Researches on the Efficiency of Diphenylamine Addition to Aged Nitrocellulose Propellants

TRAIAN ROTARIU[1], TUDOR VIOREL TIGANESCU[1], SORIN RAZVAN ESANU[1], CONSTANTIN ENACHE[1], RADU STEFANOIU[2*]

[1] Military Technical Academy, Faculty of Mechatronics and Integrated Armament Systems, 39-49 George Cosbuc, 050141, BucharestRomania

[2] Politehnica University of Bucharest, Faculty of Materials Science and Engineering,313 Splaiul Independenţei, 060032, Bucharest, Romania

In the paper some data are presented on experimental investigations of safety and performance characteristics for aged nitrocellulose propellants, after supplementary diphenylamine (stabilizer) impregnation. Impregnated propellants were tested relative to new and aged nitrocellulose propellants having the same initial composition and shape.

Keywords: nitrocellulose, propellant, diphenylamine, stabilizer

It is well known that natural ageing of ammunitions during storage and service causes modification of mechanical, physico-chemical and ballistic characteristics. After long periods of time these modifications become so important that the ammunition does not longer perform according to its specifications and usage/storage are considered dangerous.

It is also known that propellant charge is the most vulnerable part of these systems relative to natural ageing especially when energetic polymers are involved as energetic base. Among the energetic polymers used in propellant charges nitrocellulose (NC) is usually preferred but glycidylazidopolymers [1] and polyvinylnitrates [2] can also be used. Even when they are stored at normal temperature and humidity levels, nitrates will slowly decompose producing nitrous vapours and consuming the stabilizer. The mechanism of this decomposition process was detailed by Rychly et al. [3] and will not be discussed here. When stabilizer content decreases under some specific values the stability reserve of the propellant is no longer considered satisfactory and it must be disposed.

Compared to all other ammunition parts simple base propellants have the shortest service life which is not usually longer than 35 years (when pass reception and all periodic tests).

Romania, like other countries from eastern block, has to deal with large stocks of ammunitions produced in the last 50 years, many of them containing simple base propellants approaching the end of their service life. Among them, there are large quantities of aged simple base propellant produced in the first decade after the Second World War that suffered the so called process of “revival” which consisted in supplementary addition of stabilizer (diphenylamine - DPA) and volatile solvents.

The idea of reusing aged propellants became very attractive for the MoD and explosives producers in our country before 1989 and it was put in practice in 1988 when some of simple base propellants batches produced between 1952 and 1985 were reprocessed in order to restore the initial stabilizer content. The principle of this reprocessing was that chemical evolution of nitrocellulose is measurable by determining stabilizer content decrease and stability reserve (total number of hours at 106.5°C Vieille test). Minimal conditions for propellants to be accepted for reprocessing were considered: 0.7% stabilizer content and 35 hours Vieille test stability. Periodic testing interval was set at 8 years.

In short description the “revival” process consisted in successive sprinkling of aged propellant with DPA solution in 5% diethyl ether and 95% ethyl alcohol, in closed vessel, during a period of ten days and under periodic mixing. Then the propellant was dried in open air for 24 h, washed several times with water and dried again with warm air (65°C).

It is obvious that technology was rudimentary and had shortcomings especially regarding homogeneity of impregnation and profoundness of colloidal reconstruction, but at that time it was considered satisfactory and many lots of aged propellants were processed and reused in new or repaired ammunitions calibre 57, 85 and 100 mm.

Laboratory and real firing tests were done on these propellants in order to establish their stability and performance characteristics. Reported results for a simple base propellant (canon ammunition type 14/7 – 1.4 mm combustion width, 7 perforations) produced in 1952 and reprocessed in 1989 are presented in table 1, comparative to some technical specifications for this type of product.

Since there are large stocks of ammunition containing this kind of propellant that was never in detail investigated

Table 1
RECEPTION TEST RESULTS FOR “REVIVED” PROPELLANT

	Physical, chemical and ballistic characteristics							
	Vieille (h)	DPA (%)	V_e (%)	V_r (%)	V_o (m/s)	r_{vo} (m/s)	$P_{max.avg}$ (bar)	$P_{max.max}$ (bar)
Rev. propellant 14/7	108	1.40	1.28	2.01	793	1.07	2497	2559
Technical spec.	>60	1.0÷2.0	1.0÷1.8	>1.3	793	<2.3	<2550	<2700

(DPA – diphenylamine content; V_e – eliminable volatiles content; V_r – residual volatiles content; V_o – muzzle velocity; r_{vo} – velocity deviation; $P_{max.avg}$ – average of maximum pressures; $P_{max.max}$ – maximum of maximum pressures)

* email: radu.stefanoiu@upb.ro; Tel.: 021 4029521

Propell. no.	Prod. year	Characteristics						
		Vieille (h)	DPA (%)	N (%)	V_e (%)	V_r (%)	Q_e (J/g)	V_{sp}* (L/kg)
1	2006	90	1.37	13.10	1.80	1.83	3890.5	823.0
2	1952 (1989)	>70	1.29	12.86	1.4	3.03	3715.3	833.0
3	1978	>70	1.35	12.79	1.21	2.79	3858.8	805.8

*- *without water. (N – nitrogen content in the nitrocellulose base; V_e – eliminable volatiles content; V_r – residual volatiles content; Q_e – explosion heat; V_{sp} – specific volume)*

Table 2
NATIONAL TESTS RESULTS

it was the aim of this study to determine at this stage some important physical and chemical characteristics that will allow us to draw a conclusion about the effectiveness of the revival process and make proper judgement regarding further destination of the ammunition.

Target propellant (no. 2) was analysed comparative to a new similar propellant (no. 1) produced in 2006 and also an aged similar propellant (no. 3) produced in 1978. Experimental techniques that we used included:

- National standard procedures for technical status evaluation: chemical stability (Vieille test), nitrogen content, eliminable volatiles content, residual volatiles content, DPA content, explosion heat, specific volume;
- International (NATO) standard procedures: thermal characterisation by differential scanning calorimetry (DSC), differential thermal analysis (DTA), vacuum stability.

Using modern thermal analysis methods allowed us not only to determine propellants temperature sensitivity and caloric effect but also to estimate and compare kinetic parameters of high temperature exothermic decompositions. Kissinger [4] and Ozawa [5] methods were employed to compute activation energy (E_a) and pre-exponential factor (A) for decomposition reactions of chemical compounds in many scientific publications [6-10].

Both methods use computation of DSC curves at multiple heating rates to obtain a plot of log (heating rate) or log (heating rate/T_p^2) versus $1/T_p$. Lin et al. [10] demonstrated that DSC approach gives best results when estimating efficiencies of stabilizers and NC's E_a of thermal decomposition process. They also determined the influence of different scanning rates on thermal decomposition E_a.

The popular Ozawa method is based on equation (1) for the activation energy (E_a) and equation (2) for pre-exponential factor (A):

$$E_a = 2.19 \cdot R \cdot d\left[\log \Phi / d(1/T_p)\right] \quad (1)$$

$$A = \frac{\Phi \cdot E \cdot \exp(E_a / RT_p)}{R \cdot T_p^{\,2}} \quad (2)$$

where: Φ is the heating rate (°C/s) and T_p is the peak temperature.

Kissinger method use equation (3) to determine activation energy and also equation (2) for pre-exponential factor:

$$E_a = \frac{2.303 \cdot R \cdot d \log\left(\Phi / T_p^{\,2}\right)}{d(1/T_p)} \quad (3)$$

Knowing E_a and A allow us to determine rate constant for high temperature decomposition using well-known Arrhenius equation.

Experimental part

National standards tests

Chemical stability was determined first using Vieille method [11] at 106.5°C, in closed glass tubes, in the presence of litmus paper. Total number of hours needed to turn red the litmus paper was determined.

Eliminable and residual volatiles content were determined according to the military technical standard (SMT) 04164/3 [12].

Diphenylamine- content was determined by titration with sodium nitrite according to SMT 040164/1 [13].

Nitrogen content was determined using Lunge nitrometer according to SMT 40395 [14].

Explosion heat and specific volume were determined under vacuum, using an isothermal calorimeter produced by AVL and a Julius-Peters gas-meter [15] on 2 g samples.

NATO standards tests

Vacuum stability tests were performed according to NATO standard agreement (STANAG) 4556 [16] method 2A with calibrated pressure transducer. 5 g of sample is heated at 100°C in a constant temperature bath (metal block type), 40 h, under vacuum. Evolved volume of gas is calculated based on pressure variation. Pressure was monitored at all time in order to appreciate its evolution. Special designed transducers and test tubes supplied by OZM Research were used. Data acquisition and storage were realized using a Omega OM320 data logger.

Thermal analysis for all three kinds of propellants was done using Perkin Elmer Diamond DSC apparatus on 1÷1.5 mg samples, under nitrogen flow. The heat flow and temperature calibrations of DSC were done using indium standard. Temperature sensitivity was determined using OZM DTA 551 apparatus on 30 mg samples, in open air. DTA temperature calibration was done using indium standard.

During sampling it was observed that propellant no. 2 (reprocessed) presents two types of granules: some of them light colored (yellow-brownish) and some dark colored (green-brown). Samples were drawn from both types of granules for comparison.

Results and discussions

National standards test results

Test results for National standards test tests are presented in table 2.

Thermal analysis results

DSC curves were determined for five different heating rates (5, 10, 15, 17 and 20°C/min.). Representative thermogrames and results of Ozawa and Kissinger computations are presented in figure 1 - 9. Figure 10 presents DTA thermograms for 10°C/min. heating rate and

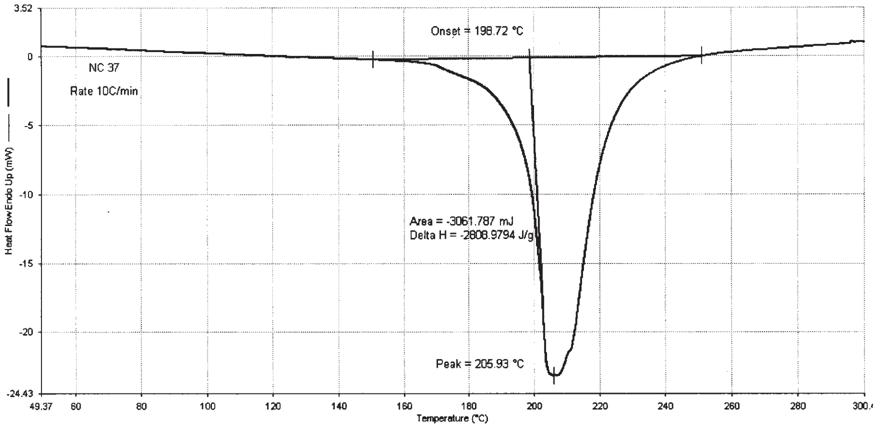


Fig. 1. DSC curve for Propellant 1

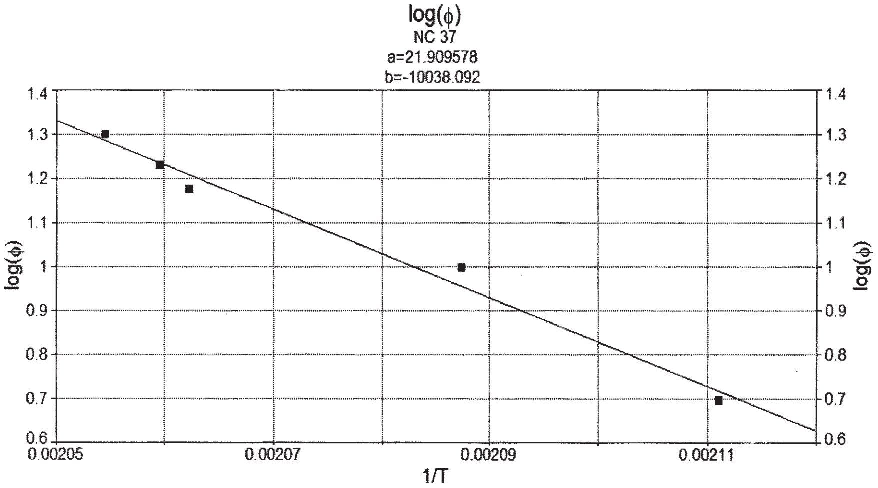


Fig. 2. Ozawa plot for Propellant 1 (E_{Ozawa} = 182.8 kJ/mol; A= 1.242 x 10^{18} s^{-1})

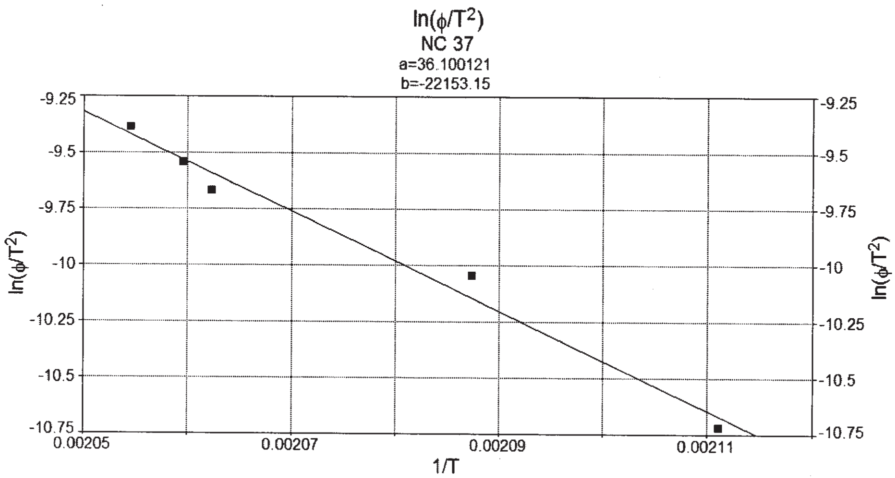


Fig. 3. Kissinger plot for Propellant 1($E_{Kissinger}$ = 184.2 kJ/mol; A= 1.763 x 10^{18} s^{-1})

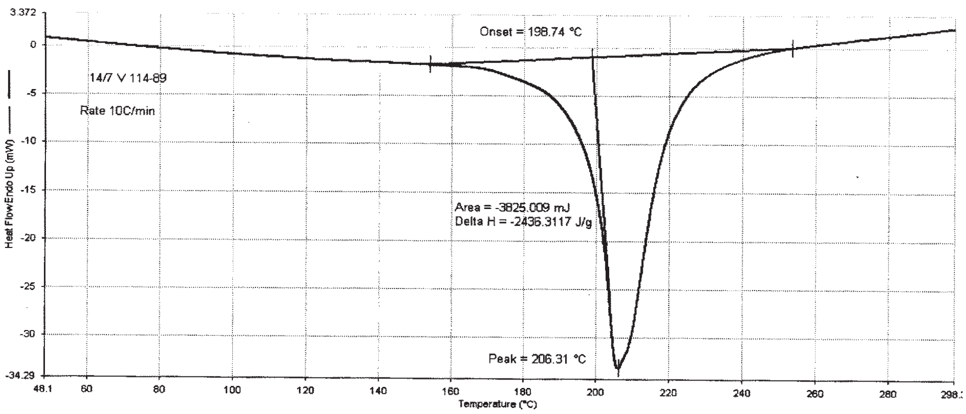


Fig. 4. DSC curve for Propellant 2

also onset temperatures for all four (5, 10, 15 and 20°C/min) heating rates used.

Vacuum stability tests were performed on samples without any preliminary conditioning (heating or vacuum drying). Results are presented below as pressure vs. time curves; calculated evolved volume is also indicated.

Nitrogen content for propellant 2 and 3 is lower compared to reference propellant no.1, as expected, due to their age, and might generate lower ballistic performance but not in an important degree. DPA content is very good, slightly lower for propellant no.3.

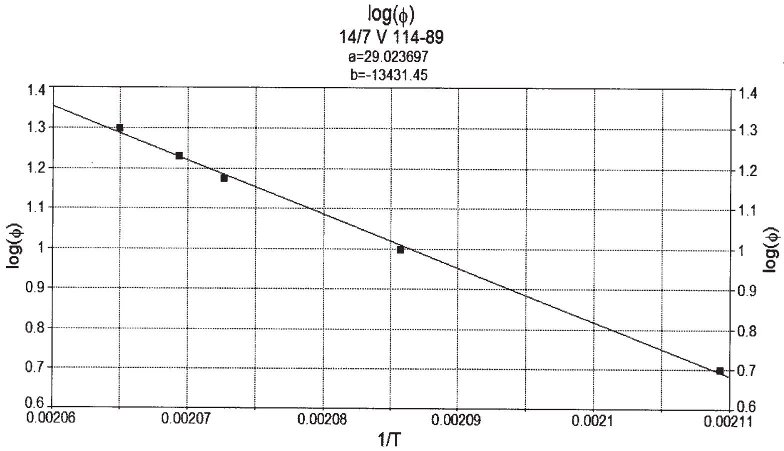


Fig. 5. Ozawa plot for Propellant 2
(E_{Ozawa} = 244.6 kJ/mol; A= 9.699 x 10^{24} s^{-1}).

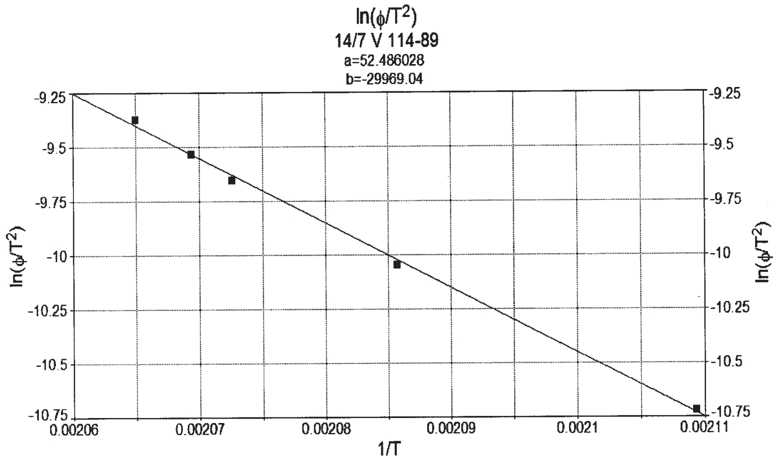


Fig. 6. Kissinger plot for Propellant 2
($E_{Kissinger}$ = 249.2 kJ/mol; A= 3.111 x 10^{25} s^{-1}).

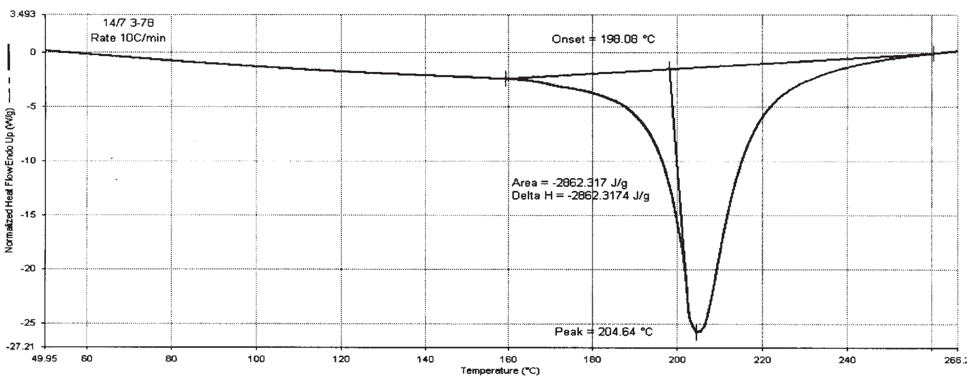


Fig. 7. DSC curve for Propellant 3

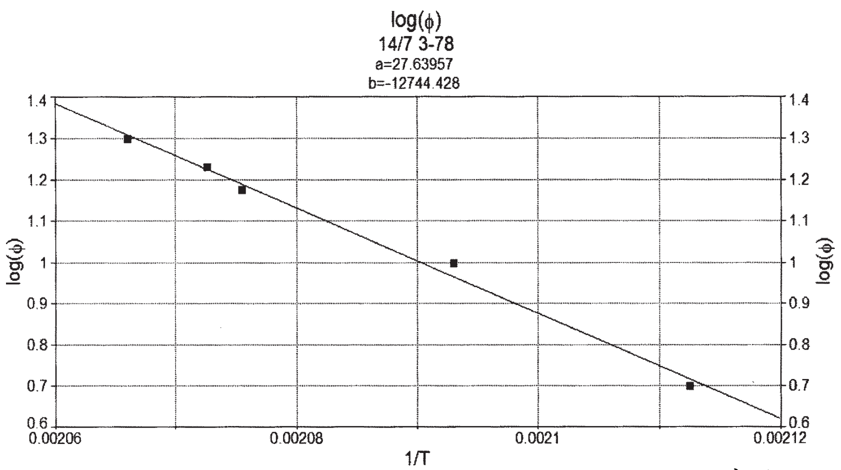


Fig. 8. Ozawa plot for Propellant 3
(E_{Ozawa} = 232.1 kJ/mol; A= 4.460 x 10^{23} s^{-1})

Volatile content tests indicated less eliminable volatiles and more residual volatiles for propellants 2 and 3. Especially residual volatiles content for propellant no.2 is much bigger compared to propellant 1 and could have an impact on the energetic performances.

Explosion heats for all three samples are situated in usual ranges for this kinds of simple base propellants (3800±100 J/g). As expected, the explosion heat decreases as the age of nitrocellulose increases. Propellant no. 2 is close to lower limit so it must be further checked in ballistic tests regarding performance.

DSC study at different heating rates allowed us to evaluate kinetic parameters for high temperature decomposition reactions. As indicated in figures 5÷9, the kinetic parameters have higher values for aged propellants.

Arhenius equations and Ozawa E_a and A values give the following rate constants (k): 0.014 s^{-1} for propellant 1, 0.020 s^{-1} for propellant 2 and 0.018 s^{-1} for propellant 3. This indicates an increase in activation energy and reaction rate for aged propellants and must be further investigated in ballistic tests in order to verify compliance on safety characteristics (max. pressure values). Kinetic results are also in accordance with those presented by Lin et al. [17] that NCs with lower nitrogen content have higher E_a and A.

DTA shows normal temperature sensitivity for all three samples, onset temperature being very close to 180°C while 172°C is considered as lower limit for this kind of propellant. Propellant 2 gives onset temperatures very similar to propellant 1 especially for 20, 15 and 5°C/min heating rates.

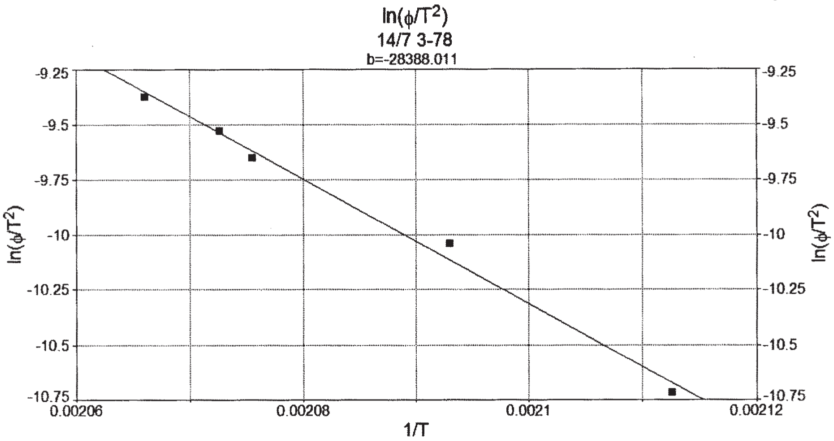
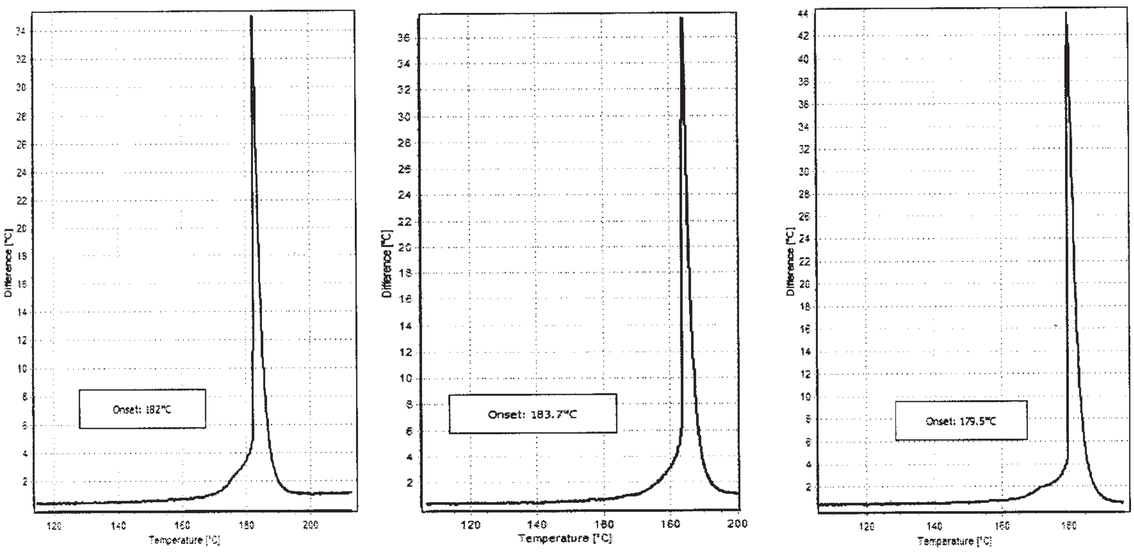
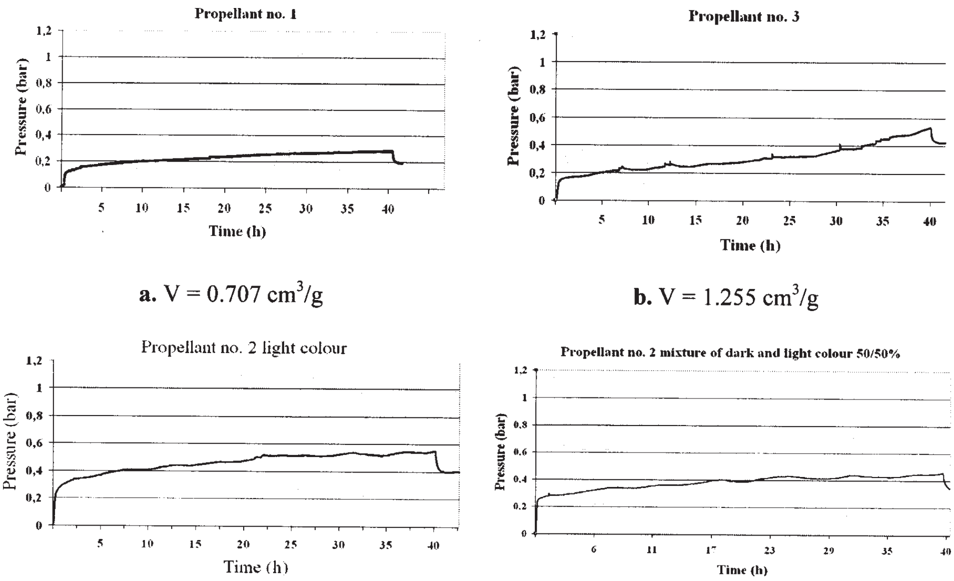


Fig. 9. Kissinger plot for Propellant 3($E_{Kissinger}$ = 236.0 kJ/mol; A= 1.220 x 10^{24} s^{-1})



a b c

Fig. 10. DTA curves: *a. Propellant 1* - Onset: 186.5°C (20°C/min); 185,1°C (15°C/min); 182°C (10°C/min); 180.5 °C (5°C/min); b. Propellant 2 - Onset: 186°C (20°C/min); 185.6°C (15°C/min); 183.7°C (10°C/min); 180.4°C (5°C/min); c. Propellant 3 - Onset: 183°C (20°C/min); 180.6°C (15°C/min); 179.5°C (10°C/min); 179.4°C (5°C/min)



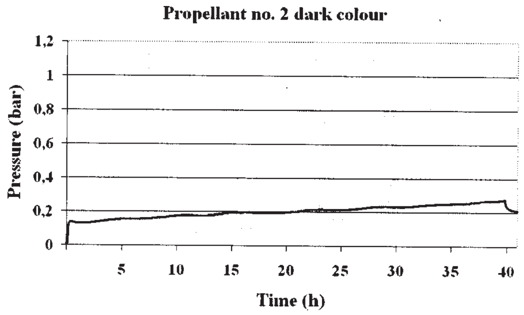
a. V = 0.707 cm^3/g

b. V = 1.255 cm^3/g

c. V = 1.610 cm^3/g

d. V = 1.284 cm^3/g

Fig. 11. Vacuum stability test results



e. V = 0.770 cm^3/g

Fig. 11. Vacuum stability test results

While DSC and DTA did not show any difference between light and dark granules of propellant 2, vacuum stability tests indicated better stability for darker granules. Also considering those presented by Lindblom [17] it can be supposed that a higher content of DPA is present in darker granules and raise questions about the homogeneity of DPA impregnation process. Mixtures of dark/light granules generated 1.284 cm^3/g volumes of gas and are in good correlation with results obtained in separate tests (1.61 cm^3/g for light colored and 0.77 cm^3/g for dark colored). Anyway, stability being a safety characteristic, we must take into consideration the most disadvantageous situation and take 1.61 cm^3/g as a final result which will not be acceptable in many NATO countries. Propellant 3 also gives bad results in vacuum stability tests having an evolved volume of 1.255 cm^3/g (bigger than 1 cm^3/g). This is contradictory to Vieille results because all three propellants have passed the litmus paper test giving over 70 h stability reserve.

Looking at pressure vs. time curves in figure 11 we can observe that light colored propellant 2 evolves important volume of gases at the very beginning of heating and this affects drastically the final result. It is obvious that such important evolution in such short period of time (0.002 bars in the beginning to 0.3 bars after 5 min) cannot be produced by a decomposition reaction and rather produced by a bigger content of volatiles. This could explain contradictory the results obtained in vacuum stability vs. litmus paper tests.

Conclusions

All national tests performed indicated that "revived" propellant fulfils requirements for at least 5 years of service life. On the other hand, vacuum stability tests gives over 1 cm^3/g results for gas evolution indicating chemical instability. Shape of pressure vs. time curve suggests that vacuum stability results could be affected by a higher volatiles content. Having this in mind we concluded that further investigations involving ageing protocols and HPLC chemical analysis are required in order to make a final judgement regarding the real stability reserve of the propellant.

Temperature sensitivity of "revived" propellant fulfils requirements and is comparable to those of similar new propellants. Estimated values for kinetic parameters of high temperature decompositions indicate that in spite of lower nitrogen content, aged propellants give higher decomposition rates, so further ballistic tests are required in order to determine if ballistic safety characteristics could be affected.

At this stage, can be concluded that, in spite of obvious shortcomings, the simplistic "revival" process proved to be effective in extending service life of aged simple base propellants. Stability and sensitivity tests do not indicate abnormal behaviour but must be confirmed by artificial ageing and stabilizer consumption measurement.

References

1. T. ROTARIU, GH. HUBCA. U.P.B. Sci. Bull., Series B, Vol.66, No**. 2-4**, 2004, p.51.

2. T. ROTARIU, GH. HUBCA. U.P.B. Sci. Bull., Series B, Vol.66, No**. 2-4**, 2004, p. 61.

3. J. RYCHLY, A. LATTUATI-DERIEUX, L. MATISOVA-RYCHLA, K. CSOMOROVA, I. JANIGOVA, B. LAVEDRINE, Journal of Thermal Analysis and Calorimetry, Vol. 107, **No. 3**, March 2012. p. 1267.

4. H. E. KISSINGER. Anal. Chem., **No. 29**, 1957, p. 1702.

5. T. OZAWA. J. Therm. Anal., **No. 2**, 1970, p. 301.

6. A. FULIAS, B. TITA, G. BANDUR, D. TITA. Rev. Chim. (Bucharest), **60**, no. 10, 2009, p. 1079.

7. A. FULIAS, T. VLASE, G. VLASE, Z. SZABADAI, G. RUSU, G. BANDUR, D. TITA, N. DOCA. Rev. Chim. (Bucharest), **61**, no.12, 2010, p.1202.

8. B. TITA, A. FULIAS, G. RUSU, D. TITA. Rev. Chim. (Bucharest), **60**, no. 11, 2009, p.1210.

9. T. ZECHERU, A. LUNGU, P. IORDACHE, T. ROTARIU, Combustion, Explosion, and Shock Waves, Vol. 49, **No. 2**, 2013, p. 204.

10. C.-P. LIN, Y.-M. CHANG, J. GUPTA, C.-M. SHU, Process Safety and Environmental Protection, **88**, 2010, p. 413.

11.*** STP-M 40294/1. Solid propellants. Methods to determine the chemical stability by blue litmus indicator paper at 106.5 ^{0}C., Romanian MoD, Bucharest, 1993.

12.*** SMT 04164/3. Simple base propellants. Volatile content determination using precipitate method, Romanian MoD, Bucharest, 1996.

13.*** SMT 040164/1. Simple base propellants. Diphenylamine content determination methods, Romanian MoD, Bucharest, 1996.

14.*** SMT 40395 Nitrogen content determination method, Romanian MoD, Bucharest, 1995.

15. O. ORBAN, D. GOGA, T. PARASCHIV. Explosives and Propellants. Analysis and identification methods, A&C International, Bucharest, 1994, p105

16.***: STANAG 4556. Ed.1 – Explosives. Vacuum stability test, NATO-MAS, Brussels, 1999.

T. LINDBLOM. Propellants, Explosives, Pyrotechnics, **No. 27**,

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