Influence of processing solvents on decomposition of nitrocellulose in smokeless powders studied by heat flow calorimetry

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A B S T R A C T

The influence of processing solvents (water, diethyl ether and ethyl alcohol) on thermal stability of nitrocellulose in smokeless powders was investigated by heat flow calorimetry. Powders subjected to different methods of volatiles removing were used for measurements. The dependence of accumulated heat on temperature was applied for analysis. The results indicate that residual water destabilizes studied powders most of all. Experiments proved that thermal effects during the first step were controlled by reactions of diphenylamine with nitrocellulose decomposition products. The relation between the heat generation constant and the diphenylamine concentration was determined. The analysis of experimental data shows that the stabilizing effect of diphenylamine can be observed only at low extent of nitrocellulose conversion.

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1. Introduction

Nitrocellulose (NC) as the basic component of single and double base powders is unstable and is susceptible to decomposition e.g. reactions of thermolysis and hydrolysis. The homolysis of $CO-NO_2$ bond generates radicals. A series of reactions then occur, some of which result in the formation of nitrogen oxides and nitrous/nitric acid. The evolved products of oxidizing properties catalyse further decomposition of NC. The reactions in nitrocellulose-based propellants are accompanied by significant heat effects [1] and molecular weight reduction [2]. The above mentioned phenomena result in a substantial risk during storage and firing. With degradation of NC chains the mechanical strength of powder grains decreases. This can finally lead to the increased burning surface and uncontrolled pressure rise. The addition of stabilizers to nitrocellulose was the most important advance in powders production. The stabilizing effect consists in chemical bonding of degradation products that accelerate further decomposition. The monitoring of reactions of stabilizers in smokeless powders is of fundamental significance for their operational and ballistic stability. Therefore the important goal of research on nitrocellulose and smokeless powders was to develop effective stabilizers [3–8], investigate the ageing processes [9,10] and determine the kinetics of decomposition [11–13]. Primary decomposition products may accelerate degradation of nitrocellulose. It is possible to slow down the catalytic process by adding stabilizers, e.g. diphenylamine (DPA). This compound preferably reacts with reactive oxides and acids forming nitroso and nitro derivatives [1,14,15], and the major reaction product is N-nitrosoDPA, whereas the content of nitro derivatives is considerably lower [14].

The powder dough consists of nitrocellulose, stabilizer and mixture of ethyl alcohol and diethyl ether. For manufacturing of smokeless powders most often DPA is used as a stabilizer. The solvent mixture is used in such an amount that the dough achieves suitable rheological properties. A thoroughly mixed mass is formed into strips or extruded into cords. The shaped forms are pre-dried to lower the solvent content and to enhance their mechanical resistance. The so-prepared product can be cut into a desirable shape without being deformed. There are no data concerning the influence of processing solvents on the degradation of powders stabilized with DPA, in the initial stage of this process. Therefore we decided to undertake a study on the influence of volatiles on thermal induced degradation of powders. The aim of this research was also to compare different methods of volatiles removal in relation to the stability of powders. The heat effects associated with the initial stage of their thermal degradation were followed by heat

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flow calorimetry (HFC). The HFC sensitivity makes possible measurements of small thermal effects observed for decomposition of nitrocellulose. The basic aim of HFC investigations of nitrocellulose based powders is to control their degradation and to estimate their operational stability.

2. Materials and methods

2.1. Heat flow calorimetry (HFC)

HFC measurements were conducted using TAM III calorimeter (TA Instruments). Measurements were performed in capped 4.3 ml ampoules. They were completely filled and the degree of filling Z was calculated as a ratio of the sample mass to the ampoule volume. The initial powder marked P-0 gives much lower degree of filling than the others. This is connected with the higher content of processing solvents, which cause the swelling of powder grains. The measurements were carried out at 90 °C to shorten them. This is the highest temperature recommended by standard procedure STANAG 4582 [16]. The results were used to evaluate the thermal stability of single based propellant before admission to further modifying stages of the burning layer. The measurements were carried out with agreement to manufacturer i.e. the analysis of calorimetric signal (P) started after 45 min (P_{45}).

2.2. Quantification of volatiles

The method based on hydrolysis of NC was carried out using procedure described previously [17]. The samples were dissolved in NaOH aqueous solutions (20% by weight). The volatiles released from powders were next distilled. The resulting distillates were analysed using a Perkin Elmer AutoSystem XL gas chromatograph with FID detector. Separations were performed on PE Elite-1701 30 m column, using nitrogen as carrier gas. The oven program was: 1 min at 50 °C then ramped at 2.5 °C/min to 70 °C and finally to 250 °C at 25 °C/min. The temperature of FID and injector was 200 °C. For quantification IS method was applied using methanol as internal standard.

2.3. Quantification of diphenylamine and derivatives

The HPLC quantitative analysis of diphenylamine and its derivatives was carried out on Agilent 1260 Infinity system. The separations were performed on 15 × 4.6 cm Supelcosil ABZ + Plus column (Sigma−Aldrich) using HPLC grade (Merck) methanol and water, 49% and 51% (vol.) respectively. The flow rate was 1.5 ml/min and oven temperature 35 °C. The quantification was based on the IS method. DPA and its derivatives were obtained from Sigma-−Aldrich. Samples of powders were poured with acetonitrile. After 2−4 h grains were completely disintegrated and went into a powdery precipitate. Next aqueous solution of calcium chloride was added to precipitate nitrocellulose. Then IS was added and the sample was filled up with water to the final volume. The obtained supernatant liquid prior analysis was filtered through 0.45 μm PTFE filter.

2.4. Materials

The initial smokeless powder P-0 was prepared in Special Production Plant Pionki (Poland) from nitrocellulose (13.2% N) using DPA as stabilizer. Powder P-0 was sampled just after cutting extruded cords into small tubes. The samples were as follows: initial powder P-0 with high content of volatiles and powders subjected to different processes of solvents removing. P-0 is a single-perforated short tubular powder (5/1) of average 1.9 mm

length, 1.3 mm diameter and 0.50 mm thickness of the burning layer. The removing of volatiles was carried out in a high-scale laboratory reactor of 25 l volume. The methods applied to prepare investigated powders can be found in Table 1. All those methods aimed at receiving powders of various content of volatiles. For comparison also a batch of initial powder P-0 dried using industrial method in SPP Pionki was used. Both the content of diethyl ether(x_E), ethanol(x_A) and water(x_W), and the initial contents of DPA and N-nitrosoDPA in studied powders are summarized in Table 2.

3. Theory/calculation

In the present state of knowledge all kinetic models which could describe decomposition of NC and reactions of stabilizers are approximate. Therefore it is easier to give a very general kinetic description, which can be reduced to simple dependencies for the condition of small degrees of conversion α. Let us note that the decomposition of examined compounds followed the first order reaction [18,19] and the degradation products act as catalysts of the subsequent reactions. We can express the whole reaction rate by the Eq. (1) [20]:

$$\frac{d\alpha}{dt} = k_1(1-\alpha) + k_2\alpha(1-\alpha) \tag{1}$$

where α is the conversions degree, k_1 and k_2 are reaction rate constants of the first order and the autocatalytic reaction respectively. This equation can be applied if the sample and its decomposition products are soluble in the reaction phase. During the real degradation process the volatile products also appear. They have catalytic properties but also have limited solubility α^*. For such assumptions Eq. (1) can be described:

$$\frac{d\alpha}{dt} = k_1(1-\alpha) + k_2\alpha^*(1-\alpha) \tag{2}$$

where α^* is the concentration of a catalyst in the reaction phase, which changes are dependent on the thermodynamic equilibrium. Rearranging Eq. (2), where α^* is the constant, a pseudo-first rate equation is obtained:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^*)(1-\alpha) \equiv k(1-\alpha) \tag{3}$$

Eq. (3) was successfully used for description of decomposition of energetic materials in the initial stage [21−23]. For a very small degree of conversion $\alpha \ll 1$, it can be assumed that the term $1 - \alpha \approx 1$. For this reason Eq. (3) takes the form.

Table 1
Summary of powders symbols and their preparation methods from initial powder in consecutive processes of volatiles removing.

Powder	Preparation methods
P-0	Initial powder
P-1W	Distillation of a water slurry (rp), drying in rotary evaporator (rp)
P-2	Dry distillation (rp)
P-2W	Dry distillation (rp), drying in rotary evaporator (rp)
P-3	Dry distillation (rp) with prolonged processing time
P-3W	Dry distillation (rp) with prolonged processing time and drying in rotary evaporator (rp)
P-4W	Removing of diethyl ether in dry distillation (rp), and ethanol in distillation of a water slurry (rp), drying in rotary evaporator (rp)
P-4WS	As for P-4W and drying in air drier
P-5	Water extraction + drying in diffuser

Note: rp means reduced pressure used for the process.