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THERMAL ANALYSIS IN PROPELLANT STABILITY EXAMINATIONS

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Abstract

The thermal analysis of powders and propellants extends the possibilities of study of their chemical stability. Two models of double and triple base powders were analysed by differential scanning calorimetry. Their chemical stabilities were determined by using classical analytical methods. The thermal explosions of the powders were analysed. It was shown that the thermal decompositions of double and triple base powders are controlled by the consumption of nitro-ester stabilizers.

Keywords: aged propelliant, chemical stability, differential scanning calorimetry, double base propellant, triple base propellant

Introduction

The chemical stability of chemical explosive materials (explosives, pyrotechnic mixtures, powders and propellants) changes during storage and manipulation. The stability is determined by the kinetics of slow degradation which occurs at ambient temperature under the conditions of the surroundings [1, 2].

The decomposition of explosive materials, depending on the sources of initiation of the process, can be divided into: chemical, thermal, mechanical, photo, X-ray and biological. In nature, these sources of initiation are not isolated, and the processes of decomposition are related. During storage, explosive materials are primarily exposed to heat and temperature changes and to mechanical strain during manipulation.

Experimental

Because of the importance of the slow thermal degradation of explosive materials [3–5], the chemical stabilities of a few models of double and triple base powders were examined in several steps:

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- preparation and examination of the powder model compositions [6];
- examination of the chemical stabilities of the powders at 65°C [7], 'aged' for 3, 6, 9 or 12 months.

These conditions were used because of the relatively small temperature increase as compared to the upper temperature limit of use, 50°C, and the relatively significant sample mass, 50 g (in order to establish the natural storage conditions for propellants in service packages) [7].

The 'aged' propellant samples were stored in a storehouse for 24 months, under the conditions of the propellants, with the aim of prolonging the beginning of thermal decomposition. 'Unaged' reference propellants were stored in the same storehouse.

The chemical stabilities of reference and 'aged' propellant samples were examined by classical methods:

- Bergmann & Junk test at 120°C [7];
- heating at 100°C [7];
- methyl violet test at 120°C [7];
- Hansen test at 110°C [8].

Thermal analyses of the reference and 'aged' propellants were performed on a Thermal Analyzer series 99 with a DuPont 910 Differential Scanning Calorimeter (DSC). The samples (2 mg), cut into plates, were sealed in aluminium pans. The nitrogen flow was 50 ml min^{-1}. The samples were scanned at heating rates of 5, 10, 20 or 30°C min^{-1}. All measuremens were performed five to ten times.

The stabilizer contents in the reference and 'aged' propellants were determined by gas chromatography (GC). The GC analyses were performed on a Hewlett-Packard Model 5890 gas chromatograph equipped with a flame ionization detector. The chromatogram was evaluated with a Hewlett-Packard Model 3396A integrator. A 10 m×0.53 mm I. D. fused-silica capillary column coated with cross-linked methylsilicone stationary phase of film thickness was programmed from 100 to 200°C at 10°C min^{-1}. The detector temperature was 250°C. Helium was used as the carrier gas, at 15 ml min^{-1}. The injected sample volume was 5 μL; it was split, with a split vent flow of 200 mL min^{-1}. The internal standard method was used for the quantitative determination of the sample components, acetanilide (AA) being used as the internal standard. Dichloromethane was used as solvent.

Results and discussion

The double base propellant (B_{00}) consists of two energetic components, nitrocellulose (NC) and nitroglycerine (NG) as a nitrocellulose gelatinizer; dibutyl phthalate (DBP) as a nitrocellulose plasticizer; and centralite I (CI-ethyl phenyl amine) as a nitrocellulose stabilizer. The triple base propellant (B_{50}) contains nitroguanidine (NGV) as a third energetic component.

The chemical compositions, and physico-chemical and energetic properties of the propellant models (moisture content (H_2O), ignition temperature (T_i) and heat of explosion (Q)) determined after their production, are presented in Table 1.

Table 1 Chemical compositions, and physico-chemical and energetic properties of the propellant models

Models	NC	NG	NGV	DBP	CI	H_2O	ρ/ $g\ cm^{-3}$	T_i/ °C	Q/ $J\ g^{-1}$
	mass%								
B_{00}	57.04	37.53	–	2.97	2.26	0.20	1.592	168	4323
B_{50}	24.69	21.16	48.88	3.25	1.95	0.07	1.641	172	3456

The results of the classical chemical stability tests on the reference samples (B_{00}, B_{50}) and propellant samples 'aged' for 3 ($B_{00/3}$, $B_{50/3}$), 6 ($B_{00/6}$, $B_{50/6}$), 9 ($B_{00/9}$, $B_{50/9}$) or 12 months ($B_{00/12}$, $B_{50/12}$) at 65°C, after storage in a stroehouse for 36 months or 24 months, respectively, are given in Table 2.

Table 2 Results of chemical stability tests

	B_{00}	$B_{00/3}$	$B_{00/6}$	$B_{00/9}$	$B_{00/12}$	B_{50}	$B_{50/3}$	$B_{50/6}$	$B_{50/9}$	$B_{50/12}$
Heating at 100°C, day	6.5	4.5	3.5	1.17*	0.6*	>14	>14	>14	>14	>14
Bergmann-Junk at 120°C/cm^3	4.25	4.61	4.54	5.45	4.81	4.52	4.99	5.17	4.36	5.54
Hansen test at 110°C, pH	3.59	3.48	3.45	3.33	3.16**	3.72	3.74	3.67	3.58	3.65
Methylviolet test at 120°C/min	70	70	70	70	45	80	80	95	90	85

*unstable
**limit of stability

The results and the adopted criteria for propellant stability showed that only the method of heating at 100°C indicated that the propellant samples $B_{00/9}$ and $B_{00/12}$ were unstable. Otherwise, during the accelerated 'ageing' for propellant sample B_{00} at 65°C, nitrogen oxides were detected after 3 months of heating, while in the case of triple base propellants, they appeared after 9 months of heating. During ageing, the samples changed colour (B_{00} from yellow to dark-red, and B_{50} from light to dark-yellow), because of the interaction of the stabilizer with the products of primary thermal degradation of the propellants.

DSC curves of the reference samples B_{00} and B_{50} and of the same samples 'aged' for 3, 6 or 9 months, scanned at heating rates of 5, 10, 20 or 30°C min^{-1}, are shown in Figs 1 and 2 (a, b, c, d). The heating rates for sample $B_{50/12}$ (curves e) were 5 and 10°C min^{-1}.

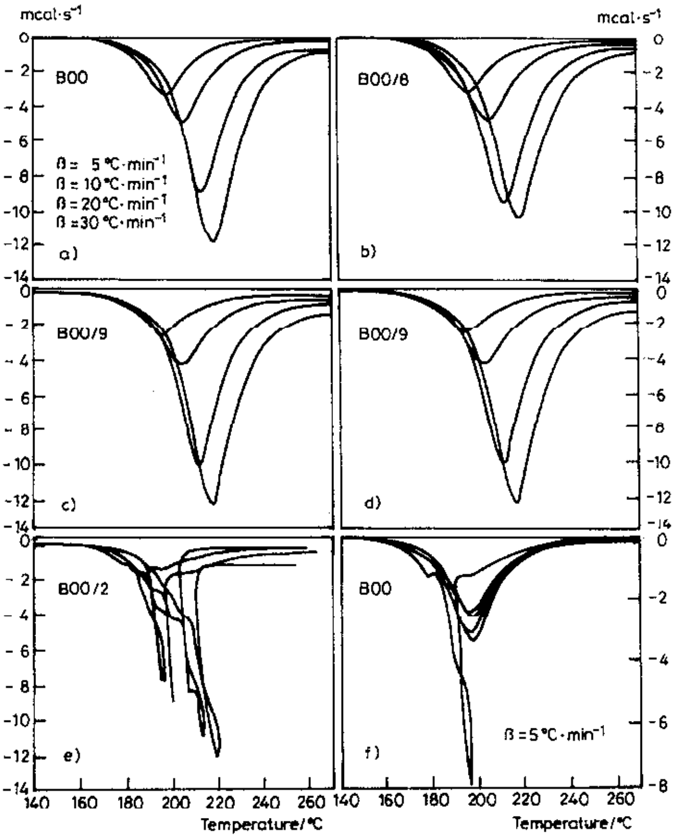

Fig. 1 DSC curves of propellant sample B_{00}

During the examination of sample $B_{50/12}$, the reactions were so exothermic that the sample pans were opened and displaced from their positions, and the system became dirty. The samples were not examined at higher heating rates. The DSC curves of the reference propellants and the same 'aged' propellants are given in Figs 1 and 2(f), with scanning at the lowest heating rate, 5°C min^{-1}.

The propellants B_{00} and B_{50} exhibit differences in thermal behaviour. In the case of samples B_{00}, 'aged' for 3, 6 or 9 months or 'unaged', one peak can be seen representing the decomposition of the double base propellant. In the case of samples B_{50} 'aged' for 3, 6 or 9 months, one peak is split into two, the secondary, smaller peak of which originates from NGV [9] present in the sample in roughly 50 mass%.

The values of the 'onset' and peak maximum temperatures and enthalpy changes are not as important for these investigations as are the shapes of the DSC curves.

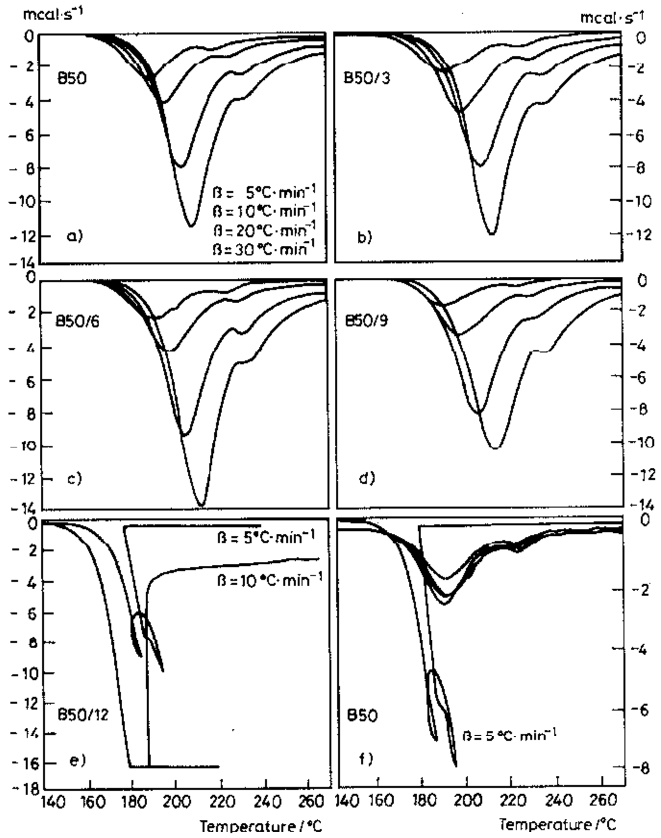

Fig. 2 DSC curves of propellant sample B_{50}

The shape of the DSC curves of samples B_{00} and B_{50} 'aged' for 12 months differs from the shapes of the other 'unaged' and 'aged' curves. In the case of $B_{00/12}$, one loop can be seen in the DSC curve, while the $B_{50/12}$ curve has two loops.

The loops are characteristic of unstable samples. The appearance of loops is probably a result of the thermal explosion of samples $B_{00/12}$ and $B_{50/12}$ during DSC measurements.

The phenomena which occur in the sample correspond to the mechanism of self-ignition of the unstable propellant: autocatalytic exothermic reactions which then act as a heat source. As the temperature increase in the sample, after a critical time it becomes the source of reaction propagation. The further thermal degradation of the propellants follows the mechanisms of autocatalytic reactions. When an outside heat source exists, as in DSC, the equilibrium between the generated heat and the heat which has been removed is disturbed. The heat accumulation inside the propellant is rapid, and thermal explosion of the propellant occurs.

It is questionable why thermal explosions occurred only in the case of samples $B_{00/12}$ and $B_{50/12}$.

To find an answer, it was necessary to analyze the content of stabilizer in the propellants. Using gas chromatography, it was found that all the stabilizer was consumed in samples $B_{50/12}$ and $B_{00/12}$, Fig. 3. Therefore, as long as there is any stabilizer in the propellant, no critical temperature or thermal explosion are evident.

The thermal decomposition of the propellant is directly controlled by the consumption of the nitro-ester stabilizer. In that case the rate of reaction is independent of the sample mass.

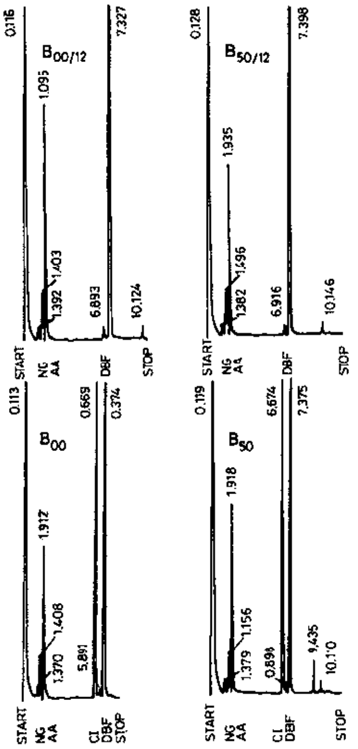

Fig. 3 Chromatograms of propellant samples

Conclusions

The thermal analysis of propellants permits conclusions on their stability. Of the classical methods of stability investigation, the heat test at 100°C gives the most reliable results.

DSC allows the examination of propellant sensitivity to thermal explosion, which occurs when all the stabilizer in the propellant is consumed. The thermal degradation of the propellant is controlled directly by the consumption of the nitro-ester stabilizer.

None of these methods give precise and certain results which can prove the stability of the propellant.

When one of these methods indicates propellant instability, it is necessary to continue the investigations to prove this.

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