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## The Applicability of Chromatographic Methods in the Investigation of Ageing Processes in Double Base Rocket Propellants

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**Abstract:** The ageing of double base (DB) rocket propellants is the result of chemical decomposition reactions and physical processes, causing degradation of a number of relevant propellant properties (such as reduction in stabilizer and nitroglycerine (NG) content, reduction of the mean molecular mass of nitrocellulose (NC) *etc.*), which is reflected in a decrease in the reliable service life time of DB propellants. This is the reason why the study of processes of ageing and their consequences (effects) is so important.

In this paper we have studied the kinetics of DB rocket propellant decomposition during their artificial ageing, *i.e.* at elevated temperatures. The kinetic parameters were obtained by measurements of the stabilizer/Ethyl Centralite (EC) content and the mean molecular mass reduction of NC, during artificial ageing at temperatures of 80, 85 and 90 °C. Consumption of the EC was observed using High Performance Liquid Chromatography (HPLC), whilst the reduction in the mean molecular mass of NC was monitored using Gel Permeation Chromatography (GPC).

It has been shown that artificial ageing of DB propellant causes significant EC consumption and a reduction in the mean molecular mass of NC, from the very beginning of ageing. EC is entirely consumed after 120 days at 80 °C, and is followed by the intensive reactions of NC decomposition. Significant changes in the mean molecular mass of NC starts after 60 days of ageing at 90 °C (or ~250 days at 80 °C). The results obtained from the kinetic data have shown that the activation energy of DB propellant decomposition, determined on the basis of changes in the mean molecular mass of NC is 145.09 kJ·mol<sup>-1</sup>, whilst the activation energy

of decomposition obtained on the basis of EC consumption is  $142.98 \text{ kJ}\cdot\text{mol}^{-1}$ , which is consistent with available literature values [1, 2].

**Keywords:** activation energy, artificial ageing, DB rocket propellants, decomposition, Ethyl Centralite (EC), Gel Permeation Chromatography (GPC), High Performance Liquid Chromatography (HPLC), kinetics of degradation, mean molecular mass of NC

## Introduction

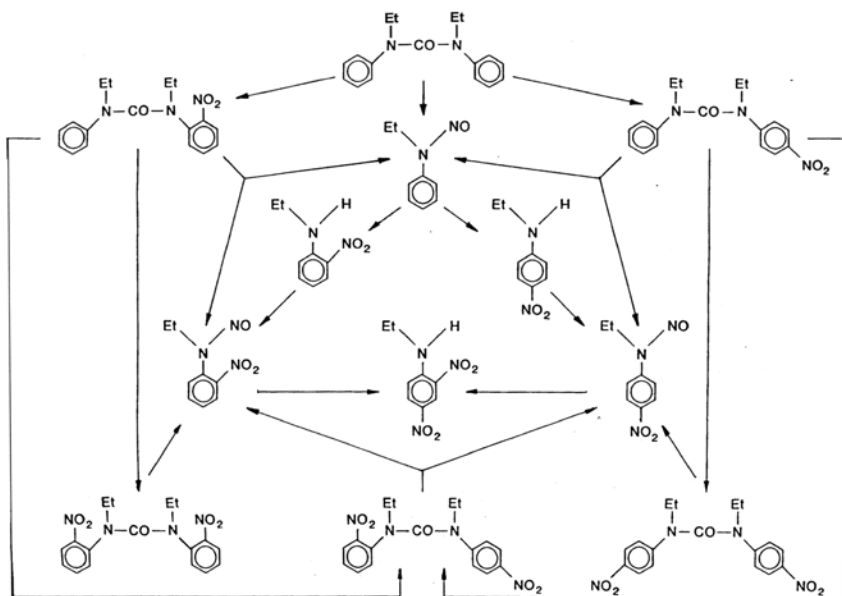
The ageing of double base (DB) rocket propellants is the result of chemical decomposition reactions and physical processes, causing degradation of a number of relevant propellant properties (such as reductions in stabilizer and nitroglycerine (NG) content, reduction in the mean molecular mass of nitrocellulose (NC) *etc.*). These degradation processes cause a reduction in the reliable period of DB propellant suitability. Thus, studies on the mechanism and kinetics of the processes that cause such types of propellant deterioration during ageing has great practical and theoretical importance.

It is well known that NC, which is the main ingredient of DB rocket propellants, is subject to a slow chemical decomposition even at room temperature [1-7] because of the relatively low activation energy ( $120\text{-}190 \text{ kJ}\cdot\text{mol}^{-1}$ ). The thermal decomposition of NC and NG is initiated by the homolytic cleavage of the O-NO<sub>2</sub> bond of these aliphatic nitrate esters, resulting in the formation of nitrogen dioxide and the corresponding alkoxy radicals [2-4, 7, 8]. The NO<sub>2</sub> radicals released immediately undergo consecutive reactions with other decomposition products, or with other propellant ingredients. During this process NO<sub>2</sub> is reduced to NO, N<sub>2</sub>O, N and HNO<sub>2</sub> [2-4, 7]. Another main decomposition pathway is the neutralisation by acid hydrolysis of the nitrate esters. The reaction is catalyzed by moisture and residual acids, or by water and acids formed during the decomposition process [8]. The resultant reaction of thermal decomposition is autocatalytic, and accompanied by heat generation [7]. Due to the low thermal conductivity of propellants, the heat released can accumulate in the propellant grain, and under certain conditions, such as high storage temperature, large diameter propellant grains *etc.*, it can lead to the propellant's 'self ignition' or 'thermal explosion' [7, 9].

The primary processes of propellant decomposition cannot be prevented, but the addition of stabilizers can delay/retard the process of autocatalytic degradation of the propellant. Chemical substances, so called 'stabilizers', react

with the degradation products released during the propellant ageing – primarily with degradation products such as nitrogen oxides, nitric acid and nitrous acid.

Stabilizers that are added to DB rocket propellants are often aromatic compounds whose benzene ring is significantly more susceptible to nitration than the other components in the DB propellant. Stabilizers for DB and nitroguanidine rocket propellants are often derivatives of urea (sometimes in combination with diphenylamine, DPA). Typical representatives for these types of stabilizers are Centralite I (Ethyl-Centralite, N,N'-diethyl-N,N'-diphenylurea, EC), Centralite II (Methyl-Centralite, N,N'-dimethyl-N,N'-diphenylurea), Akardite I (1,1-diphenylurea), and Akardite II (N-methyl-N',N'-diphenylurea).



**Figure 1.** Conversion reactions of EC and its daughter reaction products during DB rocket propellant decomposition under artificial ageing conditions at elevated temperatures.

There is not much information in the available literature about the behavior of EC during its stabilizing activity. The reason for this lies in the difficulty in identifying and quantifying the products formed from EC. However, F. Volk, applying thin layer chromatography (TLC) for propellant samples subjected to artificial ageing, identified two main groups of EC products. The first group of products consists of EC nitro-derivates (2-nitro-EC (2-NEC), 4-nitro-EC

(4-NEC), 2,2'-dinitro-EC (2,2'-DNEC), 2,4'-dinitro-EC (2,4'-DNEC)), while the second group of products consists of products formed by cleavage of the urea skeleton, such as N-nitroso-N-ethylaniline (NOEA), 2-nitro-N-ethylaniline (2-NEA), 4-nitro-N-ethylaniline (4-NEA), N-nitroso-2-nitro-N-ethylaniline (NO-2-NEA), N-nitroso-4-nitro-N-ethylaniline (NO-4-NEA), 2,4-dinitro-N-ethylaniline (2,4-DNEA), nitrobenzene and dinitrobenzene) [10, 11]. A schematic presentation of the conversion of EC to its derivatives/daughter products, during the stabilization process of DB propellant decomposition, is shown in Figure 1.

One of the most important consequences of DB rocket propellant ageing is the reduction in the viscoelastic and mechanical properties as a consequence of reductions in NG content and the mean molecular mass of NC.

Many researchers have studied the ageing of DB propellants caused by chemical reactions, often indirectly (following stabilizer content), but rarely directly – following the reduction in the mean molecular mass of NC [1-5, 7, 8, 12-15].

The aim of this research was to investigate the ageing processes and the kinetics of DB rocket propellant decomposition during artificial ageing. The kinetic parameters were obtained by following/monitoring the chemical changes in the stabilizer EC and the reduction in the mean molecular mass of NC, during the artificial ageing of the propellant samples at elevated temperatures (80, 85 and 90 °C). The decrease in the EC content in DB rocket propellant was observed using High Performance Liquid Chromatography (HPLC), whilst the reduction of the mean molecular mass of NC was monitored using Gel Permeation Chromatography (GPC).

## Experimental

### Tested materials – DB rocket propellants

The studies were performed on DB rocket propellant samples of the following chemical composition: ~57.9 wt% of NC, ~26.7 wt% of NG, 8.5 wt% dinitrotoluene, 2.9 wt% of EC, and 4 wt% of other additives.

### Methods

#### *Accelerated ageing of DB rocket propellant samples*

DB rocket propellant samples of size 40×10×2.5 mm were prepared and artificially aged in closed glass tubes at 80, 85 and 90 °C. The volume of the glass tube was 100 cm<sup>3</sup>, whilst the mass of the sample in each tube was

approximately 10 g. The aged propellant samples were periodically taken out from the oven and their stabilizer/EC consumption and NC molecular mass distributions were measured using HPLC and GPC respectively.

### ***High performance liquid chromatography (HPLC) measurements***

High performance liquid chromatography (HPLC) measurements were conducted using a Varian high performance liquid chromatography (HPLC) apparatus, model Prostar 500 with a Lichrosphere, Supersphere (4  $\mu\text{m}$ , 250 $\times$ 4.6 mm) separation unit (HPLC column-stationary phase) and UV/VIS detector operating at 254 nm. The mobile phase was acetonitrile/methanol/water (36/22/42 vol.%), with a flow rate of 0.7  $\text{cm}^3\cdot\text{min}^{-1}$ . The sample injection volume was 20  $\mu\text{l}$ , and the separation unit temperature was 28  $^\circ\text{C}$ .

The propellant samples for the HPLC measurements were prepared according to the standardization NATO Allied Ordnance Publication (AOP-48) [16]. 1 gram of the propellant was weighted into a 500  $\text{cm}^3$  flask, and 250  $\text{cm}^3$  of acetonitrile was then added. The sample was dissolved by shaking the closed flask for a minimum of 4 hours at room temperature, avoiding exposure to direct sunlight. Then, 50  $\text{cm}^3$  of a 2 wt% aqueous solution of calcium chloride was added to the flask to precipitate the NC. In cases where the samples were not analyzed immediately, they were kept under cool, dark conditions ( $5 \pm 3$   $^\circ\text{C}$ ) to prevent any further reactions of the stabilizer.

### ***Measurements of NC molecular mass distribution in DB rocket propellant samples***

The molecular mass distribution measurements for NC in DB rocket propellant samples were performed using Polymer Laboratories, GPC-20 analyser. The measurements were done under the following experimental conditions:

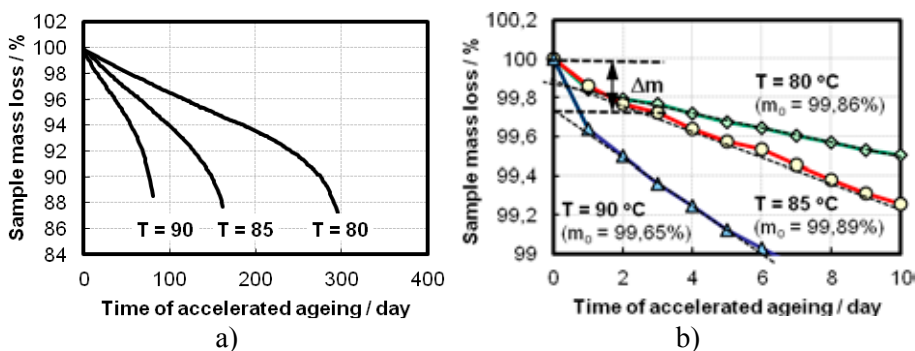
- separation unit: two serially connected PLGel™ Mixed-B columns filled with polystyrene-divinylbenzene copolymer gel, particle size 3-100  $\mu\text{m}$ ,
- eluent: tetrahydrofuran (THF),
- mobile phase flow rate: 1  $\text{cm}^3\cdot\text{min}^{-1}$ ,
- sample injection volume: 100  $\mu\text{l}$  (approximately 5 wt% NC solution in THF).

Samples for GPC measurements were prepared by dissolving 30 mg of the propellant sample in 5 ml of THF. Measurements were carried out at ambient temperature. For the hydrodynamic volume ( $V_e$ ) conversion to molecular mass, specific calibration curves of polystyrene were used. As a standard, five samples of polystyrene of very narrow polydispersivity were used.

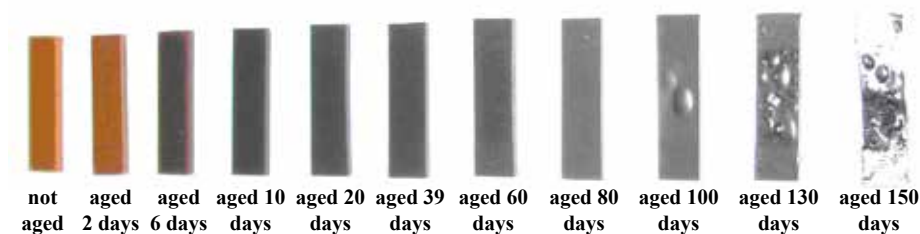
## Results and Discussion

### Artificial ageing of DB rocket propellants

In order to study the ageing process of the DB rocket propellant, the propellant samples were aged at elevated temperatures (80, 85 and 90 °C). Accelerated ageing of the DB rocket propellant caused mass loss in the tested samples (Figure 2), and visible changes in their colour, shape and structure (Figure 3).



**Figure 2.** The mass loss of DB rocket propellant samples as a function of time of accelerated ageing at 80, 85 and 90 °C; (a) total range of the sample mass loss; (b) early stages of the sample mass loss.

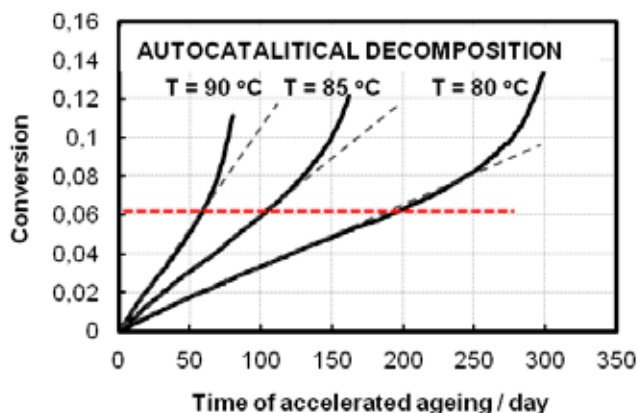


**Figure 3.** Visible changes of DB rocket propellant samples artificially aged at 85 °C.

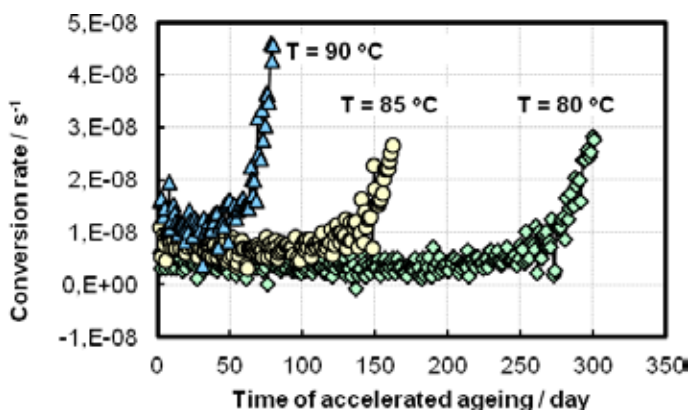
At all temperatures of accelerated ageing, a sharp decrease in the sample mass ( $\sim 0.11$  to  $\sim 0.35$  wt%) was noticed, as a consequence of the evaporation of the more volatile constituents of the propellant (humidity, residual solvents, NG), Figure 2b.

For the solid state reaction kinetics, a degree of reaction advance expressed as the reactant mass conversion fraction ( $\alpha$ ). The results of the sample mass changes with the duration of ageing, were converted to sample conversion degree

with ageing time dependency (Figure 4), and then to dependence of conversion rate ( $da/dt$ ) on time (Figure 5) and temperature of ageing. Thus the data as presented, gives a clearer picture of the ageing/degradation process of the DB propellant and allow kinetic interpretation of these data [17].



**Figure 4.** Degree (fraction of propellant total mass conversion) of DB rocket propellant samples; mass conversion vs. time of accelerated ageing at 80, 85 and 90 °C.



**Figure 5.** Conversion rate of DB rocket propellant mass vs. time of accelerated ageing at 80, 85 and 90 °C.

The shape of the curves describing DB propellant mass loss vs. time of ageing (Figure 2) is typical for most solid state reactions [18], namely, a typical decomposition reaction in the solid state is initiated after a primary decomposition reaction (decomposition of the most unstable components), followed by an



induction period and a period of acceleration of the reaction.

At the beginning of the ageing of DB rocket propellant samples, their mass loss increases almost linearly with time. After a mass loss of ~6%, the rate of mass loss increases due to the intense autocatalytic decomposition reaction of the energetic components (NG, NC) of the propellant. This is particularly obvious from Figure 5, where it is clearly seen that the mass loss rate at the beginning is almost constant, and is followed by the sudden increase in reaction rate as a consequence of the initiation of the intense decomposition reaction.

The fact that during the accelerated ageing of the DB rocket propellant different reactions take place in the propellant mass, is indicated by the change of propellant colour and shape. For example, at an early stage (time (t)) of accelerated ageing of the propellant sample ( $2 < t < 80$  days at  $85\text{ }^{\circ}\text{C}$ ,  $\alpha < 6\%$ ), the colour of the samples had changed from light brown through dark brown, to black, as a consequence of the release of brown coloured, gaseous products ( $\text{NO}_x$ ) formed during the decomposition of the nitro-esters, Figure 3.

As a result of the further advance of the autocatalytic processes of propellant decomposition, the amounts of gaseous products released increases significantly, and in the second stage of accelerated ageing ( $t > 80$  days at  $85\text{ }^{\circ}\text{C}$ ,  $\alpha > 6\%$ ) visible structural changes (swelling of the sample, occurrence of bubbles, change in the sample shape) in the propellant mass take place, Figure 3.

### **Consumption of the stabilizer (EC)**

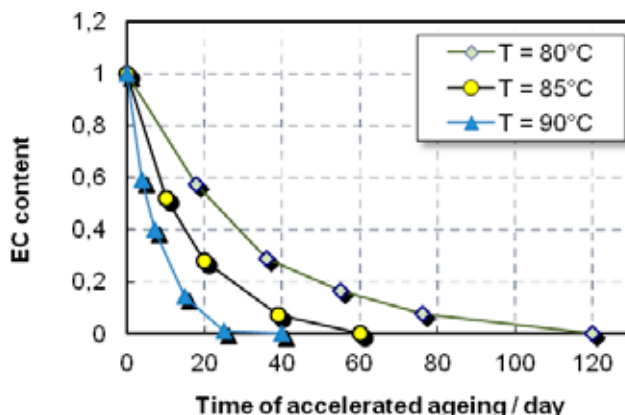
Hitherto, various analytical methods have been used in order to follow the consumption of the stabilizer (EC) during the ageing of DB rocket propellants. The kinetics of stabilizer consumption during the ageing of the propellant samples tested has been successfully modelling by first order kinetics. It has been assumed that ageing experiments combined with kinetic analysis could be efficiently used to determine quantitatively the lifetime of the propellant.

In the present work the changes in EC content of the DB rocket propellant samples were determined using HPLC. The results are presented in Table 1 and Figure 6, where the EC content changes as a function of ageing time and temperature are given.

The mass loss of DB rocket propellant samples in the early stage of their decomposition is connected with the evaporation of water and other volatile substances such as residual solvent, NG, *etc.*, decomposition of NC and NG, and the separation of low molecular mass products such as  $\text{NO}_x$ , and  $\text{HNO}_2$ . These processes occurring in propellant aged at  $90\text{ }^{\circ}\text{C}$  lasted for 55 days (100 days at  $85\text{ }^{\circ}\text{C}$ , 186 days at  $80\text{ }^{\circ}\text{C}$ ) and resulted in a mass loss of approximately 6%. During this period EC was completely consumed, Figure 6.

**Table 1.** Consumption of the stabilizer (EC) in DB rocket propellant samples during their artificial ageing at 80, 85 and 90 °C

Temperature / 80 °C		Temperature / 85 °C		Temperature / 90 °C	
Ageing time [day]	Stabilizer content [wt%]	Ageing time [day]	Stabilizer content [wt%]	Ageing time [day]	Stabilizer content [wt%]
0	0.0301	0	0.0301	0	0.0301
18	0.0172	10	0.0156	4	0.0178
36	0.0087	20	0.0084	7	0.0121
55	0.0050	39	0.0022	15	0.0043
76	0.0023	60	0.0000	25	0.0003
120	0.0000			40	0.0000

**Figure 6.** Normalised decrease in EC content in DB rocket propellant samples artificially aged at 80, 85 and 90 °C.

For example, EC reacting with nitrogen oxides generated during the decomposition of DB rocket propellant aged at 90 °C, is completely consumed after about 25 days (after 60 days at 85 °C and 120 days at 80 °C). Due to the reaction of EC with nitrogen oxides, nitro derivatives of EC are generated, which also have a stabilizing effect. At the moment when the stabilizer content and its derivatives (2-NEC, 4-NEC, 2,2'-DNEC, 2,4'-DNEC), NOEA, 2-NEA, 4-NEA, NO-2-NEA, NO-4-NEA, 2,4-DNEA, nitrobenzene and dinitrobenzene, Figure 1 [10, 11]), fall to zero, the intense autocatalytic reaction of nitro ester decomposition begins to manifest itself by an intense mass loss (mass loss > 6%). Figure 6 shows that the time for complete consumption of the stabilizer (EC) is approximately half the time for which intense autocatalytic reaction occurs for

all temperatures of accelerated ageing. Similar behaviour was also observed for the other propellants (examples of DB gun propellants) [11]. That means that, based on monitoring of stabilizer consumption, it is possible to predict the period after which autocatalytic reactions of the propellant decomposition start.

### ***DB propellant ageing kinetics on the basis of stabilizer consumption***

In order to calculate the kinetic parameters for the decomposition of DB rocket propellant samples, curves of the decrease of stabilizer (EC) content in the propellant samples (Figure 6) were subjected to kinetic model processing. It was proved that the first order kinetic model may describe well the experimentally obtained data. According to this model the content ( $S_t$ ) of stabilizer (EC) at any time ( $t$ ) is given by the equation below:

$$S_t = S_0 \cdot e^{-k \cdot t} \quad (1)$$

where  $S_0$  is the initial stabilizer content ( $S_0 = 0.0301$ ) in the propellant (*i.e.* just before accelerated ageing).

Using a non-linear curve fitting procedure on the data given in Figure 6 in accordance with the first order kinetic model (Eq. 1), the reaction rate constant ( $k$ ) of DB propellant decomposition/degradation/ageing processes is determined for each temperature of ageing, Table 2.

**Table 2.** Rate constants ( $k$ ) and their ( $\ln k$ ) values for the decrease in EC content in DB rocket propellant samples during their accelerated ageing at elevated temperatures ( $T = 80, 85$  and  $90$  °C)

Temperature of accelerated ageing, [°C]	$k$ [s <sup>-1</sup> ]	$r$	$\ln k$	$1000/T$ [K <sup>-1</sup> ]
80	$4.00 \cdot 10^{-7}$	0.9998	-14.73207	2.832
85	$7.55 \cdot 10^{-7}$	0.9996	-14.09718	2.792
90	$1.53 \cdot 10^{-6}$	0.9994	-13.39064	2.754

Then, the activation energy and pre-exponential factor are calculated from the reaction rate constant – temperature dependence, in accordance with the Arrhenius equation ( $k = A \cdot e^{-E/RT}$ ), where:

$$E = 142.98 \text{ kJ} \cdot \text{mol}^{-1};$$

$$A = 5.56 \times 10^{14} \text{ s}^{-1}.$$

The values obtained for the activation energy (E) of the process of EC content decrease in DB propellants are consistent with literature values. For example, F. Volk, on the basis of the consumption (content decrease) of EC in DB powder stabilized with 1% of EC and 1.5% of Akardite II, determined the activation energy as 142.5 kJ/mol. Data on consumption of the stabilizer (Figure 6) confirm the assumption that even in the initial stage of DB propellant ageing, intense reactions take place. For example, the entire stabilizer was consumed during about 30 days of ageing at 90 °C or 120 days at 80 °C.

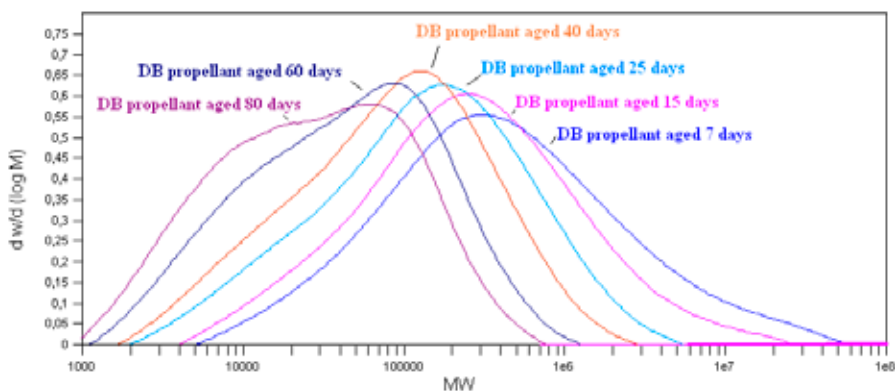
**Table 3.** The sampling frequency for the GPC analysis of DB rocket propellant samples and the results of their GPC analysis ( $\overline{Mn}$ ,  $\overline{Mw}$ ,  $\overline{Mz}$ , PD)

Sample	Time of artificial ageing, [day]	$\overline{Mn}$ , [g·mol <sup>-1</sup> ]	$\overline{Mw}$ , [g·mol <sup>-1</sup> ]	$\overline{Mz}$ , [g·mol <sup>-1</sup> ]	PD
Polystyrene (standard)	/	102114	220561	404895	2.16
Unaged DB propellant	0	171245	1069741	4094508	6.25
DB propellant artificially aged at 80 °C	36	129910	637824	2149668	4.91
	76	100802	454483	1435881	4.52
	120	39160	228736	716271	5.84
	180	23403	147783	479957	6.31
	220	19972	269412	2732091	13.49
	260	15218	85709	267937	5.63
DB propellant artificially aged at 85 °C	20	104185	1601381	14470518	15.37
	39	62295	339499	1169864	5.45
	60	39964	267696	893725	6.70
	90	22862	128128	407047	5.60
	130	11537	63340	195283	5.49
	150	3062	37254	159117	12.17
DB propellant artificially aged at 90 °C	7	116384	1713729	12920553	14.72
	15	81628	5166801	11583803	6.33
	25	42327	320239	1094096	7.57
	40	29442	184393	566706	6.26
	60	16350	93076	266761	5.69
	80	11125	60597	173107	5.45

### Changes in mean molecular mass of nitrocellulose during artificial ageing

DB rocket propellant samples artificially aged at 80, 85 and 90 °C were analysed by GPC in order to study the degradation process of NC in the propellant.

The sampling frequency of DB propellant for GPC measurements and the results of the analysis (differential molecular mass distribution curves of the samples aged at 90 °C, number-average molecular mass,  $\overline{Mn}$ ; weight-average molecular mass,  $\overline{Mw}$ ; average molecular mass,  $\overline{Mz}$  and polydispersivity degree, PD) are shown in Table 3.



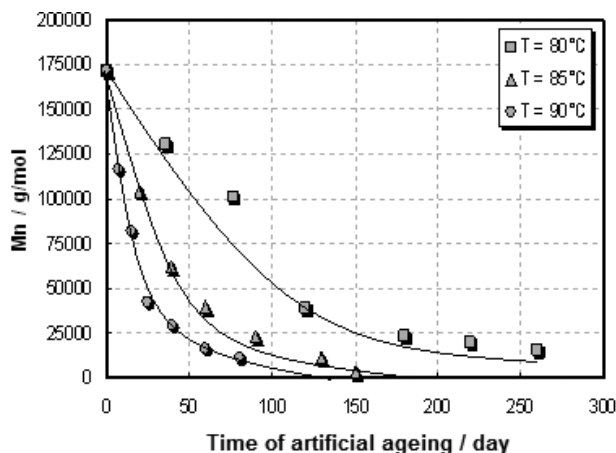
**Figure 7.** Differential molecular weight distribution ( $dW/d\log M$ ) curves of DB rocket propellant samples aged for 7, 15, 25, 40, 60 and 80 days at 90 °C.

The differential molecular mass distribution curves for DB propellant samples aged at 90 °C are shown in Figure 7.

The main feature of each differential curve is the position of its maximum and the total width of the peak/curve of the NC molecular mass distribution. A larger peak width means greater non-uniformity of the system [19]. Curves shown in Figure 7 show that by ageing the DB propellant samples, the maximum/top of the peak/curve shifts towards to lower values of the weight-average molecular mass,  $\overline{Mw}$ , while the peak corresponding to an advanced stage of decomposition is deformed (the appearance of new peaks – see the curve for DB propellant aged for 60 and 80 days at 90 °C). These changes indicated that ageing caused a decrease in the mean molecular mass of NC and an increase in non-uniformity of the DB propellant system (increase in the range of different molecular masses), where significant changes occur after 60 days ageing at 90 °C (which corresponds to the moment when the intense reaction of autocatalytic degradation appears).

Changes in the number-average molecular mass ( $\overline{Mn}$ ) as a function of ageing temperature and time, are shown in Figure 8. The results shown in Figure 8 indicate that the value of  $\overline{Mn}$  in the first part/stage of ageing changes significantly

(from an initial value of 171 245 to approx. 30000 g·mol<sup>-1</sup>). After attaining the value of  $\overline{Mn}$  of approx. 30000 g·mol<sup>-1</sup>, the rate of change of  $\overline{Mn}$  decreases with time, which indicates a slowing of the NC degradation process.

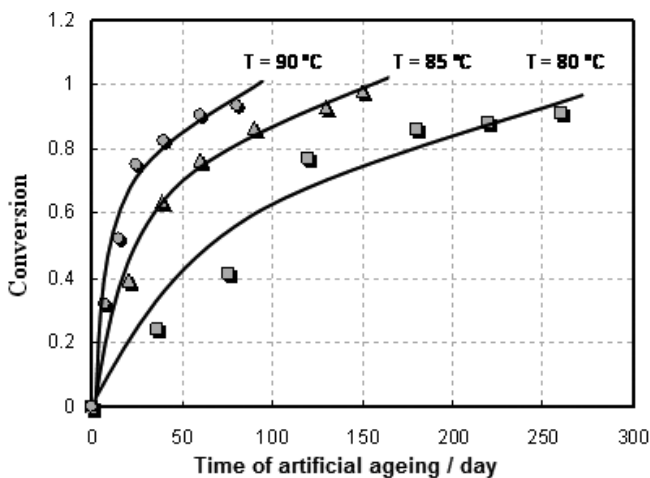


**Figure 8.** Change of number-average molecular mass ( $\overline{Mn}$ ) of NC vs. temperature and time of accelerated ageing of DB rocket propellant samples.

In addition to the time of ageing, the rate of NC degradation is also influenced by the temperature of ageing. The NC degradation rate increases with increased ageing temperature. For example, a decrease of  $\overline{Mn}$  from the initial value of 171 245 to the final value of 23000 g·mol<sup>-1</sup> was achieved in approx. 180 days of ageing at 80 °C, and in 90 days of ageing at 85 °C.

***Kinetics of NC decomposition in DB propellants on the basis of changes in the NC number-average molecular mass***

In order to describe the kinetic process of NC decomposition in DB propellants, isothermal curves of NC number average-molecular mass,  $\overline{Mn}$ , depending on ageing time have been transformed into the curves for its conversion degree as a function of ageing time, Figure 9.



**Figure 9.** Conversion degree ( $\alpha_t$ ) of  $M_n$  of NC vs. time of accelerated ageing of DB rocket propellant samples at different temperatures, *i.e.* 80, 85 and 90 °C.

The conversion degree of decrease in  $\overline{Mn}$  of NC was expressed by the equation below:

$$\alpha_t = \frac{\overline{Mn}_0 - \overline{Mn}_t}{\overline{Mn}_0 - \overline{Mn}_f} \quad (2)$$

where  $\alpha_t$  is the conversion fraction of the  $\overline{Mn}_t$  of NC for an ageing time  $t$ ;  $\overline{Mn}_0$  is initial value of  $\overline{Mn}$ ;  $\overline{Mn}_f$  is the value of  $\overline{Mn}$  for NC at the end of the decomposition process of the propellant,  $\overline{Mn}_f = 0$ ; and  $\overline{Mn}_t$  is  $\overline{Mn}$  of the NC at time  $t$ .

By means of regression analysis of the experimentally obtained data shown in Figure 9, it was found that the fraction/degree of conversion of  $M_n$  of NC with time of ageing can be described by the first order kinetic reaction model, expressed/described by Eqs. 3 and 4, in integral and differential form, respectively:

$$-\ln(1 - \alpha) = k \cdot t, \quad \text{integral form} \quad (3)$$

$$\frac{d\alpha}{dt} = k \cdot (1 - \alpha), \quad \text{differential form} \quad (4)$$

From the nonlinear regression analysis of the dependence of the degree of conversion of  $M_n$  of NC on time, (using Eq. 3), the values of the rate constants  $k$  for each temperature of ageing was calculated. The results obtained are shown in Table 4.

**Table 4.** The values of the reaction rate constants ( $k$ ) and their ( $\ln k$ ) values for decomposition of NC expressed by the decrease in  $M_n$  for DB rocket propellant samples aged at temperatures 80, 85 and 90 °C

Temperature of artificial ageing, [°C]	$k$ [s <sup>-1</sup> ]	$r$	$\ln k$	$1000/T$ [K <sup>-1</sup> ]
80	$1.16 \cdot 10^{-7}$	0.981	-15.9663	2.832
85	$2.81 \cdot 10^{-7}$	0.982	-15.0841	2.792
90	$4.53 \cdot 10^{-7}$	0.974	-14.6073	2.754

On the basis of the data given in Table 4, and using the Arrhenius dependence of the reaction rate constant ( $k$ ) on the ageing temperature ( $k = A \cdot e^{-E/RT}$ ), values of the activation energy ( $E$ ) and the pre-exponential factor ( $A$ ) were calculated:

$$E = 145.096 \text{ kJ} \cdot \text{mol}^{-1},$$

$$A = 3.6 \times 10^{14} \text{ s}^{-1}.$$

The values of activation energy obtained for NC decomposition in DB propellant are consistent with analogous values of activation energies given in literature data. For example, M.A. Bohn using the kinetic models for the degradation of the molecular mass of polymer [2], on the basis of the decrease in  $M_w$  of NC in the rocket propellants type RP RPC 470/20/TM 5, determined the activation energy of NC decomposition in the temperature range from 40 to 110 °C. It was noted that the activation energy of NC decomposition is significantly dependent on the temperature of ageing. Thus, the activation energy determined in the temperature range 40-60 °C was 58.7 kJ·mol<sup>-1</sup>, whilst the activation energy in the temperature range 60-110 °C was significantly higher and increased to 144.0 kJ·mol<sup>-1</sup>.



## Conclusions

- The results obtained showed that under the conditions of accelerated ageing of DB rocket propellant at elevated temperatures, the ageing of the propellant is caused by three main processes:
  - the process of physical ageing of the propellant, which refers to the decrease in NG content inside the DB rocket propellant grain due to its migration (exudation) to the propellant surface and further evaporation,
  - the process of thermal decomposition of energetic components of the DB propellant (NG, NC) in the initial stage of the propellant ageing, which is characterized by a loss of the stabilizer mass/content in the propellant and a reduction/decrease in the mean molecular mass of NC, and
  - the processes of autocatalytic exothermic decomposition of the energetic components of the DB propellant (NG, NC) that occur after consumption of the stabilizers (EC and its daughter reaction products).
- In the initial stages of accelerated ageing of DB propellant samples (reduction in propellant mass less than 6%) evaporation is dominant, but not the only process. It was found that the mass loss of the sample at this stage of its ageing is a result of several parallel processes, such as evaporation of NG, and decomposition of NG and NC.
- In the second stage of ageing of DB propellant (reduction of propellant mass more than 6%) the dominant process is autocatalytic degradation of the propellant, which leads to significant structural changes in the propellant mass and its structure (swelling, and changes in the shape of the DB propellant samples). This confirms the results obtained for stabilizer consumption, and for the activation energy determined on the basis of the mass loss of the sample in the second stage of ageing ( $E = 137.9 \text{ kJ}\cdot\text{mol}^{-1}$ ) [16], which is close to the value of the activation energy determined on the basis of changes in the mean molecular mass of NC in DB propellant during artificial ageing ( $E = 145.09 \text{ kJ}\cdot\text{mol}^{-1}$ ).
- Stabilizer consumption in DB propellants under conditions of their accelerated ageing is very intense from the very beginning of ageing. The stabilizer is consumed totally after 200 days at 80 °C, followed by intense thermal decomposition reactions.
- The period needed for complete consumption of the stabilizer is approximately half the period after which intense autocatalytic reactions begin. Similar ageing process/behaviour was also observed for other propellants (*e.g.* DB gun propellant) [11]. This means, that on the basis of stabilizer consumption

monitoring, it is possible to predict the time at which autocatalytic reactions of propellant decomposition occur.

- The artificial ageing of DB propellant causes a significant decrease in the mean molecular mass of NC, where significant changes start after 60 days of ageing at 90 °C. The activation energy obtained this way is 145.09 kJ·mol<sup>-1</sup>, which corresponds to the values obtained by M. Bohn [2].
- The very intense decomposition processes of NC during artificial ageing of DB propellants, is influenced by relatively high temperatures of artificial ageing (80-90 °C) and relatively high sample size (shape of rectangular bar of 40×10×2.5 mm). Specifically, some tests have shown that the geometry of DB propellant samples significantly influences the kinetics of the ageing processes, since for the larger size of samples the influence of diffusion and heat transfer are present, which can result in self-heating of the propellant sample and, in consequence, in acceleration of the NC degradation processes [12].

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