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X-ray Diffraction Study of Single-base Propellant Ageing

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Abstract: Ageing of single-base propellants, extending over a storage period of more than 50 years, was investigated by X-ray diffraction analysis. X-ray degree of crystallinity and interplanar spacing were determined. Analysed was the effect of nitrogen content, degree of substitution (DOS) and diphenylamine (DPA) content on structural changes in propellants.

Key words: ageing; propellant; X-ray diffraction analysis; nitrocellulose (NC)

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1　Introduction

X-ray diffraction analysis is used for determining structural parameters in various processes of nitrocellulose (NC) in propellants. Variation of interplanar spacing d in NC on nitration and denitration has been investigated in Ref. [1]. In Ref. [2], it has been reported that X-ray diffraction analysis is used also for quantitative characteristics of propellant additives of quantities grater than 1%. For the characterisation of mixes in Ref. [3], spectra of addition of salts were used as internal standard. Combustion rate of propellants has been investigated with X-ray diffraction analysis in Ref. [4], with attention being paid also to the effect of the state of propellants before the analysis, without giving quantitative changes with the storage time.

The aim of the investigation is to study the effect of ageing on structural changes in propellants in case of long storage through determining the X-ray degree of cristallinity K_α and interplanar spacing d.

2　Experimental

Investigated were seven-perforated single-base propellants with a nitrogen content of 13.05% ~ 13.85%, stored in military storehouses with maintenance of temperature and moisture conditions for a period of time extending over more than 50 years. Propellants were analyses with X-ray diffractometer Phillips (Germany), 34 kW, 20 mA. Diffraction curves were obtained with Cu K_α radiation with continuous scanning and rotation of powder pressed sample over an angle range of $2\theta = 3° \sim 40°$. Interpretation was done with a software package belonging to the diffractometer. Nitrogen content in propellants was determined by Lunge G nitrometer according to Ref. [5]. DPA was determined by Pye Unicam (England) chromatograph.

3　Results and discussion

Propellant ageing is characterised by different types of destruction processes going on together or complementing each other. Therefore, its interpretation is not unambiguous and there is no full picture of those processes. An important stage is the investigation of structural changes during propellant ageing.

Diffraction patterns of investigated propellants, stored for 5, 17, 45 and 56 years, are distinguished for two rounded diffraction peaks in the range $2\theta = 12° \sim 20°$, characteristic of highly nitrated NC. From them, X-ray degree of cristallinity K_α and interplanar spacing d were determined.

Degree of cristallinity K_α was determined according to the method proposed by Hermans P and Weidinger A by the formula:

$$K_\alpha = \frac{\sum S_{cr}}{\sum (S_{cr} + S_{cr})}$$

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where:

S_{cr}—area of crystal part;

S_{am}—area of amorphous part.

Data for variation of K_α, nitrogen content N_2, degree of substitution γ, NO_2-groups content and DPA versus time of propellant storage are given in table 1.

Table 1　Variation of K_α, N_2, γ, NO_2 and DPA versus storage time of propellants

Storage time /years	K_α/%	N_2/%	γ	NO_2/%	DPA/%
5	12.36	13.85	2.889	61.34	1.70
17	2.23	13.05	2.723	57.79	1.56
45	3.67	13.12	2.737	58.10	1.21
56	5.09	13.22	2.758	58.55	1.12

From table 1 it is seen that the degree of cristallinity K_α decreases in case of long storage of propellants, with existing dependence on the nitrogen content in NC. It is possible that effect on K_α of highly nitrated NC of propellants has also the different content of alcohol-ether mixture[6]. These results coincide completely with the on-going destruction processes of ageing in the propellants. Unlike the nitration reaction of NC, in which the degree of substitution γ of ON groups with NO_2 groups has an effect, during ageing, the non-uniformity of the substitution increases, and the lengths of the macrochains decrease, with their polydispersity increasing at that. Therefore K_α decreases. Ageing depends also on intensity of going on of the process of destruction of the initial ordered supermolecular structure of NC, whereupon new structures are formed.

With the decrease of the DPA stabiliser, the ageing is accelerated, wherefrom follows that the hydrogen bonds among the functional groups in NC of propellants are destroyed.

For the analysis of crystal structure of propellants, the determination of interplanar spacings d at $2\theta = 4°, 6°, 8°, 10°, 11°, 19°$ and $22°$, which are given in table 2, is used.

From the data in table 2 it is seen that at different values of 2θ, there is both decrease and increase of d. In Ref. [1], a detailed variation of d has been described. It has been established that with decrease of the degree of substitution d of the ON groups with NO_2 groups, the d (110) spacing in the lattice of NC decreases from 7.28 to 6.81■. The values for d (110) on denitration do not vary at γ from 2.8 to 2.2, whereas on nitration, there is a decrease of d (110) with the decrease of γ. Variation of phase state of NC during nitration reactions has been investigated with X-ray diffraction analysis also in Ref. [7]. Recorded have been variations for d dependent on nitriting mixes.

Table 2　Variation of interplanar spacings d versus storage time of propellants　(■)

2θ/(°)	Storage time/years			
	5	17	45	56
4	8.84	16.67	11.05	—
6	6.81	8.19	9.11	—
8	5.34	5.98	—	—
10	4.35	4.27	—	—
11	4.07	4.13	—	—
19	2.02	2.37	2.40	2.35
22	2.35	2.06	2.07	2.02

It can be assumed that in a consequence of ageing simultaneously with the process of structural destructions in NC of propellants, there goes on also rearrangement allowing formation of new structures. The values of d for $2\theta = 2°, 10°$ and $11°$ for propellants, stored for 45 years, were not registered, and in case of 56 years of storage-also for the angles $2\theta = 4°$ and $6°$. This is explained with the decrease of molecular weights: number-average (M_n), average (M_w), viscosity-average (M_η) and coefficient of polydispersity (n) of the investigated propellants during ageing[8]. For the propellants stored for 17 years, M_η = 1 480 000 and $n = 4.34$, whereas for 56-year-old propellants M_η has already decreased to 19 700, and $n = 7.00$. All of the above mentioned leads to destruction of intermolecular bonds as well as crystal structure.

Investigations made allow to apply X-ray diffraction analysis to characterise the ageing of NC of propellants, thus completing other investigation methods.

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