Characterization of gun propellants by long-term mass loss measurements

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Abstract: Three different gun propellants (A5020, JA-2 or L5460, NK1074) have been investigated up to 35 years by mass loss at isothermal temperatures between 30 °C and 90 °C. From these data, activation energies for the different reactions of zero order (mass loss increase up to stabilizer consumption) and first order (solvent evaporation at begin) are derived. The mass loss data are described very well by a combination of these two reactions. Stabilizer consumption has been determined by HPLC. In case of diphenylamine (DPA), several consecutive products (mononitro-DPA up to tetranitro-DPA) have been regarded also. Activation energies are in the range of energies obtained by other methods: 84 kJ/mol [A5020], 150 kJ/mol [JA-2], 100 kJ/mol [NK 1074]). Long term measurements show seasonal influence in the mass loss data. Respective graphs are shown in this work. At least four years of measurement are recommended to compensate for the signal drift caused by seasonal changes.

Introduction

NC based energetic materials, such as single and double base gun propellants, are often monitored with mass loss to determine their ageing characteristics. Mass loss is a robust but nevertheless reliable and well-known method to describe reaction kinetics [1]. Three different propellants, A5020, JA-2 or L5460, NK1074, see Table 1, have been investigated by mass loss over extended time periods up to 35 years, starting at low isothermal temperatures in the range 30°C and going up to 90°C. Techniques such as mass loss, heat flow calorimetry and gas generation were performed at temperatures well above 25°C due to the low reaction rate at these temperatures. If one wants to measure at low temperatures, long observation and measurement times are necessary. However, to predict the in-service times of propellants, mostly one has to extrapolate with data gained at higher temperatures. To investigate, if such extrapolations are valid and reasonable, three different propellants were stored at Fraunhofer ICT (initiated by former Dr, Fred Volk) at low temperatures namely 30°C to 55°C as well as at some higher temperatures over 35 years and their mass losses have been recorded up to recent time. To our knowledge this is the first study that covers a period of 35 years in constant monitoring of the ageing of propellants. Table 1 lists the composition of each propellant, the abbreviations mean: Nitrocellulose (NC), Dibutylphthalate (DBP), Dioctylphthalate (DOP), Diphenylamine (DPA), Nitroglycerine (NGL), Diglycoldinitrate (DGDN), Ethylphenylurethane (EPU) and Dinitrotoluene (DNT). Akardit II or Acardite II is N-methyl -N‘,N‘-diphenyl–urea. Centralite I is N-ethyl-N-phenyl-N‘-ethyl-N‘-phenyl–urea. JA-2 means Jeck Alfons, lot 2. Mr. Jeck was the developer of this type of gun propellant, produced without solvent (Pulver ohne Lösungsmittel POL), at former company WNC Nitrochemie in Aschau am Inn, Germany.

Table 1. Compositions of the investigated gun propellants in mass-%, as N-content of NC

A5020 (single base)		JA-2 (L5460) (double base)		NK 1074 (double base)	
NC (N=13.2)	95 %	NC(N=13.0)	59.5 %	NC (N=13.1)	51.8 %
DBP /DOP	2.6 %	NGL	14.9 %	NGL	40.5 %
DPA[a]	0.8 %	DGDN	24.8 %	DPA[a]	1.0 %
Centralite I[b]	1.5 %				
$Na(C_2O_4)$	0.6 %	Akardite II[a]	0.7 %	Centralite I[b]	1.5 %
Graphite		MgO	0.05 %	EPU	3.7 %
		Graphite	0.05 %	DNT	1.5 %
				Pb stearate	1.4 %

[a] Stabilizer;

[b] surface (burning) phlegmatizer

Experimental Section

Propellant samples were stored in glass vials with a diameter of 17mm or 30 mm depending on sample mass, which varied between 1 g and 4 g. The vials were closed with a loosely inserted ground stopper without any grease or clamps. The samples were stored in the basement of a large building within PID-controlled aluminum block ovens, which were regularly checked for functionality and temperature drift. Vial masses were recorded with an analytical balance with a precision of 0.1 mg.

Stabilizer consumption was determined by means of HPLC. Remaining stabilizers and consecutive products were extracted using Soxhlet extraction method over 48 h with dichloromethane. The solvent was removed by rotary evaporator and the extract residue dissolved in acetonitrile. HLPC was carried out using an Agilent 1100 instrumentation equipped with Kinetex 2.6 µm 100x4.6 mm reversed phase C18 column and Phenomenex pre-column. The eluent was water / acetonitrile mixture (53:47) with

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a flow of 0.6 ml/min at 35°C and quantification was by UV/Vis photodiode array detector at 410 nm.

Results and Discussion

Mass loss

In this paper, mass loss ML is obtained by Eq.(1), where M(0) is the start mass of the vial and M(t,T) is the mass at time t and temperature T.

$$ML(t,T) = \frac{M(0)-M(t,T)}{M(0)} \qquad \text{Eq.(1)}$$

Figures 1and 2 show an example of a set of mass loss curves.

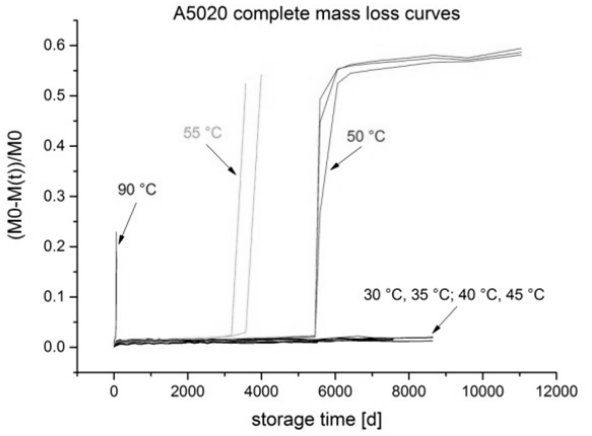

Figure 1. Mass loss curves of A5020 single base propellant (overview)

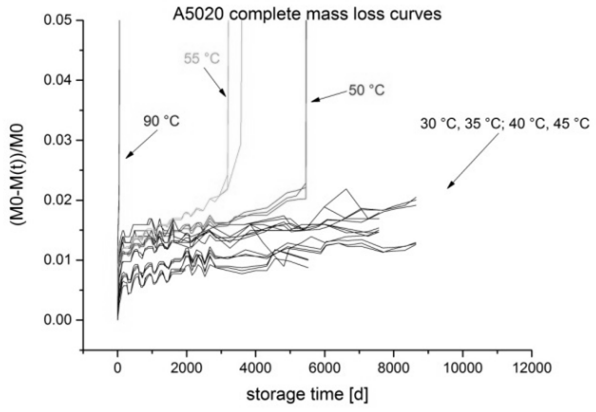

Figure 2. Mass loss curves of A5020 single base propellant (lower temperatures).

Kinetic description of these mass loss curves is given by a superposition of two kinetic reactions, one fast first order reaction, which handles solvent and water evaporation and a slower zero order reaction, to describe the mass loss increase.

As long as stabilizer is active in the propellant, the mass loss increases mostly linear. At the end of stabilizer action because of its consumption, mass loss increases very rapidly, which is often called autocatalytic decomposition. From the kinetic reaction equations the following formal model can be derived[2], Eq.(2):

$$ML(t,T) = OF + ML_e\left((1-a) * k_0(T) * t + a * \left(1 - e^{-k_v(T)*t}\right)\right)$$
Eq. (2)

with offset *OF*, scaling factor ML_e (here assumed to be 1, i.e. complete decomposition of the sample into gases), partitioning factor *a* between the two processes and the reaction rates k_0 and k_v for the zero order reaction and for the evaporation (first order reaction). This formal model is compared with an empirical model, Eq.(3).

$$ML(t,T) = A * \left(1 - e^{-k_v(T)*t}\right) + k_0 * t \qquad \text{Eq. (3)}$$

using the amount of solvent *A* and the two reaction rates as in Eq. (2).

For the processing and evaluation of the data, all mass loss curves of one propellant at one specific temperature were combined into one set of curves (mostly 4 samples were measured in parallel). Each set was fitted using either Eq. (2) or Eq. (3) using a so-called “global fit”. This allows differing between shared parameters, i.e. one value calculated and used in all curves, and individual parameters, which can have different values for each curve in one set. For the same temperature, shared parameters are the reaction rates k_0 and k_v, whereas partitioning factor *a* and offset *OF* respectively solvent amount *A* are individual parameters. With these two models reaction rates for different temperatures are calculated and activation energies E_A are estimated using the Arrhenius equation, Eq.(4).

$$k(T) = Z * e^{-\frac{E_A}{RT}} \iff ln(k(T)) = \ln(Z) - \frac{E_A}{RT} \qquad \text{Eq. (4)}$$

As usual, ln(k(T)) is plotted against reciprocal absolute temperature and the activation energy E_A is derived from the slope. Figures 3 to 5 show the corresponding Arrhenius plots.

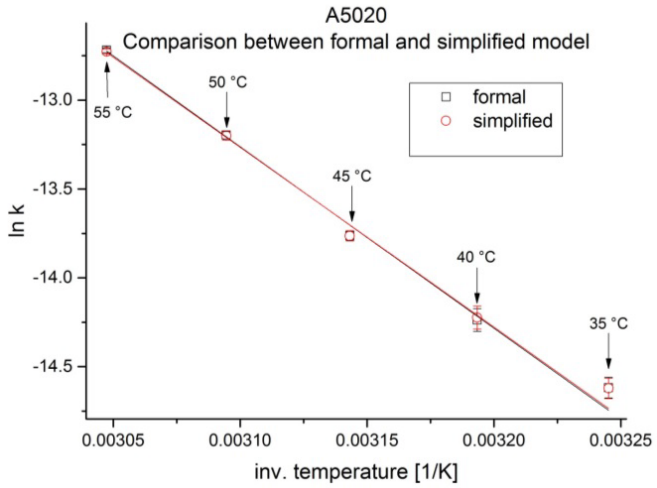

Figure 3. Arrhenius plot of single base propellant A5020.

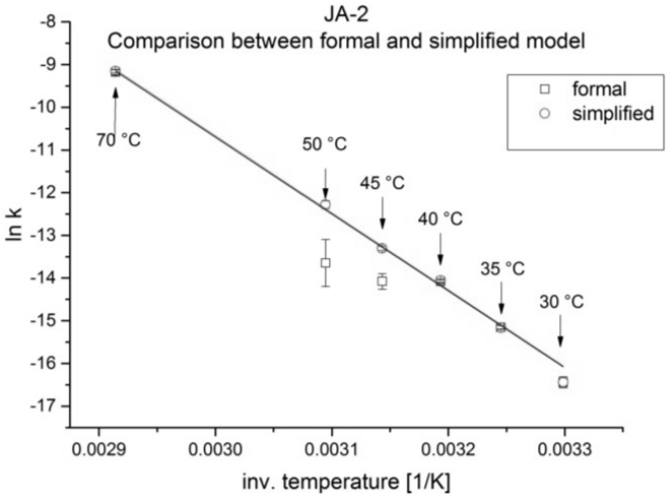

Figure 4. Arrhenius plot of double base propellant JA-2 (L5460).

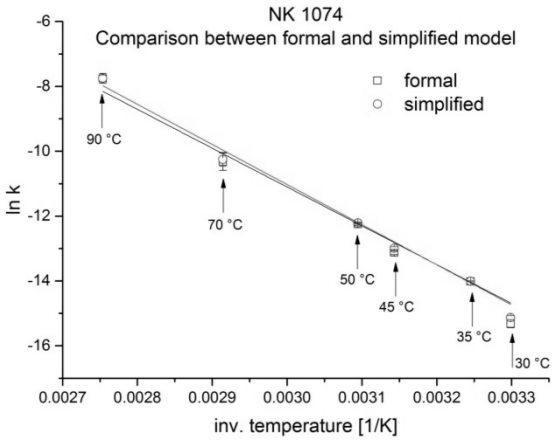

Figure 5. Arrhenius plot of double base propellant NK 1074

The two models show very good correlation ($R^2 > 0.98$) resulting in similar values for the activation energies as listed in Table 2.

Table 2. Activation energies for zero order reaction (stabilizer degradation)

	Formal model		Empiric model	
Propellant	E_A [kJ/mol]	Std. dev. [kJ/mol]	E_A [kJ/mol]	Std. dev. [kJ/mol]
A5020	84.14	3.02	84.14	3.02
JA-2	149.60	5.25	149.88	3.07
NK 1074	99.51	5.74	102.81	5.39

These values coincide with activation energies for the corresponding stabilizer decrease found by other means[3][4] or obtained from shorter measurement times at higher temperatures[5]. These short term measurements have the advantage getting quite fast results. However, the higher thermal load can favour other reaction pathways as are preferred at low temperatures. This leads to the necessity of performing long term measurements to check for possible different reactions. In this study, similar results are obtained suggesting the same reaction paths happen at both high and low temperatures. While measured activation energies for stabilizer consumption are very good, those for solvent evaporation are not. Table 3 lists the calculated activation energies along with the corresponding adjusted R^2 values. Adjusted R^2 values are based on the R^2 values by

$$R^2_{adj} = 1 - \left[\frac{(1-R^2)(n-1)}{n-k-1}\right]$$

with the number n of data points and k of parameters used. Note that adj. R^2 can be negative for low R^2 values.

Table 3. Activation energies for first order reaction)

	Formal model		Empiric model	
Propellant	E_A [kJ/mol]	Adj. R^2	E_A [kJ/mol]	Adj. R^2
A5020	26.8 ± 5.72	0.840	23.76 ± 7.08	0.720
JA-2	2.80 ± 9.61	-0.224	28.45 ± 37.43	-0.092
NK 1074	98.04 ± 28.20	0.735	80.99 ± 12.86	0.906

Figure 6 shows a mass loss curve of JA-2 at low temperature (30°C). It is notable that the noise is much larger than any mass loss signal from solvent evaporation. This decreases the fit quality, resulting in large deviations for the activation energy of the first order reaction part as listed in Table 3.

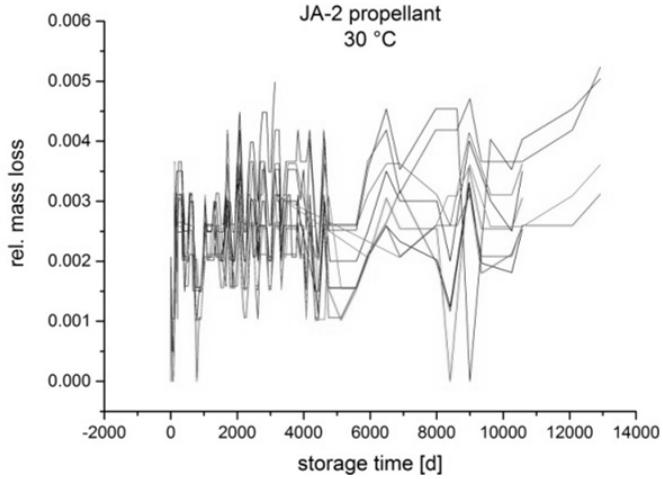

Figure 6. Mass loss curve of JA-2 at 30 °C.

For A5020 a special behaviour is observed. Mass loss signals show oscillating mass losses over an extended time period as can be seen in Figure 7.

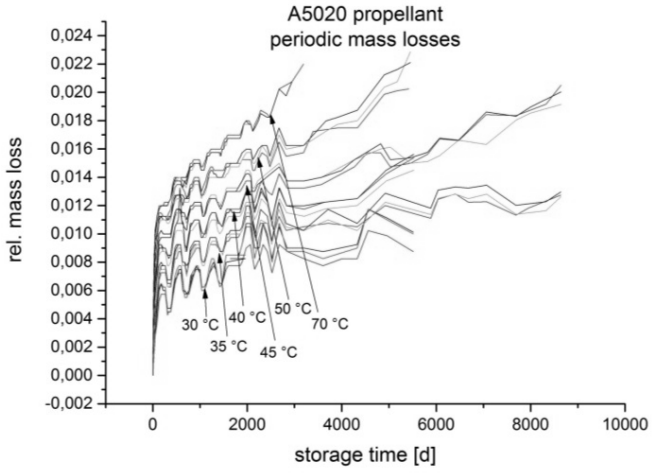

Figure 7. Periodic oscillations in A5020 single base propellant.

These oscillations can be observed at all temperatures from 30°C to 70°C. At higher temperatures decomposition is quick and the linear part in ML showing stabilizer consumption is much shorter than the time range of 2000 days for observable oscillations. The oscillation period is temperature independent which excludes chemical processes since they would obey the Arrhenius law. The oscillations are very clear in the first 2000 days, and then the measurement intervals are too long to see the oscillations properly. The oscillation period is about 350 days which strongly suggests seasonal influence on the experiment. As mentioned in the experimental section the PID-controlled ovens are located in the basement of a large building providing. Possible explanations are

- a slight influence of ambient temperature changes on the PID controllers resulting in small storage temperature variations
- and / or a slight influence of changing relative humidity on either the PID controller or the samples or both.

It is assumed that for A5020 two different decomposition mechanisms exist [3] [4], resulting in two different lines in the Arrhenius plot intersecting at ~60°C. Figure 8 shows the results for A5020 over the complete temperature range. The 90°C value is higher than anticipated from the determination result between 35°C and 55°C. Other samples of A5020 were measured at temperature between 55°C and 90°C. However, they were manufactured using a different batch of nitrocellulose But all samples of A5020 presented in this work are from the same NC batch. These samples showed values inconsistent with these data, which indicates an influence of the NC on the propellant behaviour. It is difficult to compare results from a propellant made in different batches. Figure 9 shows the same data as Figure 8 with two more reaction rates at temperatures 70°C and 80°C obtained with a propellant containing another batch of NC.

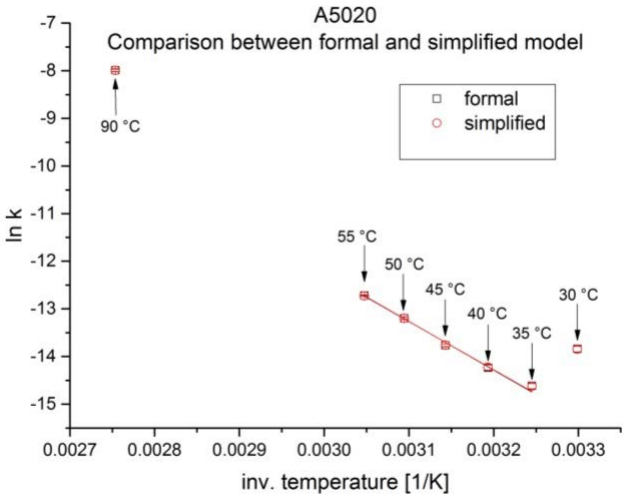

Figure 8. Arrhenius plot of A5020 single base propellant (complete temperature range).

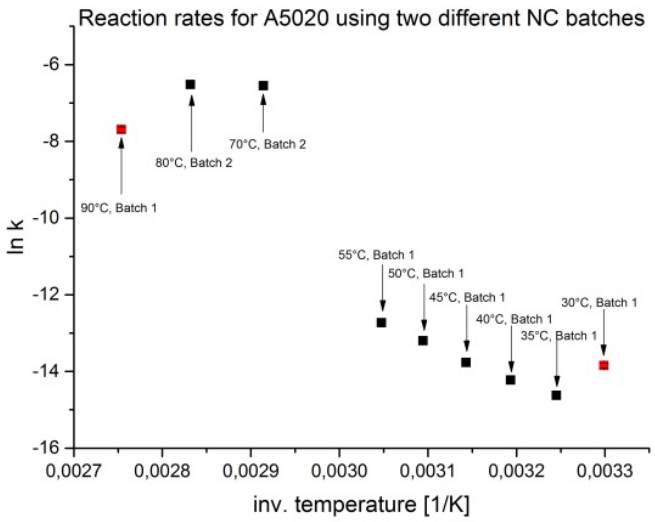

Figure 9. Arrhenius plot of A5020 single base propellant containing two different batches of NC

Stabilizer consumption

Figures 10 to 12 illustrate the concentrations of the stabilizers and the various consecutive stabilizer products. Figure 10 shows the concentration of Akardite II in JA-2 (L5460) over the storage. Each sample has been isothermally stored about 35 years at the given temperature. A clear decrease in Akardite II is notable with a formal starting concentration of 0.7 mass-%. It is possible to find 0.2 mass-% of Akardite II even after 35 years at 45°C.

Figures 11 and 12 show a selection of the different consecutive products of DPA. Most notable is the rise of higher nitrated compounds (tri- and tetranitro-DPA) at higher temperature storage, whereas at lower temperatures, these compounds do not appear. For A5020, 2,2',4,4'-tetranitro-DPA is only observed at storage temperatures of 45°C and higher over 35 years. Samples of the same age stored at 35°C or 40°C contain a significant amount of 2- and 4-nitro-DPA, which means that only the first nitration step of DPA has occurred. This leads to the conclusion that DPA is very active as a stabilizer even after 35 years at slightly elevated temperatures. The dinitro-DPA compounds appear in between at 40°C, being not present before and reacting to higher nitrated compounds thereafter. The results for NK 1074 are deviating from A5020. As can be seen from Figure 12, the 2- and 4-nitro-DPA are only present in the samples stored at 30°C. Samples stored at higher temperatures do not contain these compounds. However different dinitro-DPA compounds appear with maximum at 35°C storage temperature. 2,4,4'-trnitro-DPA starts to rise at 35°C whereas 2,2',4,4'-tetranitro-DPA is only present in the sample stored at 45°C.

To summarize, JA-2 (L5460) shows the expected decrease of Akardite II starting with 0.7 mass-% for unaged powder ranging down to 0.2 mass-% for a sample aged 35 years at 45°C. A5020 and NK 1074, which are both stabilized with DPA, show consistent behavior with respect to higher nitrated consecutive products. Tri- or tetra-nitro-DPA compounds are only present at samples aged at 45°C or higher, while dinitro-DPA disappears. Different behavior is observed for samples aged at lower temperatures. A5020 shows a significant amount of 2- and 4-nitro-DPA indicating a very good stabilizing property of the original DPA. Dinitro-DPA starts to show up at intermediate temperatures before decreasing. NK 1074 shows lower contents of 2- and 4-nitro-DPA with higher ratios of dinitro-DPA compounds. Another difference is 2,4,4'-trinitro-DPA, which can only be detected in NK 1074 but not in A5020.

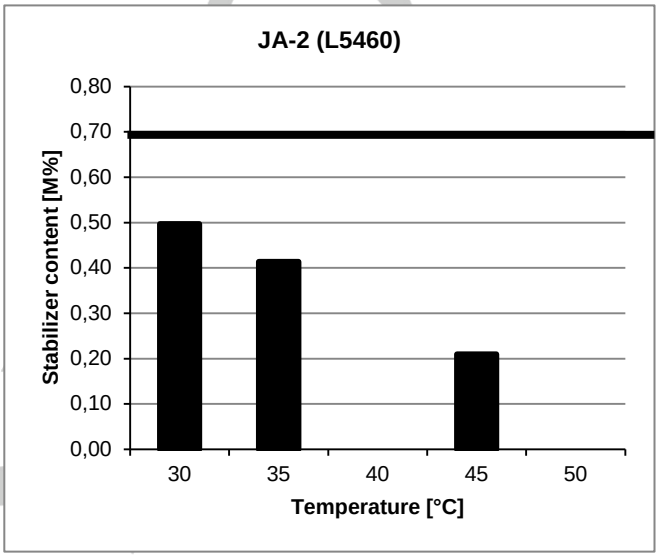

Figure 10. Stabilizer consumption of Akardite II in JA-2 (L5460) propellant

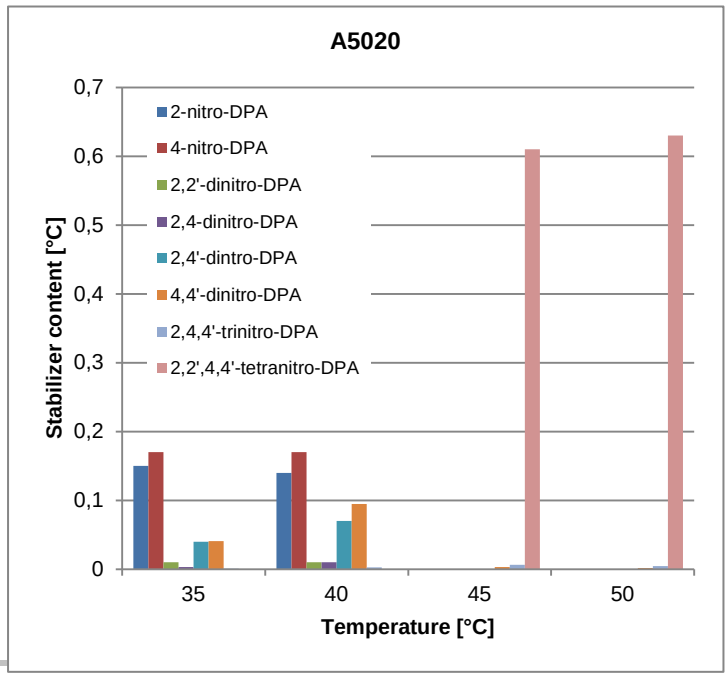

Figure 11. Stabilizer consumption of DPA and consecutive products in A5020 propellant

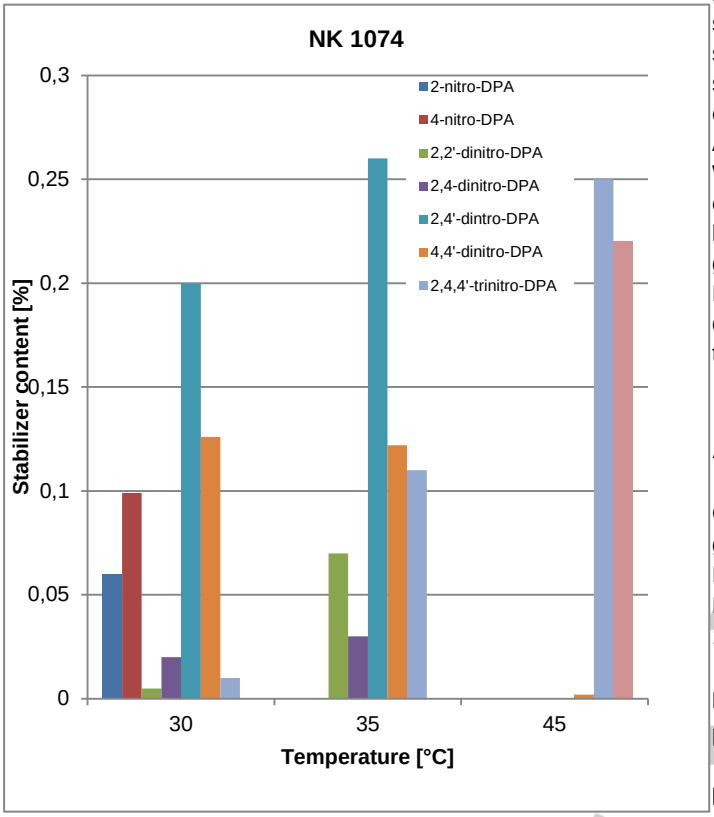

Figure 12. Stabilizer consumption of DPA and consecutive products in NK 1074 propellant

Conclusions

The investigated propellants have provided mass loss data at low temperatures over an extended time of over 30 to 35 years. The kinetic mechanisms used to describe the mass loss of propellants at higher temperatures are applicable to low temperature measurements also. The activation energies obtained for the mass loss increases reflect also stabilizer degradation and are in good correlation with the activation energies found with other methods. Low temperature measurements may suffer from bad signal to noise ratios. Larger sample amount for storage is proposed to increase signal to noise ratio, an amount of 10 to 20 g is suggested. In addition, low temperature measurements put demands on the sample storage and the quality of oven temperature control, otherwise small ambient temperature changes can influence the mass loss signal. The observed oscillations caused by seasonal influences can be averaged, if measurements are conducted long enough. A period of at least four years is suggested.

While original DPA cannot be found in any sample, different consecutive products are present. It is notable that in A5020 at lower temperatures 2- and 4-nitro-DPA can be found indicating a good stabilization. Higher nitrated products (tri- and tetranitro-DPA) appear as expected at higher temperatures. The different dinitro-DPA variants appear as an intermediate product at temperatures in midrange.

Acknowledgements

Over this long time period several persons have helped to gather all the data. Three should be mentioned: Ms Anna Dürk, Mr Reinhold Nowara, Ms Jasmin Aniol. The authors MH and MAB are grateful to Dr. Fred Volk (died in 2005, DOI: 10.1002/prep.200590010), who initiated this long term project.

Keywords: Long term mass loss • kinetic description • propellant stabilizer consumption • nitrocellulose decomposition

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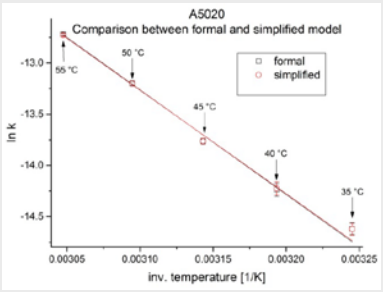
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Three gun propellants are investigated by mass loss and the activation energy of the stabilizer depletion is calculated. The consecutive products of stabilizer reaction are investigated by HPLC.



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