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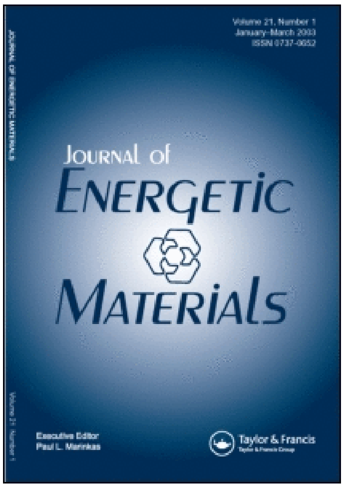

Journal of Energetic Materials

Publication details, including instructions for authors and subscription information:
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Catalytic effects of lead citrate on the HMX azide polymer propellants

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To cite this Article Kimura, Eishu , Oyumi, Yoshio and Yoshida, Tadao(1995) 'Catalytic effects of lead citrate on the HMX azide polymer propellants', Journal of Energetic Materials, 13: 1, 1 — 14

To link to this Article: DOI: 10.1080/07370659508019341

URL: http://dx.doi.org/10.1080/07370659508019341

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CATALYTIC EFFECTS OF LEAD CITRATE ON THE HMX AZIDE POLYMER PROPELLANTS

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ABSTRACT

Thermal decomposition and the burning properties of BAMO and HMX based propellants have been investigated. Lead citrate with carbon black significantly altered the burning properties of the based propellants. Especially the content of 2.9% yielded high value of the burning rate with the low pressure exponent. Although the lead citrate played an important role in the increase of the temperature gradients in the gas phase close to the burning surface of the propellant, the content of 2.9% affected both

Journal of Energetic Materials Vol. 13, 1-14 (1995)
Published in 1995 by Dowden, Brodman & Devine, Inc.

the temperature gradient and the burning surface temperature. The gas composition at the burning surface was also altered by the lead catalyst. The burning rate of the propellant increased with NO_2, HONO, HCN and NO increase and also with N_2O, CO and CH_2O decrease in the thermolysis gas composition. Since the lowest CH_2O content showed highest burning rate, CH_2O might be one of the key reactant in the rate controlling steps of the burning rate.

INTRODUCTION

In the solid rocket propellant arena, the desire for the minimum signature (smoke and flame) has eliminated ammonium perchlorate (AP) from consideration in a wide variety of modern applications. For the increased specific impulse at reduced flame temperatures, a cyclic nitramine (HMX) has been selected as an energetic material in the propellant ingredients[1)]. However, HMX has low burning rate coupled with a relatively high pressure exponent problem[1-4)]. The object of this research was to increase the burning rate of HMX via energetic material containing azide side chains[5-7)] and to characterize the catalytic site of the lead citrate during the combustion. The azide copolymer of BAMO (3,3–bis(azidomethyl)oxetane) (0.7 mole%) with NMMO (3–nitratomethyl–3–methyloxetane) (0.3 mole%) was chosen as an energetic binder material.

EXPERIMENTAL

The propellant compositions tested here were listed in Table 1. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were conducted by using a Seiko SSC5200 TG/DTA220 with a helium flow rate of 150 ml/min. The cubic

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Table 1. Propellant Compositions

Sample	BDR	HMX	LC	CB
1	25.0	75.0	–	–
2	24.6	73.9	1.0	0.5
3	24.2	72.5	2.9	0.5
4	23.5	70.4	5.6	0.5

BDR: BAMO/NMMO(7/3) binder
HMX: cyclotetramethylene tetranitramine
LC: lead citrate CB: carbon black
Ratios of BDR/HMX are 25/75 in all the samples.

samples, weighing approximately 0.2–0.3 mg, were placed in a small unconfined aluminum cell 3 mm high with an inside diameter of 5 mm. Since these cells were not hermetically sealed, gaseous products could escape. Differencial scanning calorimetry (DSC) was carried out by using a Seiko SSC5200 DSC120 with a helium flow rate of 150ml/min and a heating rate of 0.17 K/s in order to observe the heat release during the reation. 0.3–0.5 mg of the cubic samples were placed in a small confined aluminum cell, whose inside depth was 2 mm with an inside diameter of 4 mm.

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All burning rates and temperature profile measurements were performed with a chimney type strand burner which was pressurized with nitrogen. The size of the propellant samples was 7 x 7 mm in cross–section and 70 mm in length. Three fuse wires were passed through the strand sample in 20 mm intervals. The ignition of the samples was conducted by an electrically heated nichrome wire attached on the top of the strand sample. The burning rates were measured at 4–10 MPa with the help of the fusing wires. In order to determine the heat feedback process from the gas phase to the burning surface of the propellants, the temperature profile in a combustion wave was measured at 1.5 MPa with microthermocouples made of Pt–Pt10%Rh wires 5 μm in diameter.

Gases products were measured by a rapid scan Foulier transform infrared spectroscopy and the thermolysis cell was given elsewhere[8]. The relative percent concentrations of the gas products were obtained by a procedure employing the effective width factors and absolute intensities of non-interfering absorbances for each product[8]. H_2O and HNCO were omitted in the calculation because H_2O has complicated band and absolute intensity of HNCO is unknown. The propellant samples were heated to 773K with a heating rate of 6,300K/s, which simulated the combustion surface.

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Ignition energy measurements were made with an electric spark generating device, which was developed by Y. Mizushima and described in elsewhere[9]. 20 mg of powdered propellant sample was packed to an average density of 0.47 g/cm^3 in a Teflon tube 8 mm high with an inside diameter of 4 mm. It was judged to be "ignited" when the sample holder burst or shrunk. Otherwise, it was "unignited". Twenty trials were conducted for each samples to obtain the ignition energy with 50% probability. The ignition energy E in joule was obtained by the following equation:

$$E = \eta (1/2)CV^2$$

where C is the capacity (0.1795 and 0.5044 μF) of the condenser, and V is the electric voltage (kV). Though the efficiency η was important to determine the real ignition energy of each propellant[10], η was assumed to be 1.0 in here. Since the gap length between the two steel electrodes and the packing density of the sample were almost exactly the same in all the measurements, η should be equal in all the experiments. The catalytic effects on the ignitability were focused in this study.

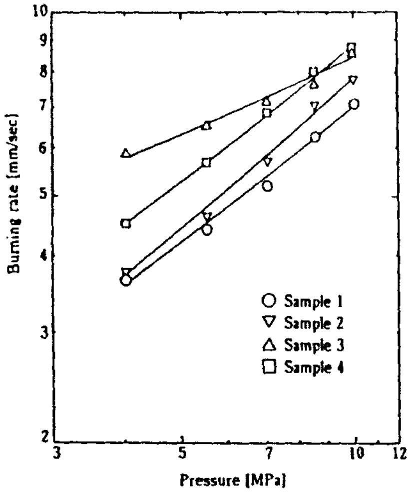

FIGURE 1

Burning rate behavior of HMX based propellants with and without additives at 293K.

RESULTS AND DISCUSSION

Burning rates

The relationships between the propellant burning rate and pressure at 293K were shown in Fig. 1 and they showed good linearity in log scale. It was evident that the catalyst used here affected not only the burning rate but also the burning rate pressure exponent. The addition of 2.9% lead citrate with carbon black showed a significant increase in burning rate with a favorable decrease in the pressure exponent. The burning rate equations for HMX based propellants shown in Fig. 1 were as follows,

Sample 1 : $r = 1.269\ P^{0.734}$

Sample 2 : $r = 1.164\ P^{0.821}$

Sample 3 : $r = 3.339\ P^{0.394}$

Sample 4 : $r = 1.598\ P^{0.739}$.

These results indicate that the lead citrate plays an important role in the burning process. The burning rate became larger with the catalyst content increase. The pressure exponents of all the propellant samples except Sample 3 were almost the same. It indicates that the rate of combustion reactions was accelerated by the catalytic effects but the combustion mechanisms was not altered in the content of 1.0% and 5.6%. The content of 2.9% lead citrate, however, showed an unexpected effect on

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the combustion process. The 2.9% lead citrate was more effective than 5.6% at a pressure range below 8MPa. This caused the relatively lower pressure exponent in Sample 3. The reastion sites in Sample 3 were very active at lower pressure region and become less active with the pressure increase. This unexpected catalytic effect of 2.9% content on the combustion mechanism was focused on this study.

HMX is an energetic material but does not act as an oxidizer because of its negative oxygen balance. HMX generates N_2O, CH_2O, NO_2, HONO, NO, and HCN as the main decomposition products[8, 11, 12]. The small molecule products from azide binder are N_2, HCN from BAMO unit and NO_2, CH_2O from NMMO unit[13]. The mixture of these highly reactive species might be produced near the burning surface of the propellants and the reactions among them might play an important role in the combustion mechanism. The chemistry occurred in the condensed phase and the gas phase near the burning surface was investigated at the following sections.

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Condensed phase reaction

The thermal analyses and temperature profile measurements were conducted to investigate the reaction mechanism near the burning surface. The TGA results of HMX based propellant samples with a heating rate of 0.17 K/s in helium were shown in Fig. 2. The onset temperatures of the propellant decomposition indicated that the decomposition of HMX was initiated and accelerated by the heat generated by the azide polymer binder decomposition. The rapid weight loss occurred at a temperature between 490K and 550K. During this region, the weight losses for all the propellant samples were approximately 90%. Although the slope of the weight loss curve at around 500K was relatively steeper in Sample 1 than in other lead salt containing

Table 2. Thermal Analyses Data

Sample	DSC exotherm [K]		Q_{DSC} [kJ/mol]	Ea [kJ/mol]
1	516	525	2.49	143
2	518	524	2.49	147
3	516	521	2.45	147
4	519	523	2.41	147

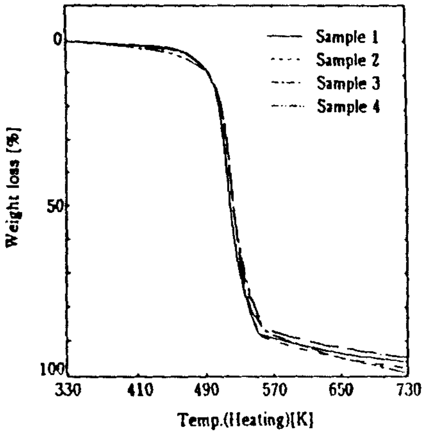

FIGURE 2

TGA thermograms of HMX based propellants with and without additives.

samples, there was less difference in the activation energies of thermal decomposition (Ea) obtained by Kissinger's method(4) as shown in Table 2. Especially, no difference existed in the catalyzed samples.

The DSC thermograms for HMX based propellant samples were shown in Fig. 3. Sample 1 showed an endotherm of phase transition of HMX at 470K(5) and an exotherm between 500K and 540K with peak temperatures of 516K and 525K. The temperature range of this exothermic reaction was exactly the same as that of rapid weight loss reaction shown in Fig. 2. It was found that Sample 1 decomposed exothermically in this temperature range. The lead citrate with carbon black less altered the decomposition reaction of Sample 1. This was completely different from the result obtained with the lead stearate(8). The reaction site of the

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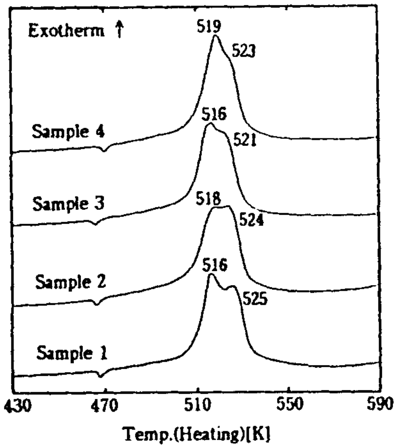

FIGURE 3
DSC thermograms of HMX based propellants with and without additives.

lead stearate was observed in the condensed phase chemistry. However, the lead citrate was less effective on the both DSC exotherm temperatures and the heat of decomposition measured by DSC (Q_{DSC}), as shown in Table 2. Q_{DSC} became smaller with the catalyst content increase because of the energy level of the propellant decrease. The condensed phase chemistry of the HMX azide propellant used in this study was less altered by the lead citrate in the thermal analysis conditions.

Temperature profiles

Temperature profiles in a combustion wave were measured with the 5 μm microthermocouple at 1.5 MPa. The average burning surface temperatures and the temperature gradients in the gas phase close to the burning surface of propellant $(dT/dx)_s$ were listed in Table 3. The temperature profiles were shown in Fig. 4. The propellant below the burning surface in Sample 1 was gradually heated compared to the catalyzed propellants. Then the temperature near the burning surface rapidly increased with an average heating rate of 6,300 K/s to the flame temperature. The microthermocouple, however, was too fragile to survive at above the burning surface and become unstable at the terminal stage as shown in Fig. 4.

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Table 3. Average Burning Surface Temperatures, Temperature Gradients at 1.5 MPa, and Ignition Energies.

Sample	Ts [K]	$(dT/dx)_s$ [K/m]	E_{50} [J]
1	700	3.43×10^8	13.0 ± 0
2	750	7.35×10^8	11.3 ± 0
3	670	3.97×10^8	15.2 ± 0.1
4	830	5.21×10^8	15.9 ± 0.1

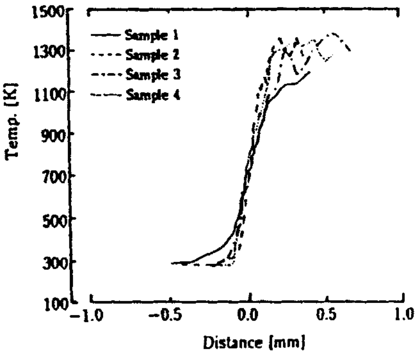

FIGURE 4
Temperature profiles in HMX based propellant combustion wave at 1.5 MPa.

The heat flux into the condensed phase will occur in two ways : by conductivity and by radiation. The contribution from the former was determined by the temperature gradient just above the burning surface in the gas phase. If the heat conductivity in the gas phase of catalyzed propellant was same as that of uncatalyzed one, the burning rate augmentation was caused by the increase of the heat input from gas phase to condensed phase. The burning rate was indicated by the following equation with considering the heat balance near the burning surface(17).

$$r = \lambda g(dT/dx)_s / Cp \rho_p (Ts - T_0 - Qs/Cp)$$

where, λg: heat conductivity in the gas phase, Cp: specific heat of the propellant, ρ_p: propellant density, Ts: burning surface temperature, T_0: initial temperature of the propellant, and Qs: exotherm at the burning surface. The burning rate depends on the

Table 4. Gas Compositions obtained by the Rapid Scan FTIR

	CH_4	CO_2	N_2O	CO	NO	CH_2O	NO_2	HONO	HCN
Binder	11	1	3	16	–	17	–	–	51
HMX	–	2	12	–	8	16	22	8	22
Theo	3	2	10	4	6	16	17	6	29
Sample 1	–	2	19	10	7	25	8	10	20
Sample 2	–	2	14	7	9	22	10	12	25
Sample 3	–	2	14	6	11	20	7	10	30
Sample 4	–	2	13	6	13	27	5	5	30

Theo; 0.25 Binder + 0.75 HMX

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magnitude of $(dT/dx)_s$, Ts, and Qs in the similar propellant composition samples in which λ_g, Cp, and ρ_p should be very close. If the Qs of the catalyzed samples show the same tendency with that of the Q_{DSC} obtained at condensed phase reaction, Qs has less influenced by the lead content. Therefore, the $(dT/dx)_s$ and Ts play important role in the rate determination steps of the burning rate.

Ts of the catalyzed propellants became higher except Sample 3 and $(dT/dx)_s$ was much larger in Sample 2 and Sample 4 as shown in Table 3. These results indicated that the reduction in Ts of Sample 3 caused an augmentation of burning rate. In other catalyzed propellants $(dT/dx)_s$ acted as a dominant role in the burning rate control mechanism.

Gas composition

The initial gas compositions obtained at the simulated burning surface condition were shown in Table 4. In these initial gases compositions highly reactive gases, such as CH_2O, NO_2, and HONO, were rapidly diminished during the experiments. According to the comparison between the gas compositions of the theoretical and the

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Sample 1, the chemical interaction between the binder and the decomposition products of HMX was so strong that CH_4 disappeared and NO_2 diminished with increasing N_2O, CO and CH_2O. The increase of HONO showed the proton transfer of NO_2 accelerated by the presence of neighbored hydrocarbon. Therfore, much CH_2O survived in Sample 1.

The lead citrate altered the gas compositions of the propellant thermolysis reaction. In Sample 1 and Sample 2, NO_2, HONO, HCN and NO were increasing with decreasing N_2O, CO and CH_2O. In catalyzed propellant NO_2 and HONO were decreasing with increasing the lead citrate concentration. CO_2, N_2O and CO were relatively independent of the catalyst. CH_2O was found to be minimum at 2.9% lead citrate. Since the smallest CH_2O showed the highest burning rate of the propellant sample, CH_2O might be one of the key reactant in the rate controlling step. The higher concentration of CH_2O in Sample 4 might be the reason for the smaller in burning rate than Sample 3.

Burning rate is determined by the heat feed-back from the gas phase where these gaseous products played an important role in the secondary reactions. The catalytic effect of 2.9% content on the burning rate was diminished at a higher pressure region as shown in Fig. 1. The gas phase reactions depend upon the pressure and the reaction rate should be faster at a higher pressure. It is possible that the 2.9% content of lead citrate may produce a special condition near the burning surface to accelerate the propellant burning rate and relatively slower reactions at lower pressure may strongly be activated in the condition. The role of the reaction diminished with the pressure increase and 5.6% content sample showed highest burning rate at above 9MPa.

Ignition characteristics

Ignition energies measured with an electric spark generating device were listed in Table 3. The reaction of the combustible gases in the gas phase played an important role in the ignition processes. Especially, the ignition process depended upon the reactivity of the combustible gases produced by the decomposition by the electric spark. The values of E_{50} were depend on the concentration of highly reactive species, such as CH_2O, NO_2 and HONO. These concentrations for each propellants were Sample 1 : 43%, Sample 2 : 44%, Sample 3 : 37% and Sample 4 : 37%, as shown in Table 4. These gases might act as a key in the combustion process and lower content needed higher ignition energy.

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CONCLUSIONS

The specific additive caused drastic changes in the combustion wave structure of HMX based propellants. The lead citrate played an important role in the increase of the temperature gradients in the gas phase close to the burning surface of the propellant and the 2.9% content of the catalyst also affected the burning surface temperature. Since the lowest CH_2O content in the thermolysis gas composition of the propellant showed highest burning rate, CH_2O might be one of the key reactant in the rate determination steps of the burning rate. The role of the reaction, however, became smaller with the pressure increase. The highly reactive gas products, such as CH_2O, NO_2 and HONO, depended on the catalyst content and they were related to the ignitability.

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ACKNOWLEDGEMENT

We are grateful to Dr. F. Hosoya, Dr. Y. Mizushima and Mr. S. Kiname of Hosoya Kako Co., Ltd. for usage of an electric spark generating device.

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