Studies Regarding the Effectiveness of Stabilizer "Revival" Process on Old Propellants

VIOREL TIGANESCU[1], TRAIAN ROTARIU[1]*, SORIN RAZVAN ESANU[1], TEODORA ZECHERU[1,2], CATALIN FLOREA[1], LIVIU - CRISTIAN MATACHE[2]

[1]Military Technical Academy, 34-49 George Cosbuc Str., 050141, Bucharest, Romania

[2] Scientific Research Center for CBRN Defense and Ecology, 217-225 Oltenitei Road, 041309, Bucharest, Romania

The paper deals with experimental investigations performed in order to evaluate the safety and the performance characteristics of some old simple base propellants used in some specific activities, after a "revival" process consisting in supplementary diphenylamine (DPA) addition. The revived propellants were tested comparative to new and old propellants of similar composition and geometry.

Keywords: nitrocellulose, propellant, simple base, diphenylamine, stabilizer

Propellants are the most vulnerable part of propulsive systems relative to natural aging, especially when nitrocellulose is involved as energetic base. Even stored at normal ambient temperature and humidity, nitrocellulose will slowly decompose producing nitrous vapours and consuming the stabilizer [1-4]. When stabilizer content decreases under some specific values, the stability reserve of the propellant is no longer considered satisfactory and, consequently, it must be disposed. Simple base propellants have the shortest service life that is not usually longer than 35 years.

Romania also has to deal with large ordnance stocks produced during the cold war, many of them containing simple base propellants at the end of their service life. These stocks include large quantities of old simple base propellant produced in the late fifties that suffered a process of "revival" consisting in supplementary addition of stabilizer (diphenylamine - DPA) and volatile solvents. Thus, many batches of old simple base propellants produced between 1952 and 1985 were reprocessed in order to restore the initial stabilizer content. Minimal conditions to be accepted for reprocessing were considered: 0.7% stabilizer content and 35 h at 106.5°C for the Vieille stability test. Propellants were thus reprocessed and reused.

Since there are large stocks containing revived propellant that has never been investigated in detail, the aim of this study was to determine, at this stage, some important physical and chemical characteristics that will allow to draw a conclusion about the effectiveness of the revival process and make proper judgment regarding further destination.

Samples from a batch of revived propellant (no. 2) were analyzed using standard procedures [5-6] in comparison to a newer similar propellant (no. 1) produced in 2006 and also an old similar propellant (no. 3) produced in 1978.

In a previous work [1], thermal analysis (DTA, DSC) and vacuum stability tests were performed using non-aged samples. Some results from national qualification/ periodical tests were also presented.

All national tests performed indicated that "revived" propellant fulfills requirements for at least 5 years of service life. On the other hand, vacuum stability tests indicated over 1 cm^3/g evolving gas for some samples and this could be considered unacceptable in some countries. But analyzing shape of pressure vs. time curve, we concluded that vacuum stability results were affected by higher volatiles content and not by accelerated chemical decomposition.

Further investigations involving ageing protocols and HPLC chemical analysis were required in order to make a final judgment regarding the real stability reserve of the propellant.

Temperature sensitivity of "revived" propellant fulfilled the requirements and was comparable to those of similar new propellants. Estimated values for kinetic parameters of high temperature decompositions indicated, as expected, that old propellants give higher decomposition rates.

At that stage we concluded that, despite of obvious shortcomings, the simplistic "revival" process proved to be effective in extending the life of old simple base propellants, while the stability and the thermal analysis tests did not indicate an abnormal behavior, while artificial ageing and stabilizer consumption measurements were used for confirmation purposes.

Experimental part

Propellants no. 2 and 3 were artificially aged at 65.5 °C, for 60 days, using closed glass tubes and 20 g samples (standard procedure [7], fig. 1).

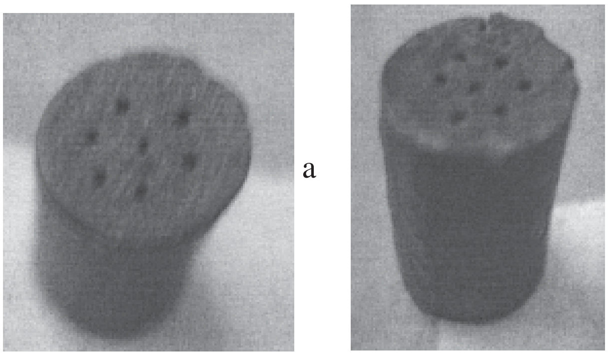


Fig. 1. 14/7 type propellant granules: a) un-aged propellant no. 2; b) aged propellant no. 2.

*email:traian.rotariu@gmail.com; Tel.: (+40)213364591

Thermal analysis of un-aged and aged propellants was performed using an OZM DTA 551 apparatus on 30 mg samples, in open air [4-5,7]. The DTA temperature calibration was performed using an indium standard.

The stabilizer content and the stabilizer consumption after ageing were determined by HPLC analysis [6,8-9], using a Perkin Elmer UV-VIS 200 Series apparatus and the following conditions:

- column: Techema RP-18, 5μm, 250x4 mm;
-eluents: methanol/water/ acetonitrile (HPLC grade) - 22%/42%/36%;
-flow: 1 mL/min.;
- detector wavelength: 234 nm;
- column temperature: 30°C;
- external standards: Diphenylamine p.a., N-Nitroso-Diphenylamine p.a., 2-Nitro-Diphenylamine p.a., 4-Nitro-Diphenylamine p.a. – Sigma Aldrich.

1g propellant samples were dissolved in 250 mL acetonitrile using magnetic stirring for 4 h. Nitrocellulose was precipitated adding 50 mL of 2% $CaCl_2$ aqueous solution and then the suspension was cooled at 0°C for 2 h. A portion of the clear liquid layer was then filtered on 0.45 μm Teflon filters and also centrifuged. 20 μL samples were injected into the column.

Vacuum stability tests were performed according to standard procedures [3-4] with calibrated pressure transducers. 5 g of sample are 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 an Omega OM320 data logger.

Results and discussions

DTA curves obtained for aged and un-aged revived propellant (no. 2) and also for reference propellants (no.1 and 3) are presented in figure 2. Heating rate used for all samples was 5°C/min. Detailed results (start, onset, top and maximum difference) of thermal analysis can be observed in table 1.

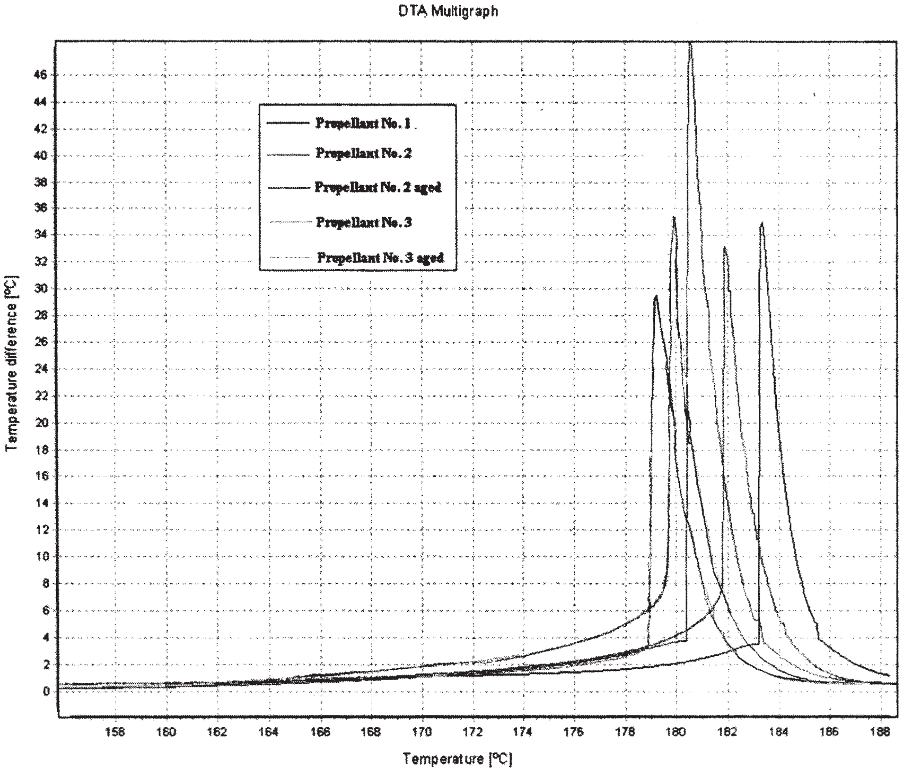
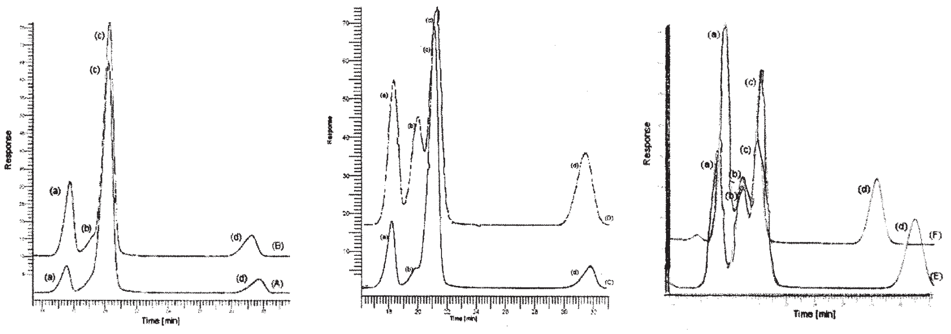


Fig. 2. DTA curves for aged and un-aged propellants

Table 1
DETAILED RESULTS OF THERMAL ANALYSIS

Propellant	**No. 1**	**No. 2**	**No. 2 aged**	**No. 3**	**No. 3 aged**
Heating rate:	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min
Decomposition start:	149 °C	138 °C	151 °C	158 °C	148 °C
Onset:	183 °C	180 °C	182 °C	179 °C	179 °C
Top:	183 °C	181 °C	182 °C	179 °C	180 °C
Max. tempertaure difference	35 °C	49 °C	33 °C	29 °C	35 °C
Final tempera-ture:	191 °C	191 °C	190 °C	189 °C	190 °C



A – unaged propellant no.1 C – unaged propellant no.2 E – unaged propellant no.3

B – aged propellant no.1 D – aged propellant no.2 F – aged propellant no.3

Peak correspondence: (a) N-nitroso-DPA; (b) 4-nitro-DPA; (c) DPA; (d) 2-nitro-DPA

Fig. 3. HPLC curves for the aged and unaged simple base propellants

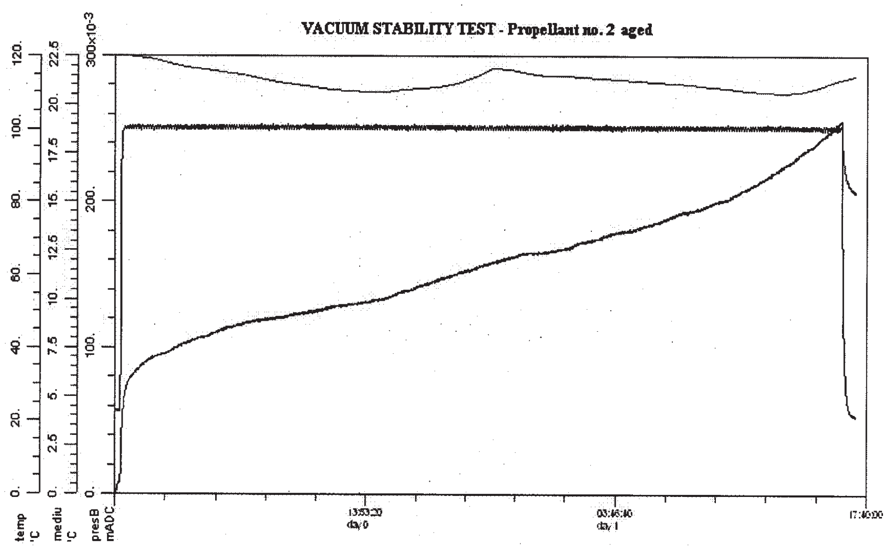


Fig. 4. Typical pressure vs. time (temperature vs. time) curves for vacuum stability tests

Table 2
DPA AND EFFECTIVE STABILIZER CONTENT BEFORE AGEING

Propellant	**N-nitroso- DPA content before ageing [%]**	**DPA content before ageing [%]**	**Effective stabilizer content before ageing [%]**
No. 1	0.12	1.69	**1.79**
No. 2	0.32	1.58	**1.85**
No. 3	0.48	1.05	**1.46**

Table 3
DPA AND EFFECTIVE STABILIZER CONTENT AFTER AGEING

Propellant	**N-nitroso-DPA content after ageing [%]**	**DPA content after ageing [%]**	**Effective stabilizer content after ageing [%]**	**DPA consumption [%]**	**Effective stabilizer consumption [%]**
No. 1	0.44	1.21	**1.58**	0.48	**0.21**
No. 2	0.58	0.94	**1.43**	0.64	**0.42**
No. 3	0.68	0.48	**1.06**	0.57	**0.40**

The DTA results do not indicate significant differences between the target propellants. Revived propellant (no. 2) shows a slightly lower onset temperatures versus the new propellant (no. 1) and a little higher onset compared to the old propellant (no. 3). Decomposition starting temperatures are normal for simple base propellants when using 5°C/min heating rates. Aged no. 3 propellant shows, as expected, a higher decomposition rate prior to onset temperature.

HPLC curves for the three propellants are presented in figure 3 and table 2 and 3 show final results of chromatographic measurements performed on aged and un-aged propellants regarding DPA content and effective stabilizer content (%DPA + 0.85 · % Nitroso-DPA). DPA initial content of propellant no. 2 (1.58%) shows a usual value for fresh simple base propellants, superior to that of propellant no. 3. The final effective stabilizer content of

Propellant	Initial pressure [bar]	Initial env. temperature [°C]	Final pressure [bar]	Final env. temperature [°C]	Volume of evolved gas [cm^3]	Specific volume [cm^3/g]
No. 2 aged	0.008	22.92	0.206	21.48	3.85	0.77
No. 3 aged	0.006	22.35	0.255	21.22	4.76	0.95

Table 4
VACUUM STABILITY RESULTS FOR AGED PROPELLANTS

both aged propellants is much higher than 0.3% and the effective stabilizer consumption is lower than 0.5%.

Vacuum stability tests (fig. 4 and table 4) demonstrated that the bad results obtained on un-aged propellants [1] were strongly influenced by initial volatiles content, as we supposed at the time we interpreted the shape of pressure vs. time curve.

Specific volume obtained for aged propellant no. 2 is now lower than 1 cm^3/g indicating still good chemical stability. Propellant no. 3 shows a specific volume very close to 1 cm^3/g, indicating that it is approaching the end of the stability reserve.

Conclusions

The aim of the study was to supply an objective point of view regarding the actual situation of some old propellants that have suffered, in 1989, a so-called "revival" process and still posse's good ballistic characteristics.

Along with usual national qualification tests, thermal analysis, vacuum stability and stabilizer content, the stabilizer depletion methods were used. Thermal analysis (DSC and DTA) did not indicate significant modifications in temperature sensitivity and decomposition kinetics. Vacuum stability tests on un-aged propellants gave unsatisfactory outcome but further results, obtained on aged propellants, and also the allure of pressure vs. time curve demonstrated that the higher volatile content and not the decomposition reactions of the revived propellant caused an increased volume of evolved gas. HPLC chemical analysis on aged and un-aged samples showed that revived propellant still contains a great amount of effective stabilizer and its depletion after ageing is in the limits of acceptance for a minimum of 5 year-service life, at normal ambient temperatures.

We can conclude that, in spite of obvious shortcomings, the simplistic "revival" process proved to be effective in extending service life of old simple base propellants. Analyzed batches of revived propellant showed good stability characteristics and usual temperature sensitivity comparative to new and old propellants and according to standard criteria. The revival process could be recommended, with proper refinement, for a study regarding the reuse of old simple base artillery propellants that have not suffered surface treatments.

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