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LIFETIME PREDICTION OF PROPELLANTS ACCORDING TO NATO STANDARDS

This work presents the process of lifetime prediction of propellants according to new NATO standards. It shows the examples of lifetime prediction of selected nitrocellulose based propellants that are used in the ammunition of Armed Forces of Slovak republic.

1. Introduction

Slovak Republic is NATO member from 2004. This reality strongly influences our Ammunition and Explosive nation testing facilities. We must transform our national testing procedures, requirements and facilities from our national standards and traditions to procedures, requirements and facilities fulfilled NATO standards requirements. The reason this transformation is simply. Our units with our Ammunition and explosives have to train and cooperate together with armed forces from other NATO countries. The question of mutual interoperability is then very important. Mainly it means that our ammo and explosive must be safe and suitable for service according NATO standards. It means, they must be designed and tested according these requirements. We cannot applicate all NATO standards requirements on ammunition developed before our NATO membership, but these ammunition and explosives must be safe and suitable for service according NATO standards.

Practically it means, that ammunition and explosive must be tested according NATO standards requirements on safety and suitability for service. That the reason of our transformation.

The most vulnerable parts of ammunition are explosives. Problems of their stability, resistance on all environmental conditions, stability their chemical and physical properties have influence on ammunition safety and suitability for service.

2. Chemical stability of propellants

Propellants are subject to row of physical and chemical process during storage. Under these processes, there might be gradual changes their properties. It is so-called the ageing of propellants. Nitrocellulose based propellants show a slow, but constant decomposition of nitrate ester groups under the formation of nitrogen oxides and nitric acids. These components catalyse the further decomposition of the propellant and may finally lead to an autocatalytic decomposition. It can be followed with the temperature increase and ignition of propellant. To prevent autocatalysis or at least reduce the risk of it, stabilizers are added to the propellants. These substances have the ability to response with nitrogen oxides by the formation of nitrosated and nitrated compounds. Typical stabilizers for propellants are diphenylamine DPA, N-nitrosodiphenylamine NODPA and the urea derivates ethylcentralite CI and methylcentralite CII. The concentration of stabilizers in the propellant gives us important information about the actuel grade of propellant decomposition provided that we know aborigine concentration of stabilisers. The investigation of stabiliser contents is notable process of the stability assessment and plays significant role in the prediction of propellants lifetime. The artificial ageing is suitable and effective form for the investigation of propellants lifetime. It is process of accelerated ageing, which simulates spontaneous ageing in ammunition system. It is usually realized by heating at reasing temperatures which accelerate decomposition processes that will wagein the propellant number of years. Its goal is to send the propellant to such state in which it will be to occure with most probability after number of years of spontaneous ageing. It is possible by means of artificial ageing to predict the changes of stability, sensitivity, mechanical and function properties of propellants, thus their lifetime.

From previous publications in this area it results that the process of DPA chemical reactions and its derivates in the propellant is very effected by ageing conditions – it is mainly the possibility of propellant contact with air and gases escaping from propellant. Petržílek and Skládal (2) investigated the artificial ageing condition effect on DPA and CI reactions and found out that DPA loss are higher in case if the air is enterable during the ageing. From works (4,5) it results that these loss are commensurable to number of oxygen above the sample and are maximal during the initial phase of artificial ageing. I tis known from summary of work (2) that propellant samples aged with entrance o fair offer markedly higher evolve rates of gaseous products after induction period then samples artificial aged in inert atmosphere. Authors of work (3) suppose increased rate of gase evolve by means VST relates with increased ratio of skeleton urea products fission at higher initial CI concentrations. Wilker and col. (6,7) investigated the stability of different propellants during ageing and stabilizer depletion. He accented the meaning of ageing conditions. In closed and completely filled systems (HFC, VST) NO_2 is rapidly reduced to NO, it lead to a faster oxidation of the nitrocellulose. DPA is easily reacting with NO to NODPA which stabilises the propellant as well but is no more reacting with NO. In open systems (WL tests) NO and NO_2 present and NODPA is then nitrated and converted into di- and trinitro-DPA derivates. Wilker noticed that oxygen has three major effects on the samples: the nitrocellulose itself is oxidized, the stabilisers can be oxidized and it backs NO to NO_2, which is a strong oxidizing agent. So they recommended to do ageing studies in complet ammunition articles or, at least, under storage conditions as closely as possible related to the conditions in ammunition.

3. Experimental

The experiment scope is to determine the chemical stability of S053 and S060 nitrocelulose smokeless powders used for small-calibre cartridges and also it explains a calculation method of powder chemical lifetime on the base of observation of stabiliser depletion. Tested powders include DPA stabiliser. Stabiliser depletion was determined by kinetic method using multi-temperature ageing of propellant samples in accordance with II. AOP-48 allied publication that deals with stability test methods of nitrocellulose based propellants.

3.1 Multi-temperature artificial ageing conditions.

Artificial ageing was realised at various temperatures and times. Temperatures must have been chosen by minimal differences of 10°C. Ageing time was chosen by stabiliser depletion to be laid in 10 – 90 %.

Samples of propellant were subjected to ageing at 85, 75 and 65 °C in original cartridge and also sealed in the Al-PE foil. Ageing times were optimized and determined in advance considering short-term ageing at individual temperature.

3.2 Ageing time optimization

For optimal ageing temperatures determination the samples were aged at each temperature chosen from 3 values using 2 short periods of time as follows:
at 85 °C for 1-2 days
at 75 °C for 3-4 days
at 65 °C for 6-7 days

After each ageing time, the content of effective stabilizer was determined and also it was assessed whether stabiliser depletion falls in the span of 10 – 90 %. Consequentally for each temperature the kinetic parameters were calculated: aktivation energy – E and frequency factor - A. Using these parameters there is possible to calculate appropriate ageing times for 10, 30, 50 and 70 %-depletion of stabiliser at chosen temperature of the ageing.
The following equations were used:

$$\ln(t) = \ln\left(\frac{1}{A}\right) + \frac{E}{RT} + \ln\left(\frac{1-\left(\frac{100-D}{100}\right)^{1-n}}{1-n}\right) \qquad (3.1)$$

Kde:

t	-	ageing time [s]
D	-	stabilizer depletion [%]
n	-	reaction order (0,5)
A	-	frequency factor [s^{-1}]
E	-	activation energy [$kJ.mol^{-1}$]
R	-	universal gas constant [0,00831447 $kJ.K^{-1}.mol^{-1}$]
T	-	ageing temperature [K]

$$A = e^{-a} \qquad (3.2)$$

$$E = b\,.\,R \qquad (3.3)$$

$$a = \frac{\sum y - b\sum x - \sum z}{N} \qquad (3.4)$$

$$b = \frac{N\left(\sum xy - \sum xz\right) - \sum x\left(\sum y - \sum z\right)}{N\sum x^2 - \left(\sum x\right)^2} \qquad (3.5)$$

$x = \frac{1}{T}$ (3.6) $y = \ln t$ (3.7) $z = \ln \frac{1 - \left(\frac{S}{S_0}\right)^{1-n}}{1-n}$ (3.8)

Kde:
N - number of points
S - stabilizer content [%]
S_0 - inicial content of stabilizer [%]

3.3 Measuring of stabilizer content

The stabilizer content was determined by High Performance Liquid Chromatography (HPLC) using the method with the internal standard. The samples of propellants were extracted in the ultrasonic bath minimal 4 hours in acetonitrile, the nitrocellulose was precipitated by 2 % aqueous calcium chloride solution and eliminated using the centrifuging and consequently the sample supernatant liquid was filtrated through GF 50 filter.

HPLC measurement conditions:

Column	Biospher MSG P C18 4,6x250 mm
Temperature	35°C
Mobile phase	Acetonitrile/Water 55/45
Flow rate	1 ml/min
Injection volume	20 µl
Detector	UV at 205 nm

Results of stabilizer content measuring in propellant samples from multi-temperature ageing procedure are presented in the tables 1 and 2. Stabilizer content is mentioned in %.

Table 1 – stabilizer content in propellant S053

Aged in original cartridge						Aged in Al-PE foil					
85 °C		75 °C		65 °C		85 °C		75 °C		65 °C	
Days	Stab	Days	Stab	Days	Stab	Days	Stab	Days	Stab	Days	Stab
0	0,955	0	0,955	0	0,955	0	0,955	0	0,955	0	0,955
1	0,826	3	0,842	11	0,801	1	0,806	3	0,828	11	0,751
2	0,647	8	0,679	31	0,623	2	0,582	8	0,666	31	0,567
4	0,492	15	0,498	46	0,452	4	0,482	15	0,479	46	0,427
7	0,286	23	0,273	85	0,290	7	0,283	23	0,288	85	0,254

Table 2 – stabilizer content in propellant S060

Aged in original cartridge						Aged in Al-PE foil					
85 °C		75 °C		65 °C		85 °C		75 °C		65 °C	
Days	Stab	Days	Stab	Days	Stab	Days	Stab	Days	Stab	Days	Stab
0	0,947	0	0,947	0	0,947	0	0,947	0	0,947	0	0,947
1	0,835	3	0,824	10	0,851	1	0,804	3	0,789	10	0,808
2	0,633	8	0,645	34	0,657	2	0,612	8	0,594	34	0,609
4	0,406	13	0,444	46	0,468	4	0,387	13	0,395	46	0,404
6	0,245	21	0,253	83	0,282	6	0,208	21	0,191	83	0,182

3.4 Results interpretation

Measured stabilizer content values of tested propellant from multi-temperature ageing procedure were treated by program AgeKin 1,2. The program treates data ageing by sequential regression method, determines optimum n-value, calculates kinetic parameters E and A for purpose of to calculate lifetime of propellant as a storage time (years) at 25 °C after which a critical stabilizer depletion is reached. Onto the critical stabilizer depletion is considered the depletion 50 % maximum. Due to errors in storage temperature and analysis, SD values up to 20 % are considered as compatible with the kinetic model. If larger values for SD are calculated this may indicate a more complex reaction and a more detailed investigation will be necessary.[9,10]

The calculation of kinetic parameters and lifetime of propellants was performed by next equation:

$$k = A\, e^{-\frac{E}{RT}} \qquad (3.9)$$

$$t = \frac{1}{A} e^{\frac{E}{RT}} \left[\frac{1 - \left(\frac{S}{S_0} \right)^{1-n}}{1-n} \right] \qquad (3.10) \qquad\qquad SD = 100 * \sqrt{\frac{\sum (a + bx + z - y)^2}{N-3}} \qquad (3.11)$$

Kde:
SD - standard deviation [%]
k - reaction rate constant
t - storage time [years]

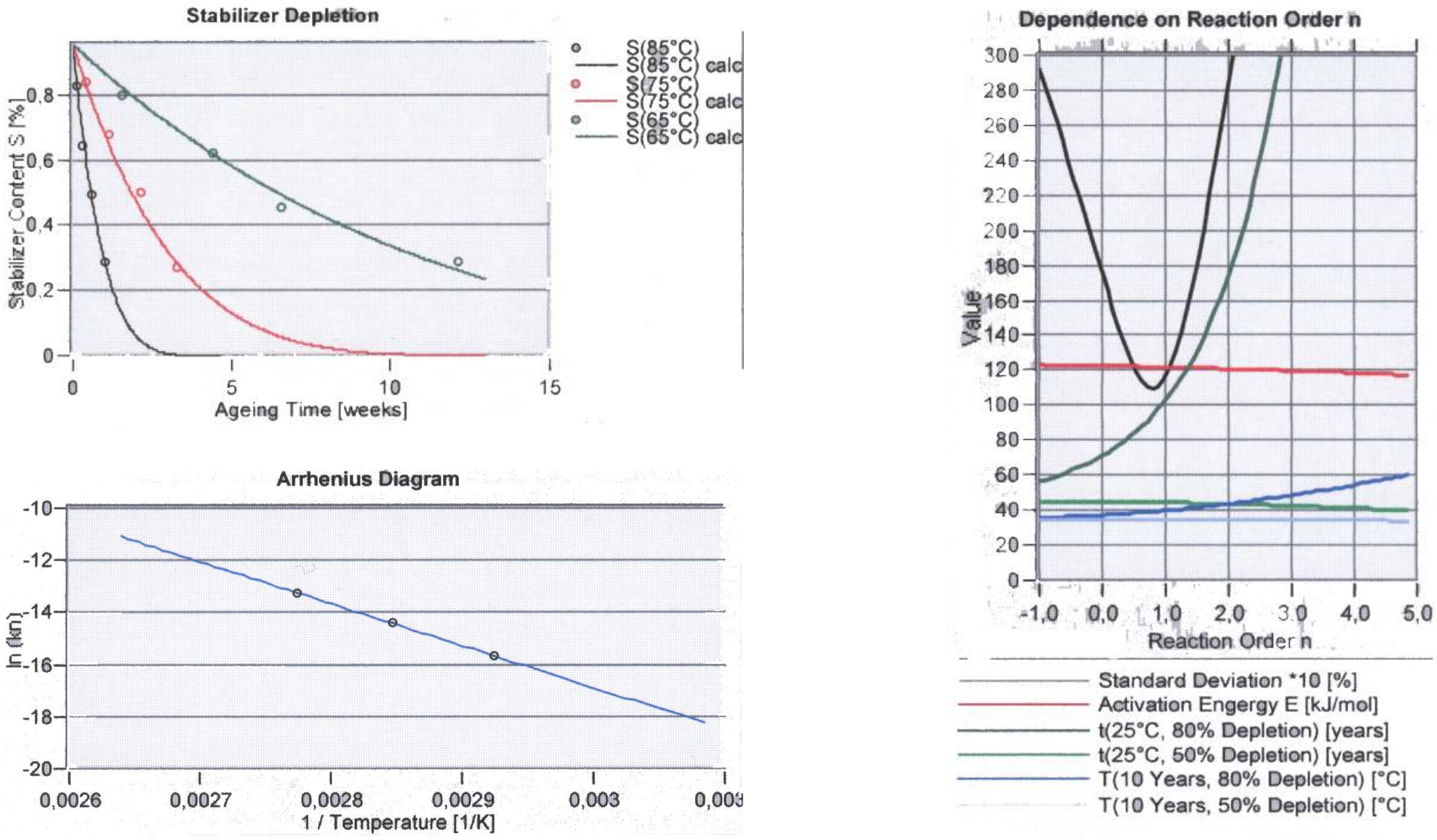
Evaluated results of data ageing treated by program AgeKin 1,2 and calculated lifetimes are presented in the table 3.

Table 3 – evaluation of data ageing

Parameters	S053 aged in cartridge	S053 aged in foil	S060 aged in cartridge	S060 aged in foil
Standard deviation [%]	10,9	16,1	10,2	8,6
Optimal n-value	0,80	1,10	0,24	0,52
Activation energy [kJ.mol^{-1}]	121,9	118,3	134,0	128,5
Frequency factor [s^{-1}]	1,068e+012	3,666e+011	6,086e+013	1,174e+013
Lifetime for 50 % stabilizer depletion[roky]	44,3	32,4	85,1	52,6

Following figure 1 displays he results of the tested propellant S053

Fig.1 - Evaluation of data ageing of propellant S053 aged in original cartridge



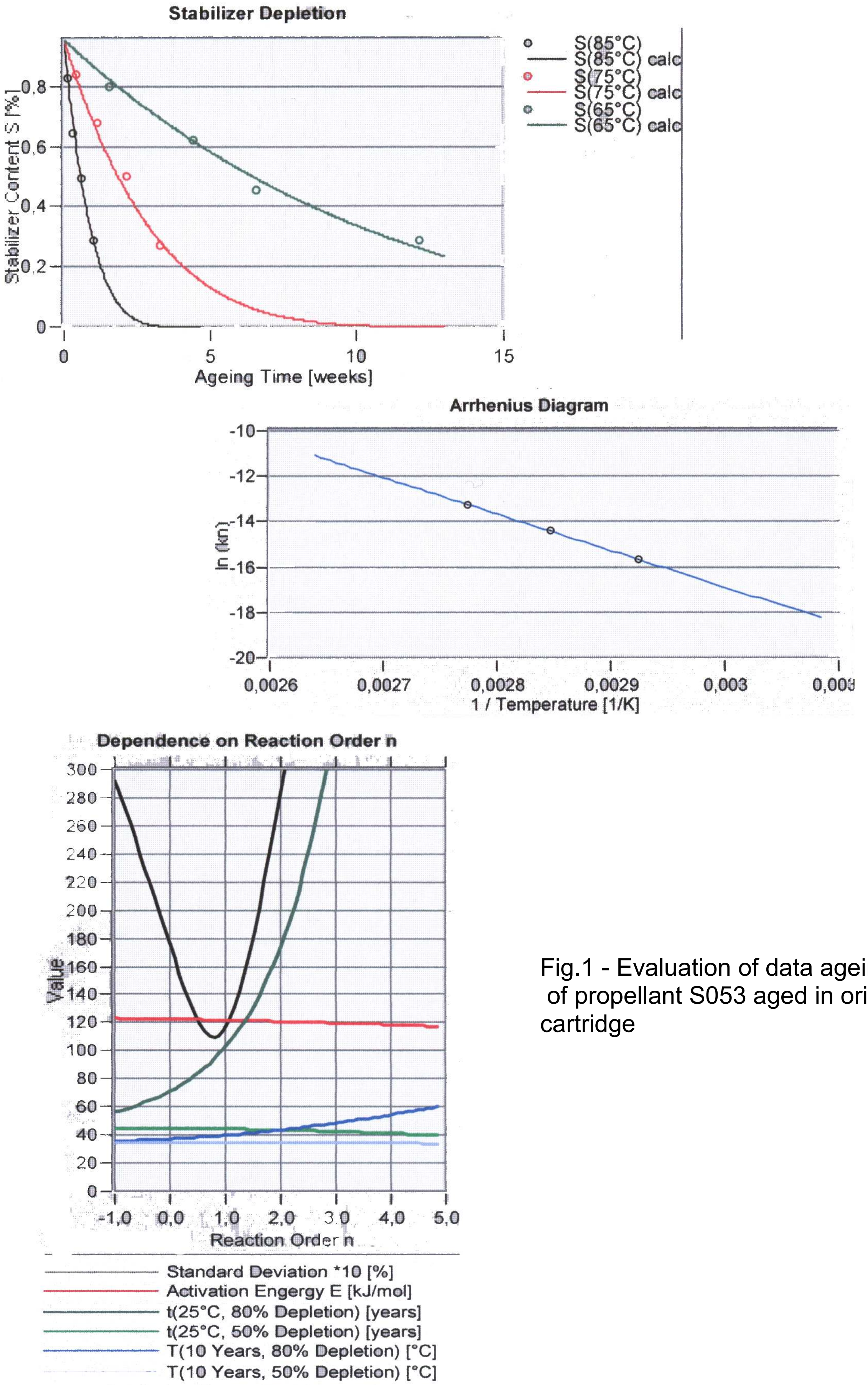


Fig.1 - Evaluation of data ageing of propellant S053 aged in original cartridge

4. Conclusion

Propellants chemical stability determination method based on stabiliser depletion allows assessing the chemical processes running in the powder grain that negatively affect its stability. In addition it predicts chemical life-time of propellant under normal storage conditions as well as forecasting the storage temperature at which the propellant remains stable for 10 years. The method requests relatively expensive facilities including HPLC assembly and detector as well as very good worked procedure of measuring of the stabiliser contents using HPLC system. There are also important thing to have precise thermoboxes for performing of multi-temperature artificial ageing.

In the point of view of sample packaging an ideal is to let the propellant to be aged in original ammunition application. If it is not possible to do so an appropriate packaging can be selaed Al-PE foil. This experimental results show on a certain difference related to packaging. The propellant samples aged in the original cartridge showed higher life-cycle than those aged in the foil. When using substitute packaging it is important the sample to be sealed to prevent negative oxygen influences on chemical processes running in smokeless propellant.

5. References

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