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Thermal decomposition of cured GAP–AP propellants containing catocene

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Abstract

Differential thermal analysis (DTA), thermogravimetric analysis (TGA) and a modified manometric vacuum stability test (MVST) were employed to investigate the thermal characteristics of cured glycidyl azide polymer (GAP)–ammonium perchlorate (AP) propellants in the presence of catocene. Various particle sizes of AP in propellants were examined. The results revealed that catocene plays an important role in catalyzing the decomposition of both AP and GAP. The DTA curves of propellants with larger particles of AP showed two exothermic reactions. However, only one exothermic reaction was found for propellants containing smaller particles of AP. The peak temperature (T_m) of the DTA curves and the onset temperature of the TGA patterns obviously shifted to a lower temperature as the catocene content increased in the propellants. Similar thermal behavior was also observed in the MVST measurements. The activiation energy of decomposition of the propellants was determined, based on the MVST results.

INTRODUCTION

Increasing both the energy content and the safety of gun or rocket propellants has become one of the major interests of researchers today. Azide polymers are a particularly important class of energetic materials. Of the azide polymers, glycidyl azide polymer (GAP) has been widely studied in recent years as an energetic binder [1, 2]. Kubota et al. [1] studied GAP-based composite propellants and found the burning rate characteristics of GAP propellants appeared to be fundamentally different from those of conventional composite propellants. Kubota and Sonobe [3] observed the significantly higher burning rate of GAP propellants. Dickinson et al. [4] investigated the adhesiveness between propellant constituents of GAP

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binder and cyclotriethylenetrinitramine filler. Ho and Fong [5] reported that propellants containing GAP as binder were less sensitive to impact than comparable propellants with HTPB or poly(ethylene glycol) as binder. Beside composite propellants, GAP has been employed in a double-based propellant to increase the burning rate and temperature sensitivity [6]. Ammonium perchlorate (AP) is extensively used as an oxidizer for composite propellants. Catocene is a general burning rate modifier of AP composite propellants. Although there are many studies related to the performance of GAP propellants, there has been no report yet on the effect of catocene on GAP–AP propellants.

In this study, the decomposition of GAP–AP propellants containing catocene was determined experimentally by both isothermal and non-isothermal methods. Thermal analyses by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out at a constant heating rate. In addition, a modified manometric vacuum stability test (MVST) was performed isothermally at assigned temperatures. The objective of this paper is to provide better understanding of the catalytic effect of catocene on the decomposition of AP and GAP in cured propellants.

EXPERIMENTAL

Sample preparation

The GAP pre-polymer examined in this paper was laboratory synthesized. it was stored in a desiccator. The specimens were formulated by curing GAP with an isocyanate curative in a NCO:OH ratio of 1:1. All the propellants were prepared by a standard blending procedure. The composite slurries were then cured in an oven at 65°C for four days. Table 1 lists the compositions of the tested samples. Four particle sizes of AP (400, 225, 50, and 5 μm) were employed in the monomodal composite propellants. A mixture containing 30 parts of GAP and 70 parts of AP (400 μm) without catocene (A4 propellant shown in Table 1) was selected as the basic propellant. To the other propellants catocene was added (0.5, 1.3, and 3.0 parts relative to AP).

DTA, TGA and MVST measurements

Thermal analysis measurements were accomplished by using a DuPont Instruments 9900 thermal analyzer with 951 TGA and 1600 DTA modules. For these measurements, samples about 2–4 mg were heated from room

TABLE 1

Summary of compositions of tested samples

Sample	GAP (wt.%)	AP (wt.%)				Catocene (wt.% of AP)
		400 μm	225 μm	50 μm	5 μm	
A1	30	70				3.0
A2	30	70				1.3
A3	30	70				0.5
A4	30	70				0.0
B1	30		70			3.0
B2	30		70			1.3
B3	30		70			0.5
C1	30			70		3.0
C2	30			70		1.3
C3	30			70		0.5
D1	30				70	3.0
D2	30				70	1.3
D3	30				70	0.5

temperature to 450°C at a constant heating rate of $10°\mathrm{C\,min^{-1}}$. A flowing nitrogen atmosphere ($50\,\mathrm{ml\,min^{-1}}$) was used.

The MVST apparatus consists of a metal heating device (Julis Peter) with a temperature controller (West 3000), pressure transducers with a data acquisition system and a personal computer (Acer 915P). Samples of less than one gram were placed in tubes and evacuated before testing. The tubes were then put into the heating device for 40 h at the desired temperature. The tubes were then moved out of the heating device for cooling to room temperature. The pressure during the experiments was recorded by a personal computer. The readings of pressure were converted to corresponding gas volumes under standard conditions using the ideal gas law. For a detailed description of the MVST apparatus and experimental procedure, see Ger et al. [7].

RESULTS AND DISCUSSION

Typical DTA thermograms are shown in Figs. 1 and 2. Figures 1 and 2 describe the decomposition of GAP-based propellants containing larger (400 μm) and smaller (50 μm) particles of AP, respectively. In Fig. 1, a small endothermic peak is found around 246°C for all samples A1–A4. The heat absorbed is believed to provide a phase transition of AP from the orthorhombic to the cubic crystal [8]. It is noted that this endotherm is independent of the catocene content. A similar result has been reported by Saito et al. [9] with other additives or at different ambient pressures. Nevertheless, the endothermic peak is not found in Fig. 2 for GAP

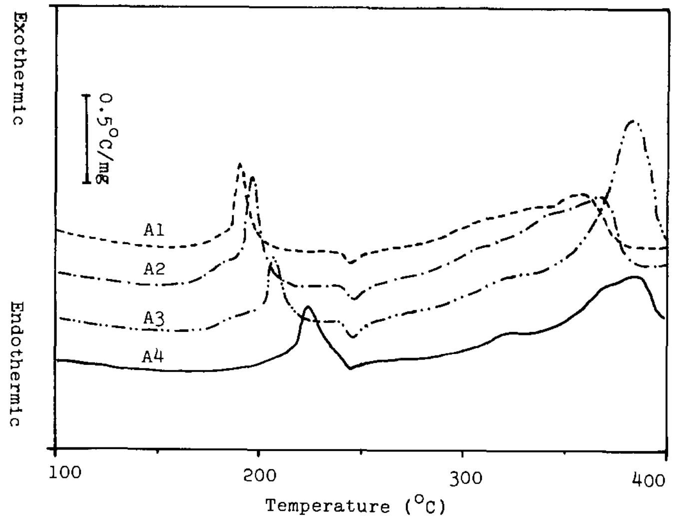

Fig. 1. DTA curves of GAP propellants containing 400 μm AP with various catocene contents.

propellants with smaller particles of AP. This might be due to the faster rate of heat transfer caused by the increase in surface area of the smaller particles of AP.

The thermal decomposition behavior of pure AP has been reported in the literature [10, 11]. Two distinct exothermic peaks have been observed in DTA scans of AP. It is also evident that the results obtained from thermal

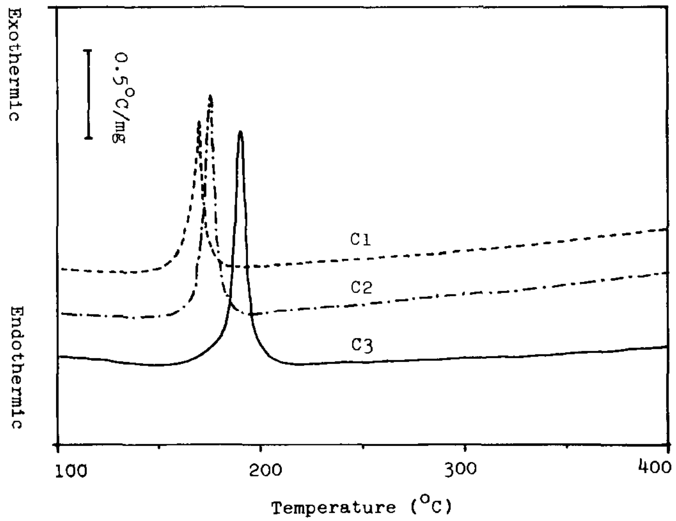

Fig. 2. DTA curves of GAP propellants containing 50 μm AP with various catocene contents.

analysis depend on the testing conditions, such as the weight of the sample, the heating rate, the testing pressure, etc. Accordingly, two maximum exothermic peak temperatures (T_m) in the DTA curve of pure AP have been reported in the ranges of 300–330 and 380–460°C, respectively. Most researchers believe that the second exothermic peak is predominantly due to the decomposition of AP. Chen and Brill [12] have reported a T_m at 221°C found on a thermogram of pure GAP from a differential scanning calorimetry (DSC) using a lower heating rate of 1°C min^{-1} under argon flow. Shen et al. [13] found T_m values of uncured and cured GAP near 251 and 240°C, respectively, by DSC with a higher heating rate of 10°C min^{-1}. In other words, if GAP is cured, the T_m value is slightly lower. The propellants examined in this article are cured composites of AP and GAP. From Fig. 1, there are two exotherms in DTA scans of the A-series propellants. The first T_m appears before 224°C. It is believed that this exotherm is due to decomposition of GAP. The second T_m is located between 359 and 386°C and should be due to the decomposition of AP. In other words, the low temperature decomposition of AP is diminished when it is blended with GAP. It is noted that the T_m values of GAP–AP propellants are apparently lower than those of either pure GAP or pure AP. In other words, the catalytic effect of catocene acts on the decompositions of both GAP and AP.

Figure 2 illustrates DTA curves of the C-series propellants containing 50 μm AP with various catocene contents. Only one exothermic peak on the DTA curves is found during the entire heating process. Those peaks of AP shown in Fig. 1, both endothermic and exothermic peaks, have all vanished. The T_m of GAP is dramatically lowered to between 170 and 191°C. Comparing Figs. 1 and 2, it is clear that the catalytic effect of catocene on the decomposition of GAP blended with smaller AP particles is much more significant than on that blended with larger AP particles.

Figure 3 illustrates a typical effect of catocene content on the exothermic peak temperature of DTA curves of GAP–AP composite propellants. As previously mentioned, the first exothermic peak on the DTA curve represents the decomposition of the GAP component and the second represents the decomposition of the AP particles. It is clear from Fig. 3 that the peak temperature of both exotherms decreases with catocene content in propellants. Nevertheless, the tendency to decrease is more apparent when the catocene content is less than 1.3 wt.% AP.

The corresponding TGA curves are shown in Figs. 4 and 5 for A- and C-series propellants, respectively. As can be seen in Fig. 4, two major stages of weight losses occur in the decomposition of A-series propellants. Less than 30% of the total weight lost occurs in the first stage of decomposition. Referring to Fig. 1 and to the compositions of the propellants, it is clear that the first stage of weight loss is caused by the decomposition of GAP. Decomposition of AP causes the second stage of weight loss.

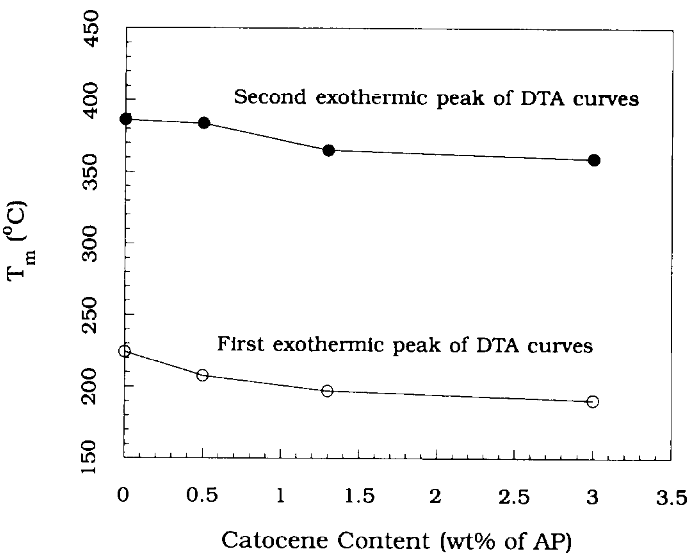

Fig. 3. Effect of catocene content on exothermic peak temperature of DTA curves of GAP propellants.

For C-series propellants, however, there is only one stage of weight loss (Fig. 5). The particle size of AP contained in these propellants was 50 μm. It is known that decreasing AP particle size increases the thermal sensitivity of the composites. Therefore, the difference between Figs. 4 and 5 could be explained as being due to reducing the particle size of AP. The AP particles are surrounded by GAP binder after complete blending. The heat liberated

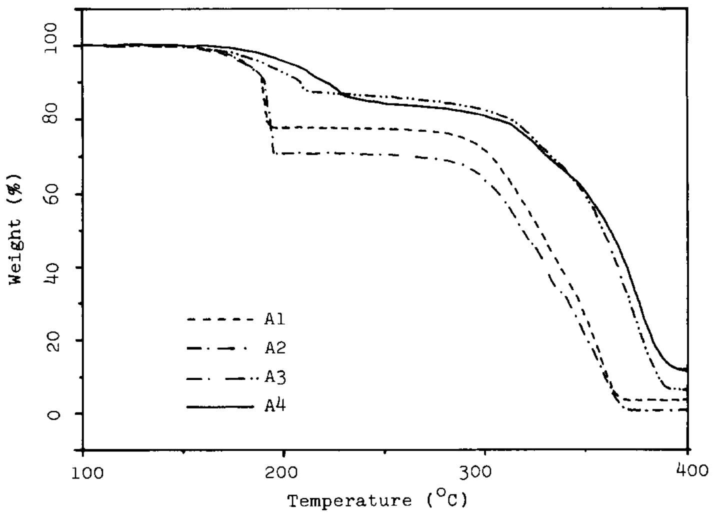

Fig. 4. Dependence of TGA curves on catocene content for GAP propellants containing 400 μm AP.

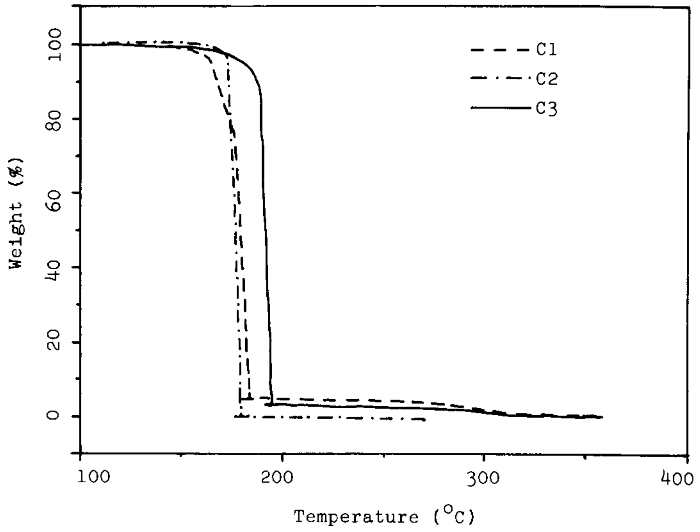

Fig. 5. Dependence of TGA curves on catocene content for GAP propellants containing 50 μm AP.

by GAP decomposition might supply enough energy to overcome the barrier of the decomposition reaction of AP. Accordingly, AP decomposes immediately after the GAP decomposition. The same results are found in the DTA measurements shown in Fig. 2.

The results of both DTA and TGA are tabulated in Table 2. From the TGA data listed in Table 2, it is found that the residue of A4 propellant (without catocene) is about 12 wt.% after two stages of decompositions, whereas that of the other propellants is less than 7 wt.%. Therefore, the decomposition behavior of GAP–AP propellants is clearly influenced by the addition of catocene. Comparing the DTA and TGA data, the results are consistent. Two exotherms are shown by DTA measurements and two stages of weight loss are shown by TGA determinations for A- and B-series propellants. For C- and D-series propellants, however, there is only one exotherm or one stage of weight loss. It is also found that the difference in the first T_m (GAP decomposition peak temperature) is small between the A- and B-series propellants containing the same amount of catocene. The same result is also observed on comparing the C- and D-series propellants. Nevertheless, the difference in the first T_m between the B- and C-series propellants is remarkable. As listed in Table 2, the first T_m values of B1 and C1 are 187 and 170°C, respectively. Accordingly, it can be concluded that the thermal decomposition of GAP–AP propellants containing catocene shows two different types of thermal characteristics. Those propellants containing larger particles (400 and 225 μm) of AP behave similarly. The other type of propellants contain smaller particle (50 or 5 μm) of AP.

Although there are several disadvantages in using a conventional

TABLE 2

Results of DTA and TGA measurements

Sample	DTA			TGA			
	1st Exothermic peak temp. (°C)	Endothermic peak temp. (°C)	2nd Exothermic peak temp. (°C)	1st stage		2nd stage	
				Onset temp. (°C)	Wt. loss (%)	Onset temp. (°C)	Wt. loss (%)
A1	190.60	245.21	359.44	174	22.4	298	74.3
A2	196.93	246.26	365.04	184	29.3	297	70.3
A3	207.48	246.10	383.67	185	12.7	303	81.5
A4	224.35	245.40	386.24	194	15.1	341	72.7
B1	187.07	246.21	355.83	170	13.9	316	79.1
B2	194.55	246.78	359.36	172	12.2	336	81.5
B3	207.42	246.01	369.12	177	14.4	340	78.7
C1	170.08	–	–	163	97.4	–	–
C2	175.64	–	–	172	100.0	–	–
C3	191.13	–	–	183	97.4	–	–
D1	168.82	–	–	162	96.4	–	–
D2	173.85	–	–	166	96.2	–	–
D3	191.18	–	–	181	98.9	–	–

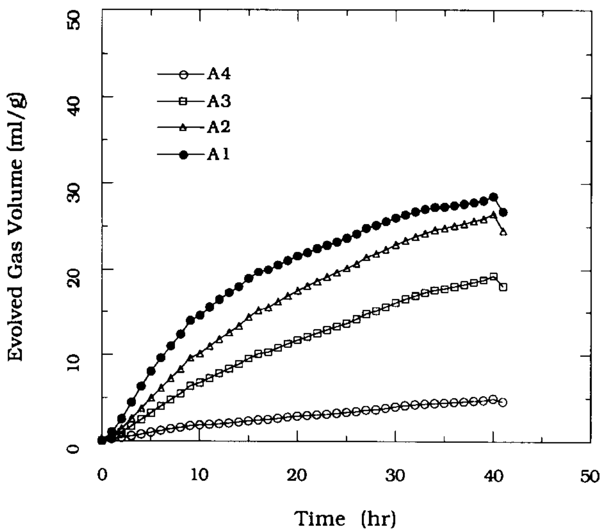

Fig. 6. The MVST results for propellants A1–A4 at 100°C.

vacuum stability test apparatus for examining the stability of energetic materials, the vacuum stability test is still used as a standard criterion for determining compatibilities between energetic compounds and contact materials [14]. Some of its limitations have been successfully improved in the MVST developed by Huang and co-workers [7, 15, 16]. The advantages of their MVST compared to conventional vacuum stability test apparatus have already been confirmed.

Typical results of the MVST are shown in Fig. 6. Figure 6 shows the evolved gas volumes from partial decomposition of propellants vs. experimental time. All gas volumes observed have been converted to values under standard conditions (0°C and 1 atm). The data at 41 h are the volumes of evolved gas after cooling to room temperature. Because of partial condensation and the temperature decrease, the evolved gas volume dropped slightly. A pseudo-zeroth-order reaction could reasonably be assumed for the linear region of each curve. The reaction rate can then be calculated as the first derivative of volume with respect to time. Furthermore, the activation energy of decomposition reaction can be obtained according to the Arrhenius law at various temperatures. The MVST measurements and the calculated activation energies are listed in Table 3.

Figure 6 shows the MVST measurements on samples A1–A4 at 100°C. The final evolved gas volumes of samples A1–A4 are 26.74, 24.53, 17.99 and 4.57 ml g^{-1}, respectively. It should be noted that the evolved gas volume of A4 is the smallest of the A-series propellants. The liberated gas volume obviously increases with increasing catocene content. Even though only 0.3 wt.% of catocene in present in A3, the gas volume generated by A3 was

TABLE 3

Final results of modified vacuum stability tests

Sample	Evolved gas volume after cooling (ml g^{-1})				E_a (kcal mol^{-1})
	80°C	90°C	100°C	120°C	
A1	7.76	16.95	26.74	44.61	23.95
A2	3.80	12.07	24.53	39.66	25.97
A3	2.36	6.85	17.99	38.25	26.14
A4	0.21	1.97	4.57	17.11	29.23
B1	7.97	18.43	30.70	40.20	24.45
B2	4.86	15.12	30.27	44.34	26.92
B3	2.19	8.78	19.23	37.66	26.46
C1	6.40	19.00	34.69	47.36	28.49
C2	4.06	14.49	29.84	45.20	29.56
C3	1.47	8.52	18.34	43.61	30.94
D1	–	23.20	34.98	52.61	25.22
D2	1.83	15.44	25.79	44.98	26.06
D3	–	6.02	15.12	42.14	28.90

about four times that of A4. In Table 3, the same results are found for the other series propellants. This illustrates that the decomposition of GAP–AP propellants is significantly accelerated by catocene. For A4 in Fig. 6 the liberated gas volume seems proportional to heating time; however, the decomposition curve of A1 is a little concave.

It is recognized that the heating temperature is an important factor in a thermal decomposition reaction. Figure 7 shows the decomposition pattern

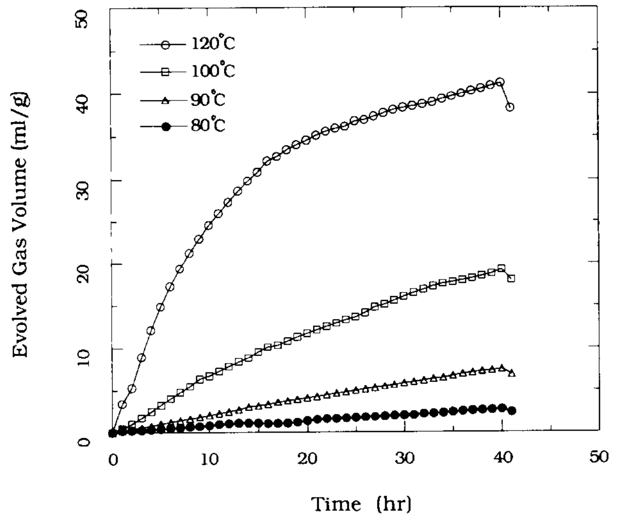

Fig. 7. Comparison of decomposition curves of B3 at various heating temperatures.

of B3 at various temperatures. It is seen that the generated gas volume increases sharply as the cooking temperature increases. At 80 and 90°C, the propellant decomposes at approximately constant rates. As the temperature increases to 120°C, the decomposition pattern obviously becomes concave. A rapid liberation of gas during the earlier part of the heating is observed. Subsequently, the decomposition reaction slows down. This implies that the activation energy of the propellant decomposition reaction is not too high and that the gas products do not promote further decomposition.

From the MVST results listed in Table 3, it is found that the evolved gas volumes of most of the C- and D-series propellants are larger than those of the A- and B-series propellants containing the same amount of catocene. Although the tendency is not absolutely clear for all cases, it seems that the catalytic effect of catocene is stronger on those propellants containing smaller particles of AP. The activation energies of thermal decomposition calculated from the MVST data are also tabulated in Table 3. Those data range from 23.95 to 30.94 kcal mol^{-1}. Chen and Brill [12] have reported that the activation energy of pure GAP decomposition is 39.4 kcal mol^{-1}. Kubota and Sonobe [3] have determined the activation energy of decomposition of GAP propellant consisting of 84.8 wt.% GAP, 12 wt.% HMDI (hexamethylene diisocyanate), and 3.2 wt.% TMP (trimethylolpropane) to be 20.8 kcal mol^{-1}. Therefore, the activation energy calculated by the MVST method is quite reasonable. From Table 3, the activation energy of GAP–AP propellants (as expected) decreases with increasing catocene content.

CONCLUSION

The thermal decomposition of cured GAP–AP propellants containing catocene has been studied by differential thermal analysis (DTA), thermogravimetric analysis (TGA) and a modifier manometric vacuum stability test (MVST). From the DTA results, the maximum peak exothermic temperatures of both GAP and AP are decreased by the addition of catocene. However, the endothermic temperature of AP is independent of catocene content for propellants containing larger particles of AP. For those propellants with 400 and 225 μm AP, two stages of decomposition are found. For those propellants with 50 and 5 μm AP, however, only one stage of decomposition is observed in DTA and TGA measurements. MVST results indicate that the evolved gas volume increases as the catocene content increases. The particle size effect of AP on isothermal decomposition (by MVST tests) shows scattered results. Nevertheless, the dependence of the decomposition of propellants on temperature was as expected. Based upon MVST data, activation energies of decomposition of propellants decrease with increasing catocene content.

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