The disposal of expired high energy materials

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Abstract. This article highlights the problem of disposal of obsolete pyroxylin powders. The main industrial methods of their utilization were considered. A method of chemical modification of cellulose nitrates that were extracted from obsolete powders with nucleophilic reagents was proposed. According to the results of physicochemical studies the major directions of the chemical reaction were established.

The disposal of explosives recovered from obsolete ammunition represents an important problem. Their production and elimination also have a negative impact on the environment. Nevertheless, these problems can be solved by the creation of safe technologies for the disposal of ammunition with the development of a resource-saving system that includes the secondary use of the released resources [1].

The explosives as well as the materials that are obtained during the disposal of weapons and military equipment can be classified as secondary material resources. These materials are potentially suitable for reuse initially or after some additional processing. One of the large-tonnage types of explosive materials that are obtained and recovered during the disposal of ammunition is pyroxylin powder. It contains up to 98% of the valuable polymer - cellulose nitrate (NC).

There are several modern trends in the recovery of recycled cellulose nitrate powders:

1) the use of unchanged powder elements and NCs contained in them as a part of industrial explosives and materials;
2) processing of them into new products - consumer goods: fuel briquettes, paints and varnishes [2];
3) production of complex mixed cellulose ethers with desired properties and development of new materials based on them.

The third direction is implemented through the synthesis of mixed cellulose ethers with improved physicochemical properties on the basis of NC regenerated from gunpowder. The obtained product can be further used in the national economy. NC shows good solubility in organic solvents in contrast with cellulose and can be chemically modified by the esterification of hydroxyl groups and the interesterification of nitrate groups [3-10].

In this work, we studied the reactions of NC with the empirical formula of the elementary unit C_6H_7O_2(OH)_{0.5}(ONO_2)_{2.5} (nitrogen content 12.75 %) with nucleophilic reagents - urea and thiourea. On the basis of the results of physicochemical methods of analysis the main directions of chemical interaction were established.

The reactions of NC with nucleophiles were carried out in homogeneous solutions with dimethylformamide (DMF) which dissolves the initial compounds without interacting with them.

In order to predict the main directions of the interaction between NC, urea and thiocarbamide, quantum-chemical calculations of the atomic point charges of urea and thiocarbamide molecules were...
carried out in the Gaussian 09 program by the Hartree-Fock method with 6-31G(d,p) basis set [11]. Figure 1 shows the optimized geometries of the studied molecules.

![Optimized geometries of molecules: a) carbamide; b) thiocarbamide](image)

**Figure 1.** Optimized geometries and atomic point charges of molecules: a) carbamide; b) thiocarbamide

The positive value of the energy of the lowest unoccupied molecular orbital (LUMO) of urea and thiocarbamide determines their nucleophilic properties in reactions with CN.

Nitrogen atoms have the highest negative point charges in the carbamide molecule, which indicates the most probable points of nucleophilic attack of NC carbons. Thiocarbamide is an ambident nucleophile; accordingly, both nitrogen and sulfur atoms can be reactive.

As a result of the reaction, solid products in the form of white odorless powders were isolated which are soluble in acetone, ethyl acetate, butyl acetate, pyridine, dimethyl sulfoxide, partially soluble in diethyl ether, alcohol, alcohol ether solvent (1:2) and insoluble in benzene, toluene, chloroform, carbon tetrachloride.

To determine the structure and study the properties of the obtained products, various physicochemical methods of analysis were used: elemental analysis, IR and $^1$H NMR spectroscopy, viscometric analysis, thermal polarization microscopy [12-14].

Analysis of the elemental composition and the results of titrimetric determination of nitrogen content showed that the increase of the reaction time leads to the decrease of the degree substitution (DS) of nitrate groups and the increase of DS by the carbamidine and thiocarbamide groups in the products.

The IR and $^1$H NMR spectra of the synthesized products indicate the presence of urea and thiocarbamide fragments in their structures. A decrease in the intrinsic viscosity of acetone solutions of the obtained products in comparison with the initial NC indicates the presence of processes of destruction and depolymerization of the chain of polymer macromolecules. The intensity of these processes increases with the growth of exposure time.

On the basis of experimental data the main reaction centers were identified: in the urea molecule - nitrogen atoms, in thiourea - the sulfur atom. The main directions of chemical modification of NC with carbamide and thiocarbamide were proposed: nucleophilic substitution of nitrate groups of NC with a thiocarbamide fragment, partial hydrolysis of nitrate groups, breaking of $\beta$-glycosidic bonds with the addition of urea and thiourea fragments at the ends of the polymer chain at the C$_1$ positions and C$_4$, as well as destruction and depolymerization of the cellulose nitrate chain.

The synthesized high-molecular compounds contain a smaller number of nitrate groups in the elementary unit, have a lower molecular weight, and, in contrast to the original NC, have new functional groups in their structure. The possibility of chemical modification of NC at different stages of synthesis on order to obtain products with controlled composition and properties was established.

The introduction of urea and thiourea fragments into the NC structure can impart some biological properties to the polymer, for example, disinfectants or fungicides, which requires additional research.
The timeliness of the research is determined by the need to solve environmental problems in the production of NCs as well as the possible conversion of gunpowder production. Most of the explosives recovered from disposal of ammunition can be used in industry, science-intensive technologies and for the creation of new materials. Quantum-chemical calculations were performed using the facilities of the Joint Supercomputer Center of Russian Academy of Sciences.

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