

Kinetic Modelling of the Chemical Transformations of the Stabiliser in Single Base Gun Propellants during Ageing

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A suitable kinetic model for the chemical transformations of the stabiliser (diphenylamine, DPA) in single base gun propellants during aging was investigated and successfully verified. This model assumes that chemical transformations of stabilisers in single base gun propellants occur in three concurrent ways, each of them representing a complex reaction, the kinetics of which can be described by the reactions of the shifting order. It was found that the experimental data were well evaluated by a first-order reaction at high concentrations of diphenylamine in the propellant, but by a zero-order reaction at low concentrations during the final phase of the propellant lifetimes. The mechanism of chemical transformations of diphenylamine was discussed in relation to the model and the ageing behaviour of these propellants.

Key words: propellant, single base gun propellant, propellant stability, stabilizers, diphenylamine, chemical stability, kinetic model.

Introduction

SINGLE-BASE gun propellants contain one energetic component, the cellulose nitrate (nitrocellulose, NC), which is gelatinized with evaporable solvent. After the formation of propellant grains, the solvent is removed from the propellants. The spontaneous chemical evolution of these propellants takes place over time and the propellants must be stabilized, since the nitrocellulose decomposition has autocatalytic character. Diphenylamine (DPA) is used as a stabilizer and it is often the only additive of single-base gun propellant composition. Apart from DPA, single-base gun propellants can contain other additives, which affect the properties and the of final product process [1, 2, 3].

The reaction and diffusion processes causing chemical transformations of the stabilizer in a gun propellant during its lifetime are very complex. Namely, because of the low binding energy of the nitric ester CO-NO₂ bond, nitrocellulose is subject to slow thermal decomposition even at moderate temperatures (normally less than 40° or 50°C). Thus, a nitrocellulose (nitric esters, RONO₂) is thermally unstable. It decomposes in an exothermic manner via thermolysis. The first step involves breakage of the nitric ester bond (RO-NO₂→RO[•]+NO₂[•]) and the formation of the free radicals RO[•] and NO₂[•]. Being free radicals, these are highly reactive with nearby molecules of RONO₂ and consequently a series of secondary reactions ensue from decomposition of nitrocellulose, all of which are exothermic [4].

One important feature of NO₂ is its capability to catalyze thermolysis of NC. As it accumulates, it accelerates further nitric ester decomposition. The result is that more heat is produced and the temperature in the propellant rises. This accelerating action of NO₂ is called self-catalysis. If it were left to occur in an uncontrolled fashion, then the rate of heat

generation could eventually become higher than the rate of heat loss to the surroundings, resulting in thermal explosion of the nitric ester after a certain induction period.

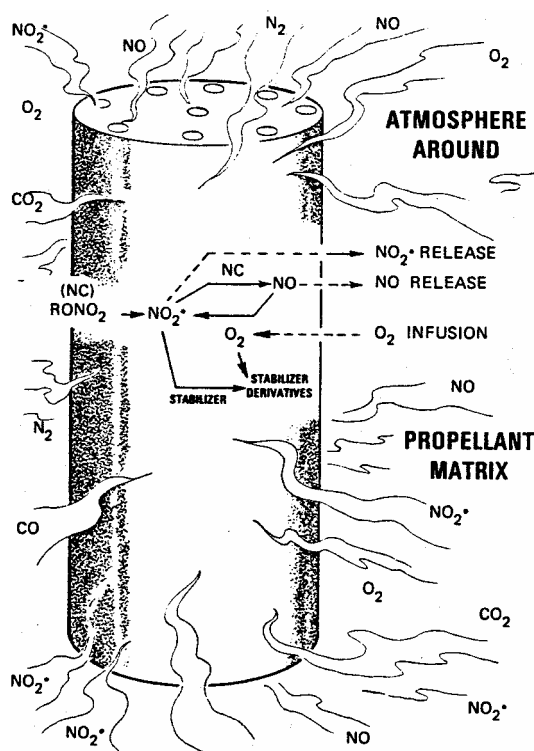


Figure 1. Chemical evolution of NC-based propellants [4]

When the nitric ester is considered as a component of the propellant, the previous reaction scheme has to be modified to account for other processes which affect decomposition

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under such conditions. The result is presented in Fig.1. Here the general formula RONO_2 is used as well as that of nitrocellulose, since it is a major component of gun propellants. Both the interior of the propellant grains and the surrounding atmosphere, are indicated since diffusion of the evolved gases outward and diffusion of atmospheric oxygen into the grains are important factors here. The presence of the stabilizer in the propellant is also critical because it inhibits the undesirable catalytic effect of NO_2 . It reacts with NO_2 to form stabilizer derivatives [4].

In the early phases of the propellant evolution, nitric ester decomposition occurs only to a small extent. The reaction between the stabilizer and NO_2 is unlikely because of the high reactivity and low concentration of NO_2 . Furthermore, the stabilizer concentration is low relative to the concentration of RONO_2 . The NO_2 reacts with other molecules of NC to give nitric oxide and carbon oxides. The small NO molecule can subsequently diffuse through the interior of the propellant and be released into the atmosphere or react with the stabilizer [4].

As further degradation of RONO_2 occurs, continued local production of NO_2 and the secondary products as well as an increased formation of the stabilizer derivatives accompany it. As the NC molecular weight decreases, small cracks begin to form. This facilitates the diffusion of NO and collision with the stabilizer molecule. Once the stabilizer is consumed, the propellant is no longer protected against the accelerating action of NO_2 . Since the situation is dangerous, it is clearly essential to avoid it.

DPA reacts with autocatalytically acting decomposition products of nitrocellulose (nitrogen oxides) forming nitrated consecutive products with an increasing degree of nitration [5-8]. The consecutive products of DPA, from the N-nitroso-DPA and mono-nitro-derivatives of the DPA to the hexa-nitro-derivatives of DPA, are formed over time (Fig.2). Some of them have a stabilizing effect as well [5-7].

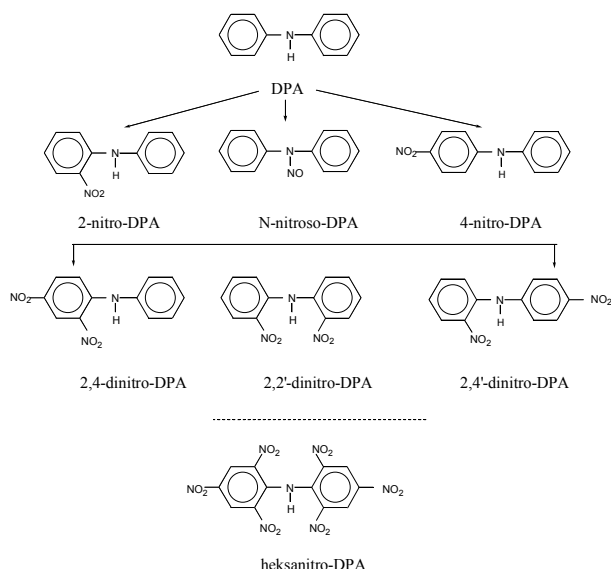


Figure 2. Chemical transformation of diphenylamine in NC-based propellants

The DPA consumption data during aging at different temperatures are used to predict a safe storage life of propellants. In accordance with the stabilizing effect of DPA, N-nitroso-DPA and mono-nitro-derivatives of DPA, there are attempts [4] to include these derivatives into the equations for predicting safe storage life of propellants.

Therefore, a fast, accurate and precise method for determining the contents of the mentioned components in propellants as well as the kinetic modelling of the chemical transformation of DPA and the formation of its mono-derivatives, are necessary.

Different instrumental methods have been used for determining the stabilizers and their derivatives' contents in propellants. The chromatographic methods [8] as thin-layer chromatography (TLC), gas chromatography (GC), and high performance liquid chromatography (HPLC) were most applicable. TLC technique has now been replaced by HPLC or GC. At one point, gas chromatography was used as a leading method for determining stabilizer contents in propellants. However, along with favourable properties, this method has disadvantages as well. With GC, the substances to be analyzed must be brought into gaseous state before entering the column and therefore, terminally unstable compounds are in danger of full or partial decomposition. Therefore, the limitation of GC methods is the inability to separate diphenylamine and its main derivatives N-nitroso-DPA, which is thermally decomposed wholly or partially into DPA [9] in the inlet port of gas chromatograph. Therefore, it can not determine the contents of DPA and its main derivative N-nitroso-DPA in aged propellants. The HPLC method does not have this problem due to its lower operating temperatures. Therefore, HPLC is nowadays used as the leading method for determining the contents of DPA, N-nitroso-DPA and other derivatives of DPA in aged propellants.

Knowledge of the stabilizer content and its consumption over a time-temperature range permits estimating their safe storage and use time. Several different approaches, which involve artificial aging of propellant samples at various elevated temperatures and measuring the change in the "free" stabilizer content of the propellant and formation of its nitrated consecutive products, have been used to obtain equations to predict the time for consumption of a given percentage of the stabilizer and a temperature coefficient to allow estimation of this time at the storage temperature [1-13]. Some of the prediction methods were investigated for specific problems and it was found that they depend on the technique used to monitor the stabilizer. Other methods were intended as basic kinetic approaches that could, at least in principle, be applied to any propellant chemical stability problem.

Kinetic modelling of the consumption of the stabilizer in single base gun propellants has been performed using different methods: model which the consumption of DPA describes by a first-order reaction [10-12], model which combines formal reactions of first and zero order [10-12] and model which assumes that reaction of the shifting order can be applied for the consumption of DPA in single base gun propellants [13].

The objective of the investigation was to find a suitable kinetic model for the chemical transformations of diphenylamine in single base gun propellants during their aging as well as to analyze the mechanism of these transformations with relation to the model and ageing behaviour of the propellants.

Description of the model

The reaction and diffusion processes causing the chemical transformations of the stabilizer in a gun propellant during its life time are very complex and a kinetic approach requires some simplifying assumptions.

It is assumed that these transformations occur in the three concurrent ways, each of them representing a complex reaction, the kinetics of which can be described by the reactions of shifting order [14]. Namely, when the diphenylamine concentration in a gun propellant is relatively high, the chemical transformations of diphenylamine approach first-order kinetics, i.e. the reactions of DPA with the evolved nitrogen oxides are dominant. When the DPA content becomes sufficiently small, the reactions of the DPA derivatives prevail, because the chemical accessibility of the unreacted DPA becomes a limiting factor. Then, the diphenylamine depletion does not depend on its concentration, i.e. the diphenylamine consumption tends to the reaction of the zero-order. Further, it is accepted that the temperature dependence of the reaction rate constants follows Arrhenius type behaviour.

In the adopted notation the rate equations describing the stabilizer transformation according to the accepted kinetic model are given by:

$$-\left(\frac{\partial C_0(t,T)}{\partial t}\right)_T = k_{0,0}(T) + k_{1,0}(T)C_0(t,T) = \sum_{i=1}^3 \left(\frac{\partial C_i(t,T)}{\partial t}\right)_T \quad (1)$$

$$\left(\frac{\partial C_i(t,T)}{\partial t}\right)_T = k_{0,i}(T) + k_{1,i}(T)C_0(t,T) \quad (2)$$

$$\sum_{i=1}^3 k_{0,i}(T) = k_{0,0}(T) \quad (3)$$

$$\sum_{i=1}^3 k_{1,i}(T) = k_{1,0}(T) \quad (4)$$

$$\left(\frac{\partial C_i(t,T)}{\partial C_{i+1}(t,T)}\right)_T = \frac{k_{0,i}(T)}{k_{0,i+1}(T)} = \frac{k_{1,i}(T)}{k_{1,i+1}(T)} \quad (5)$$

$$k_{0,i}(T) = Z_{0,i} \exp\left(-\frac{E_{a,0,i}}{RT}\right) \quad (6)$$

$$k_{1,i}(T) = Z_{1,i} \exp\left(-\frac{E_{a,1,i}}{RT}\right) \quad (7)$$

where C_0 is the diphenylamine concentration in a propellant as a function of time t and temperature T , C_i are the concentrations of DPA-mono-derivatives in a propellant as a function of time and temperature, $k_{0,i}$ and $k_{1,i}$ are the reaction rate constants for the zero-order and first-order kinetics, respectively, $Z_{0,i}$, $Z_{1,i}$, $E_{a,0,i}$ and $E_{a,1,i}$ are the corresponding pre-exponential factors and the energies of activation in the Arrhenius equation, R is the universal gas constant. The subscript $i=0$ denotes the DPA and $i=1,2,3$ denotes DPA-mono-derivatives.

Integration of eq.(1) and eq.(2) yields:

$$C_0(t,T) = -\frac{k_{0,0}(T)}{k_{1,0}(T)} +$$

$$+ \left[\frac{k_{0,0}(T)}{k_{1,0}(T)} + C_0(0,T) \right] \exp[-k_{1,0}(T) \cdot t] \quad (8)$$

$$C_i(t,T) = C_i(0,T) + \left[k_{0,i}(T) - k_{1,i}(T) \frac{k_{0,0}(T)}{k_{1,0}(T)} \right] \cdot t + \frac{k_{1,i}(T)}{k_{1,0}(T)} \cdot \left[\frac{k_{0,0}(T)}{k_{1,0}(T)} + C_0(0,T) \right] (1 - \exp[-k_{1,0}(T) \cdot t]) \quad (9)$$

Then, eq.(8) describes the decrease in the diphenylamine content and eq.(9) expresses the increase in the DPA-mono-derivatives concentrations over a time-temperature range.

Experiment

Single base gun propellant NC-27, containing about 99% nitrocellulose (NC) and 1% diphenylamine, was subjected to the artificial aging at 100, 90, 80 and 60°C for the times up to a complete consumption of the stabilizer. These tests were run on a 30g sample using pyrex tubes (150mm long by 25mm diameter), capped with loosely ground glass stoppers. In the presented work, the entire tube was contained within the cavity in the heating block to ensure uniformity of heating and to avoid condensation at the top of the tube.

The stabilizer content in the aged propellant samples was measured by the reversed-phase high performance liquid chromatography (HPLC).

The propellant samples were ground (approximately to a thickness of 2mm); 2g of each were extracted for 48 hours with 50ml of dichloromethane. By pipetting, 2ml of this solution was transferred into the volumetric flask of 10ml. The solvent was then evaporated, the internal standard solution (centralite II in acetonitrile) was added and the content of the flask was diluted with acetonitrile.

The concentration of the standard components (DPA, N-nitroso-DPA, 2-nitro-DPA and 4-nitro-DPA) in the 50ml calibration mixture solution covered the ranges expected for samples. By pipetting, 2ml of this solution was transferred into the volumetric flask of 10ml and dichloromethane was evaporated. The internal standard solution was added and the flask content was diluted with acetonitrile.

The HPLC instrument LDC/Milton Roy 3000 was used. The variable wavelength UV-detector was set at a wavelength of 220nm. Data were processed using a chromatography data system.

The column type was 150mm x 4.6mm Supelcosil LC-18-DB with a particle size of 3 μ m and the operating temperature maintained at 55°C.

The mobile phase composition was acetonitrile/water, 40/60 (v/v) with the flow rate of 2ml/min. The injection sample size was 5 μ l.

Results and discussion

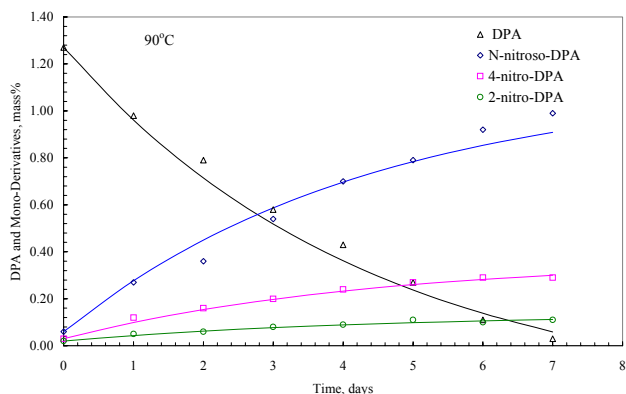
The HPLC analysis results obtained for the aged propellant samples at 90°C are presented in Table 1.

All of these results formed the basis for the kinetic and statistical analysis, which was intended to verify the proposed kinetic model.

The graphical presentation of the results is given in Fig.3. The solid lines in this figure were fitted according to the eqs. 8 and 9.

Table 1. Concentration of DPA and DPA-mono-derivatives in the single base gun propellant NC-27 as a function of time

t , day	DPA, mass%	N-NO-DPA, mass%	4-NO ₂ -DPA, mass%	2-NO ₂ -DPA, mass%	C_{total} , mass%
0	1.27	0.06	0.03	0.02	1.38
1	0.98	0.27	0.12	0.05	1.42
2	0.79	0.36	0.16	0.06	1.37
3	0.58	0.54	0.20	0.08	1.40
4	0.43	0.70	0.24	0.09	1.46
5	0.27	0.79	0.27	0.11	1.44
6	0.11	0.92	0.29	0.10	1.42
7	0.03	0.99	0.29	0.11	1.42
	Average value, AV				1.41
	Standard deviation, SD				0.03

**Figure 3.** Chemical transformations of diphenylamine in the single base gun propellant NC-27 – Description by a reaction of the shifting order

The reaction rate constants for the chemical transformations of DPA were calculated by the regression analysis according to eq.8, while the reaction rate constants for the formation of DPA-mono-derivatives were calculated in accordance with eqs. (3) – (5) by the regression analysis, as well. The results of these calculations are given in Table 2.

Table 2. Reaction rate constants for the chemical transformations of DPA and for the formation of DPA-mono-derivatives in the single base gun propellants NC-27 at 90°C

DPA	N-NO-DPA	4-NO ₂ -DPA	2-NO ₂ -DPA
k_{00} , mass%/d	k_{01} , mass%/d	k_{02} , mass%/d	k_{03} , mass%/d
0.0569	0.0399	0.0127	0.0043
k_{10} , 1/d	k_{11} , 1/d	k_{12} , 1/d	k_{13} , 1/d
0.2275	0.15950	0.05072	0.01728

As it can be seen from Fig.3, there is a good agreement between the corresponding measured and calculated concentrations of DPA and DPA-mono-derivatives for the times up to its practically complete consumption. This fact confirms the validity of the proposed kinetic model for the chemical transformations of the stabilizer in single base gun propellants. The assessment of the model was made by the standard deviation (SD) of the least square fit procedure:

$$SD = \sqrt{\frac{\sum_{i=1}^R \sum_{j=1}^T [C_{i,j}^{exp} - C_{i,j}^{calc}(k_{0,i}, k_{1,i})]^2}{R \cdot T - Nk}} \quad (10)$$

where $C_{i,j}^{exp}$ is the concentration of i^{th} reaction species measured in j^{th} time, $C_{i,j}^{calc}$ is the concentration of i^{th}

reaction species calculated in j^{th} time, R is the number of reaction species, T is the number of times at which the measurements or the calculations are made, and Nk is the number of parameters whose calculation was required.

From the results of the assessment for the considered kinetic model conclusion was drawn that the standard deviation between the calculated and measured concentrations of DPA and DPA-mono-derivatives is 0.04mass% and that this deviation is of the same magnitude as the standard deviation of the mass balance that is 0.03mass% and which represents the experimental error. This fact confirms the validity of the proposed kinetic model.

Kinetic parameters of the chemical transformations of DPA and of the formation of DPA-mono-derivatives can be determined by regression analysis in accordance with eqs.(6 and 7).

Assessment of the model using results obtained in other laboratories

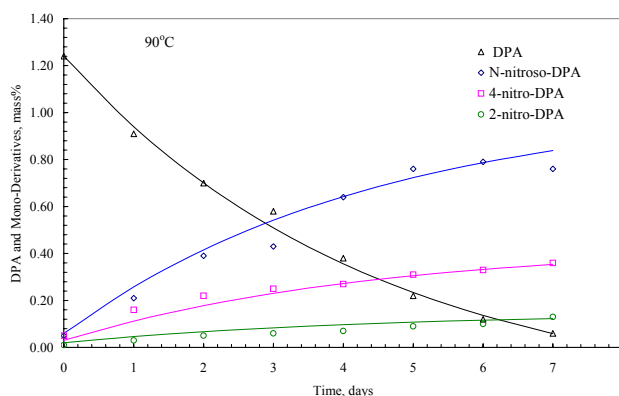
The HPLC analysis results obtained for the aged propellant samples GP A5020 [15] at 90°C are presented in Table 3.

Table 3. Concentration of DPA and DPA-mono-derivatives in the single base gun propellant GP A5020 as a function of time

t , day	DPA, mas. %	N-NO-DPA, mas. %	4-NO ₂ -DPA, mas. %	2-NO ₂ -DPA, mas. %	C_{ukupno} mas. %
0	1.24	0.05	0.05	0.01	1.35
1	0.91	0.21	0.16	0.03	1.31
2	0.70	0.39	0.22	0.05	1.36
3	0.58	0.43	0.25	0.06	1.32
4	0.38	0.64	0.27	0.07	1.36
5	0.22	0.76	0.31	0.09	1.38
6	0.12	0.79	0.33	0.10	1.34
7	0.06	0.76	0.36	0.13	1.31
	AV				1.34
	SD				0.026

All of these results formed the basis for the kinetic and statistical analyses, intended to verify the proposed kinetic model.

The graphical presentation of the results is given in Fig.4. The solid lines in this figure represent the calculated concentrations of DPA and DPA-mono-derivatives.

**Figure 4.** Chemical transformations of diphenylamine in the single base gun propellant GP A5020 – Description by a reaction of the shifting order

The reaction rate constants for the chemical transformations of DPA and for the formation of DPA-mono-derivatives are given in Table 4.

Table 4. Reaction rate constants for the chemical transformations of DPA and for the formation of DPA-mono-derivatives in the single base gun propellants GP A5020 at 90°C

DPA	N-NO-DPA	4-NO ₂ -DPA	2-NO ₂ -DPA
k_{00} , mas%/d	k_{01} , mas%/d	k_{02} , mas%/d	k_{03} , mas%/d
0.0562	0.0363	0.0151	0.0048
k_{10} , 1/d	k_{11} , 1/d	k_{12} , 1/d	k_{13} , 1/d
0.2248	0.1452	0.0604	0.0192

As it can be seen from Fig.4, there is a good agreement between the corresponding measured and calculated concentrations of DPA and DPA-mono-derivatives for the times up to its practically complete consumption. This fact confirms the validity of the proposed kinetic model for the chemical transformations of the stabilizer in single base gun propellants, as well. The assessment of the proposed model was made by the standard deviation (SD) of the used numerical procedure.

The results of this assessment indicated that the standard deviation between the calculated and measured concentrations of DPA and DPA-mono-derivatives is 0.037mass% and that this deviation is of the same magnitude as the standard deviation of the mass balance that is 0.026mass% and which represents the experimental error. This fact also confirms the validity of the proposed kinetic model.

Furthermore, based on the results from Tables 2 and 4 it can be seen that the values of the reaction rate constants for the consumption of DPA, just as for the formation of DPA-mono-derivatives, are practically the same for both gun propellants considered. This fact also confirms the validity of the proposed kinetic model, in particular from the point of view of its more general application and of the mechanism of chemical transformations of the stabilizer during ageing of gun propellants.

Diphenylamine chemically binds the evolved decomposition products of nitrocellulose and the consecutive products with an increasing degree of nitration formed. Hence, the nitrated consecutive products of DPA, from the N-nitroso-DPA and the mono-nitro-derivatives of DPA to the hexsa-nitro-derivatives of DPA are formed in time. Some of them, N-nitroso-DPA and mono-nitro-derivatives of DPA, also have a stabilizing effect [15,16].

As it can be seen in Fig. 3 - 4, the concentrations of N-nitroso-DPA and mono-nitro-derivatives of DPA increase with aging time increasing. Since these DPA derivatives have an important stabilizing effect, react with the NC decomposition products in a further step they concurrently with the remaining DPA. When the diphenylamine concentration in a gun propellant is relatively high, the chemical transformations of diphenylamine approaches first-order kinetics, i.e. the reactions of DPA with the evolved nitrogen oxides are dominant. When the DPA content becomes sufficiently small, the reactions of the DPA derivatives prevail, because the chemical accessibility of the unreacted DPA becomes a limiting factor. Then, the diphenylamine depletion does not depend on its concentration, i.e. the diphenylamine consumption tends to the reaction of the zero-order. Therefore, during this phase the reactions of the formation of the higher DPA-nitro-derivatives prevail, and the kinetics of the chemical transformations of DPA becomes more complex; for further

considerations the proposed kinetic model should be expanded in order to describe the mechanism of the chemical transformations of DPA-mono-derivatives.

Conclusion

A suitable kinetic model for the chemical transformations of diphenylamine in single base gun propellants, which assumes that these transformations occur in three concurrent ways, each of them representing a complex reaction, and the kinetics of which can be describe by the reactions of shifting order, was successfully verified.

It was found that the experimental data were well evaluated by a first-order reaction at high concentrations of diphenylamine in the gun propellant, but by a zero-order reaction at low concentrations during the final phase of the propellant life times.

The kinetic model was verified based on the results of the performed investigation of the chemical transformations of the stabilizer in the single base gun propellant NC-27, as well as the results for the gun propellant GP A5020 [15] obtained from another laboratory. A satisfactory agreement between the measured and calculated concentrations of DPA and DPA-mono-derivatives was found in the both cases.

The mechanism of chemical transformations of diphenylamine was discussed with relation to the model and the ageing behavior of these propellants.

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Kinetičko modelovanje hemijskih transformacija difenilamina tokom starenja jednobaznih baruta

Istraživan je i uspešno verifikovan kinetički model hemijskih transformacija stabilizatora (difenilamina, DFA) tokom starenja jednobaznih baruta. Ovaj model pretpostavlja da do hemijske transformacije stabilizatora u barutu dolazi na tri uporedna načina, od kojih svaki predstavlja složenu reakciju čija se kinetika može opisati reakcijama promenljivog reda. Nadenno je da se eksperimentalni podaci veoma dobro procenjuju reakcijom prvog reda pri velikim koncentracijama difenilamina u barutu i reakcijom nultog reda pri malim koncentracijama tokom završnog perioda upotrebljivosti baruta. Razmatran je mehanizam hemijskih transformacija difenilamina u odnosu na model i proces starenja baruta.

Ključne reči: barut, jednobazni barut, stabilnost baruta, stabilizatori, difenilamin, hemijska stabilnost, kinetički model.

Кинетическое моделирование химических трансформаций дифениламина в процессе старения однобазисных порохов

В этой работе исследована и удачно верифицирована кинетическая модель химических трансформаций стабилизаторов (дифениламина, ДФА) в процессе старения однобазисных порохов. Эта модель предполагает, что химические трансформации стабилизаторов в порохе происходят тремя сравнительными способами, а каждый из них представляет сложную реакцию, чью кинетику возможно описать при помощи реакций сдвигающего порядка. Здесь найдено, что экспериментальные данные очень хорошо оцениваются при помощи реакций первого порядка со высокими концентрациями дифениламина в порохе и при помощи реакции нулевого порядка со низкими концентрациями в процессе завершающего периода долговечности пороха. Здесь тоже рассматриван механизм химических трансформаций дифениламина по отношению к модели и к процессу старения пороха.

Ключевые слова: порох, однобазисный порох, устойчивость пороха, стабилизаторы, дифениламин, химическая устойчивость, кинетическая модель.

Modélisation cinétique des transformations chimiques du diphénylamine durant le vieillissement des poudres monobasiques

Un modèle cinétique des transformations chimiques du stabilisateur (diphénylamine, DFA) qui a fait l'objet des essais durant le vieillissement des poudres monobasiques, a été vérifié avec succès. Ce modèle suppose que la transformation chimique du stabilisateur dans la poudre se déroule en trois manières parallèles, que chacune représente une réaction complexe dont la cinétique peut être décrite par les réactions de l'ordre changeant. On a constaté que les données expérimentales sont très bien évaluées par la réaction du premier ordre lorsque les concentrations du diphénylamine sont grandes dans la poudre et par la réaction de l'ordre zéro quand les concentrations y sont petites, pendant la période finale de la poudre utilisable. On a étudié également le mécanisme des transformations chimiques du diphénylamine par rapport au modèle et au procès du vieillissement de la poudre.

Mots clés: poudre, poudre monobasique, stabilité de la poudre, stabilisateurs, diphénylamine, stabilité chimique, modèle cinétique.