With the reduction of the powder elements sizes the quantity of the migrating DPA into the water medium increases. For the powder elements of size 37/1, (external diameter of the powder element is 12.0 mm, diame-

ter of the channel is 4.5 mm and the height is 10.0 mm) the quantity of the washed-out DPA made 2.0·10⁻⁶ g (DPA) /g (gunpowder) · ml (solution), for particles with

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the size (0.5–1.0) mm – $12.0 \cdot 10^{-6}$ g (DPA) /g (gunpowder) · ml (solution).

To the acidic medium released the most quantity of DPA - $2.8 \cdot 10^{-6}$ g / g·ml, the fewest quantity in alkaline medium – $1.8 \cdot 10^{-6}$ g / g·ml, to aqueous neutral medium released of $2.0 \cdot 10^{-6}$ g / g·ml.

The results analysis of the composition and the stabilizers content definition in solid samples after their contact with the water medium (fig. 1) showed that after the contact with the acidic medium the quantity of DPA in gunpowder becomes slightly lower (curve 4), than in gunpowder after the contact with the neutral medium (curve 2) and alkaline (curve 3) medium.

The joint analysis of the results presented in fig. 1 and in table 3 shows that staying of gunpowder in the neutral water medium under the normal temperature doesn't affect the speed of its decomposition and safe storage terms because of almost identical DPA and N-nitroso-DPA content. Thus, the fact of direct transformation of DPA to N-nitroso-DPA at gunpowder decomposition, and interrelation of decomposition speed with storage periods were taken into account. In the alkaline medium the content of diphenylamine in powder elements is less than 0.92% by weight against 0.98% – in the neutral medium. At identical N-nitroso-DPA content in the gunpowder sustained in neutral and alkaline it is possible to claim that in the alkaline medium, DPA is more washed-out, than it is spent for gunpowder decomposition stabilization. In gunpowder at contact with the acidic medium because of the higher N-nitroso-DPA content and the smaller DPA content it is possible to state already about the influence of the acidic medium on gunpowder decomposition speed.

CONCLUSIONS. At consequences of powder elements long contact with the water medium research it is shown that at gunpowder contact with water, there is a washing-out of ecologically dangerous components such as diphenylamine and N-nitroso-DPA take place. The quantity of the washed-out components depends on pH of the contacted liquid medium; the maximum quantity of them is washed-out to the acidic liquid medium.

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ВЫДЕЛЕНИЕ ЭКОЛОГИЧЕСКИ ОПАСНЫХ КОМПОНЕНТОВ ПИРОКСИЛИНОВЫХ ПОРОХОВ ПОД ДЕЙСТВИЕМ ВОДЫ

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Рассмотрена миграционная способность стабилизатора химической стойкости дифениламина и его N-нитрозо- и нитропроизводных пироксилиновых порохов. Исследовали влияние влаги по двум направлениям. Первое направление – влияние парообразной влаги на химическую стойкость, о которой судили по составу образовавшихся производных стабилизатора химической стойкости. Второе направление – влияние жидкой влаги (жидкой среды), полностью омывающей пороховые элементы, на состав стабилизаторов химической стойкости пироксилиновых порохов и количество вымываемых стабилизаторов химической стойкости – в первую очередь дифениламина. Установлено, что при контакте пороха с водой происходит вымывание дифениламина и N-нитрозодифениламина. Количество вымытых компонентов зависит от pH контактируемой жидкой среды; наибольшее количество их вымывается в кислую жидкую среду.

Ключевые слова: дифениламин, порох пироксилиновый, водная среда, выделение.