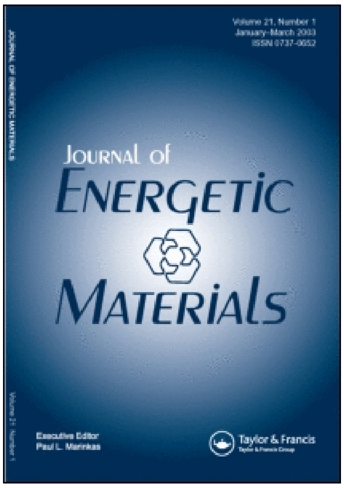


Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Insensitive munitions and combustion characteristics of BAMO/NMMO propellants

Eishu Kimura[a]; Yoshio Oyumi[a]
[a] Third Research Center, Technical Research and Development Institute, Japan Defense Agency
1—2—10 Sakae, Tokyo, Japan

To cite this Article Kimura, Eishu and Oyumi, Yoshio(1996) 'Insensitive munitions and combustion characteristics of BAMO/NMMO propellants', Journal of Energetic Materials, 14: 3, 201 — 215

To link to this Article: DOI: 10.1080/07370659608216065

URL: http://dx.doi.org/10.1080/07370659608216065

INSENSITIVE MUNITIONS AND COMBUSTION CHARACTERISTICS OF BAMO/NMMO PROPELLANTS

Eishu Kimura, Yoshio Oyumi
Third Research Center, Technical Research and Development Institute,
Japan Defense Agency
1–2–10 Sakae, Tachikawa, Tokyo 190, Japan

ABSTRACT

Burning characteristics and sensitivities to the ballistic shock were investigated for BAMO/NMMO composite propellants oxidized with HMX, AP, and AN. Tests of card gap, fragment impact (FI), electrostatic discharge (ESD), and bullet impact were conducted to evaluate their sensitivities. AP-based propellants showed plateau burning characteristics. Combined catalysts, such as lead compounds with carbon black, and copper chromite with an organic iron compound, were effective in burn rate augmentation. The use of additives and the replacement of oxidizer had little effect on the sensitivity to the shock wave. The highest sensitivity was observed for HMX-based propellants. An organic iron compound increased

Journal of Energetic Materials Vol 14, 201-215 (1996)
Published in 1996 by Dowden, Brodman & Devine, Inc.

the sensitivities to FI and ESD. It is suspected that thermal decomposition reactions played an important role in the reaction mechanisms in FI and ESD tests.

INTRODUCTION

High energy azide polymer binders have recently been investigated to improve performance of solid rocket propellants[1-6]. Azide polymers decompose exothermically with a first-order kinetics[7,8]. Their thermal decomposition characteristics are completely different from other inert binders, such as hydroxyl-terminated polybutadiene, which is the most commonly used composite propellant binder. In this study, a 3,3-bis(azido methyl)oxetane (BAMO) /3-nitratomethyl-3-methyloxetane (NMMO) copolymer[6], with a molar ratio of 7 to 3, was chosen as an energetic binder (BDR). Three kinds of composite propellants, which were oxidized with hexogen (HMX), ammonium perchlorate (AP), and ammonium nitrate (AN), were evaluated for their burning characteristics and sensitivities to ballistic shock. The combination of additives and composition of oxidizers were changed parametrically .

The purpose of this study was to improve combustion characteristics of solid propellants without sacrifice of insensitive munitions (IM) characteristics[9]. From the view point of IM, AN has been known to be an important candidate for the oxidizer of composite propellants. AN, however, has a relatively high pressure exponent and a low burn rate as a propellant. Therefore, BAMO/NMMO binders and some ballistic modifiers were evaluated to improve the propellant properties.

EXPERIMENTAL

Samples

HMX-, AP-, and AN-based propellant compositions tested here are listed in Table 1, Table 2, and Table 3, respectively. The ratios of BDR/HMX and BDR/AP in all the samples are 25/75 and 23/77, respectively. In AP propellants, ZrC acted as a suppressant for oscillatory combustion.

Table 1 HMX propellant compositions

	BDR	HMX	CuCr	PbCi	PbSt	PbHx	FeC	CB
1	25.0	75.0	–	–	–	–	–	–
2	24.0	72.2	1.9	–	–	–	1.9	–
3	23.6	70.8	2.8	–	–	–	2.8	–
4	24.2	72.5	–	2.9	–	–	–	0.5
5	24.1	72.5	–	–	2.9	–	–	0.5
6	23.7	71.2	–	–	4.6	–	–	0.5
7	23.7	71.0	–	–	2.4	2.4	–	0.5

BDR: BAMO/NMMO(7/3) binder, HMX: cyclotetramethylene tetranitramine, CuCr: copper chromite, PbCi: lead citrate, PbSt: lead stearate, PbHx: lead 2-ethylhexanate, FeC: 2,2-bis(ethylferrocenyl)propane, CB: carbon black.

TABLE 2 AP propellant compositions

	BDR	AP	Fe2O	Fe3O	FeC	ZrC
8	21.9	73.3	2.9	–	–	1.9
9	21.9	73.3	1.9	1.0	–	1.9
10	21.9	73.3	1.0	1.9	–	1.9
11	21.9	73.3	–	2.9	–	1.9
12	22.1	74.1	–	–	1.9	1.9

AP: ammonium perchlorate, Fe2O: iron(III) oxide, Fe3O: triiron tetraoxide, ZrC: zirconium carbide.

Table 3 AN propellant compositions

	BDR	AN	HMX	AP	Fe3O	CuCr	Cr2O	FeB
13	24.5	58.8	14.7	–	–	–	2.0	–
14	23.8	57.1	14.3	–	–	2.9	–	1.9
15	23.8	57.1	9.5	4.8	–	2.9	–	1.9
16	26.7	52.5	14.9	5.0	1.0	–	–	–

AN: ammonium nitrate, Cr2O: chromium oxide,
FeB: ferrocenyl grafted hydroxyl-terminated polybutadiene.

In the case of AN propellants, HMX with or without AP were added in order to alter the burn rate characteristics. The FeC and FeB are liquid organic iron compounds.

Burn rate measurement

All burn rate measurements were conducted with a chimney type strand burner which was pressurized from 4 to 13MPa with nitrogen. The size of the sample was 7×7mm in cross-section and 70mm in length. Three fuse wires were passed through the strand sample in 20mm intervals to measure burn rates. The ignition of the samples was performed by an electrically heated nichrome wire attached to the top of the strand sample.

Card gap test

This test was conducted by using a standard set forth by the Japan Explosives Society[10]. The gap material used here was a ϕ60mm aluminum plate (type 6061: density is 2.703g/cm^3, JIS H 4000). The donor explosive was pentolite, which was cast in a vinyl chloride tube (VP30), ϕ30×30mm, and was initiated by a No.6 electric cap. The acceptor propellants were cast into a steel tube that had a thickness of 2mm, an inner diameter of 37 mm and a length of 50mm. The detonation pressure generated by the donor explosive was transmitted into the propellant sample through an Al plate. The witness plate, whose size was 100×100mm in cross-section and 2mm in thickness, was placed under the acceptor propellant to determine if detonation occurs. When a propellant detonates, the witness plate shows a hole or tear. The correlation between a shock pressure and a gap thickness was determined with the ion-gap method. The minimum gap length, when no detonation was observed in all the three trials, was termed the critical gap length. The pressure at the critical gap length was defined as the critical shock pressure.

Fragment impact test

This test was performed with a method depicted in reference[10]. The impact fragment was a brass cylindrical fragment, ϕ15×15mm, 21g. The propellant sample was cast into a hard paper tube, whose size was ϕ40×50mm. The tests were conducted three times for each of five different velocities, 110, 121, 146, 214, and 400m/s.

Electrostatic discharge test

This test was conducted with an electric spark generating device, which was developed by Y. Mizushima and described elsewhere[11]. The gap length between the two steel electrodes was 1mm in all the measurements. 20mg of powdered propellant sample was packed in a Teflon tube, which was 8mm high, had an inside diameter of 4mm and an average density of 0.47g/cm^3. It was judged to be "ignited" when the sample holder burst or shrunk. Otherwise, it was "unignited". Twenty trials were conducted for each sample to obtain an ignition energy with 50% probability, which was termed E50.

5.56mm bullet impact test

This test was conducted with a bullet of 5.56mm in order to evaluate the motor case materials or the grain shapes. Although a 12.7mm projectile has been specified by the IM standard[9], a smaller, slightly faster military round, a 5.56mm bullet, was reported to be more lethal to a smaller rocket motor[12]. Therefore, a 5.56mm bullet was chosen in this screening test. The cylinder case was made of either steel or a carbon/epoxy composite material (CFRP). The cylinders were 2.2mm in thickness and ϕ99×200mm. Two types propellant grain were studied : a center-perforated grain having a 37mm inner diameter, and a three-slot grain as shown in Fig. 1.

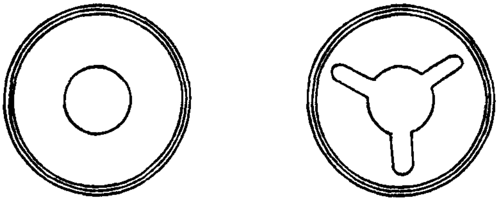


Figure 1 Cross-sections of a center-perforated grain (lelft) and a three-slot grain (right)

Thermal analyses

Differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetry (TG) were conducted using a Seiko SSC5200 DSC120 and TG/DTA220. These tests were conducted with a helium flow rate of 150ml/min and a heating rate of 0.17K/s. For DSC, cubic samples, weighing approximately 0.3mg, were placed in a confined aluminum cell, which had an inside depth of 2mm and an inside diameter of 4mm, while an unconfined aluminum cell was used for TG/DTA, whose size was 3mm height and an inside diameter of 5mm.

RESULTS AND DISCUSSION

Burning characteristics

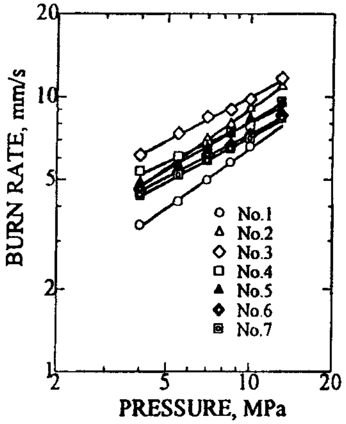
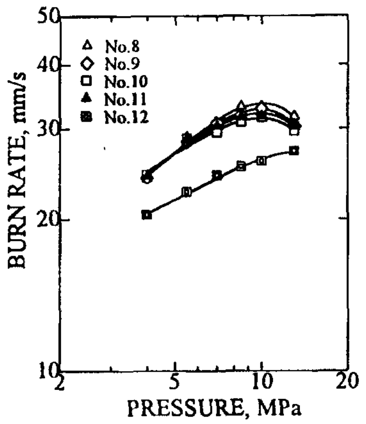


Figure 2 HMX propellants

The relationship between pressure and burn rate of HMX-oxidized BAMO/NMMO composite propellants at 293K are shown in Fig. 2. All the catalysts used here increased the burn rates. The combined catalyst of CuCr and FeC was very effective in increasing the burn rate of HMX propellant. The same result has been observed for 3-azidomethyl-3-methyl oxetane (AMMO) polymer composite propellant[13]. The effects increased with increasing



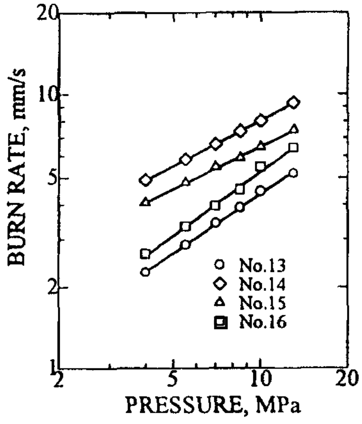


Figure 3 AP propellants

Figure 4 AN propellants

amount of catalyst. The pressure exponent of the burn rate was observed to decrease with increasing amount of additives as shown by Nos.2 and 3 in Fig. 2. In lead-catalyzed samples, Nos.4, 5, 6, and 7, PbCi was the most effective in increasing the burn rate. PbSt and PbHx were also effective in decreasing the pressure exponent of the burn rate. Although high burn rate propellants were considered important, only Nos.6 and 7 were subjected to sensitivity tests because of their lowest pressure exponent.

The catalytic effects of iron oxide on AP composite propellants are shown in Fig. 3. As shown by Nos.8 and 11, Fe2O was more effective than Fe3O in increasing burn rates. Although FeC was expected to be more effective than iron oxide, the burn rate of No.12 was lower than that of No. 8. These two samples were selected for sensitivity testing to compare the effects of organic and inorganic catalysts. All AP-azide polymer propellants showed interesting plateau burning characteristics. Such pressure insensitiveness of the burn rate indicated that condensed phase chemistry plays an important role in the catalytic mechanism of action[14].

The burn rate characteristics of AN propellants are shown in Fig. 4. Chromium oxide is a common burn rate modifier for AN-based propellants. The combined catalyst of CuCr and FeB was effective in increasing burn rates. The ammonium dichromate with CuCr was also effective in the AMMO/NMMO composite propellants[15], in which the combined catalyst activated not only the gas phase reactions but also the reactions occurring in the condensed phase. The replacement of HMX with AP altered the reaction mechanism of the combined catalyst and the burn rate was decreased by approximately 15% at 10MPa. The pressure exponent was increased by approximately 0.08 by the replacement. These results indicated that the reaction mechanisms of the burn rate of AN propellants were influenced by AP reactions. Nos.13 and 14 were selected for sensitivity testing and thermal analysis.

Sensitivity testing

Results of card gap tests are listed in Table 4. HMX propellants, Nos. 6 and 7, had a relatively higher sensitivity, since they contained greater than 71% HMX. It is noted that this composition is similar to that of some high performance explosives. The reaction of HMX was expected to dominate the initiation process. There was no difference observed between the response for the two HMX-based samples. According to thermal analysis

Table 4 Results of card gap test

No.	Gap length, mm	Judgement	Critical gap length, mm	Critical shock pressure, GPa
6	30	×××		
	25	×××	25	8.43
	20	○○○		
7	30	×××		
	25	×××	25	8.43
	20	○○○		
8	10	×××		
	5	×××	5	15.36
	0	○○○		
12	10	×××		
	5	×××	5	15.36
	0	○○○		
13	10	×××		
	5	×××	5	15.36
	0	○○○		
14	10	×××		
	5	×××	5	15.36
	0	○○○		

○; detonation, ×; no detonation

results, the decomposition rate of HMX is faster than that of AP and AN. HMX starts to decompose at a lower temperature than does AP. Further, it has been reported that it is easier to generate hot spots with an increase in the amount of HMX in the propellant[16]. The other propellants showed good sensitivity in the card gap test. AP-based azide polymer composite propellants showed exactly the same sensitivity as AN-based propellants. The use of additives, and the replacement of AN with HMX or AP, were less effective in changing the sensitivity of AN-based propellants.

All samples, except No.12, showed no reaction in the FI test. In the

Table 5 Results of thermal analyses and ESD

No.	Tp, K	Ti, K	Q, J/g	loss, %	E50, J
6	519	505	2679	56	24.1
7	517	505	2723	56	25.2
8	539	508	9510	30	23.0
	604			94	
12	476			13	
	558	471	8377	23	7.1
	601			91	
13	513	473	3776	75	25.2
14	498	460	3809	76	17.4

Tp; the peak temperature in DSC,
Ti; the onset temperature of the exothermic reaction in DSC,
Q; the heat of decomposition measured in DSC,
loss; weight loss at the end of a main reaction in TG.

case of No.12, "burning" was observed at all velocities of the fragment. The burning occurred just after the fragment passed through the sample. As the fragment velocity increased, more unburnt pieces of the propellant remained, because the kinetic energies of the fragment were large enough to break the sample into pieces before flame spreading could occur. The organic iron compound significantly sensitized AP-based composite propellants to FI.

Ignition energies, E50, which were measured with an electric spark generating device, are listed in Table 5. In general, propellants with higher burn rates are easier to ignite than those with lower burn rates. Therefore, No.8 was expected to be easy to be ignited by the electric spark. But No.8 showed almost exactly the same value as those of HMX-based propellants and AN-based propellant in ESD. This result indicates that the catalytic effect of Fe2O on AP-based propellant increases the burn rate, but does not influence the ignition in ESD.

Organic iron compounds, such as FeC and FeB, sensitized the propellant to ESD. The FeC-catalyzed propellant (No.12) was especially easy to ignite by even a the relatively low energy electric spark. The effect of organic iron compounds on ESD response appears to be related to the iron content. The low ignition energy of No.12 suggest that the sensitivity to FI was dominated by condensed phase reactions and adjacent gas phase reactions. The organic iron compounds lower the reaction temperature and the activation energy of the decomposition reactions(17).

The bullet impact test was conducted for No.14 with a 5.56mm bullet. Tests for both the center-perforated and the three-slot configurations of the grain in a steel case resulted in the generation of flames through the hole made by the penetration of the bullet approximately 5 sec after the bullet passed through the sample. After 7 sec, flames were observed from both ends of the case and continued burning for approximately 60 sec. In the CFRP case, however, no reaction was observed at all. It is concluded therefore that the CFRP case contributed to the IM characteristics of the rocket motor.

Thermal analysis

Results of DSC and TG are shown in Table 5. Thermograms for HMX and AN propellants showed only one main exothermic peak because the temperature of the BDR decomposition is relatively close to that of HMX and AN. The heat generated by the BDR decomposition accelerated HMX and AN thermolysis[6, 18]. In contrast, the exothermic reaction of AP propellants resulted in two or three peaks because the temperature of AP decomposition is approximately 100K higher than that of BDR[6, 18]. It is also possible that the thermolysis interaction and relationship between oxidizer and BDR may be weaker in the AP-based propellants than in the HMX- and AN-based propellants. The results for Ti and Tp suggest an explanation for the results of FI and ESD tests, i.e. that thermal decomposition reaction played an important role in the reaction mechanisms involved in the FI and ESD tests. Card gap test results, however, showed a different tendency and might be controlled by the mechanical properties of the propellants and the rate of reaction of the oxidizer at the shock wave. Thermal properties did not dominate the sensitivity to the shock wave of the azide polymer composite propellant.

CONCLUSIONS

AP-based azide polymer propellant showed plateau burning characteristics and burn rates that were faster than those of HMX- and AN-based propellants. For HMX- and AN-based propellants, combined catalysts, such as lead compounds and CB, or CuCr and FeB, were effective in burn rate augmentation and pressure exponent modification.

Sensitivity in the card gap test was higher for HMX-based propellants than for AP- and AN-based propellants. The use of additives and the replacement of the oxidizer appeared to have little effect on the sensitivity to shock waves. On the other hand, organic iron compound reduced the sensitivities of the azide polymer composite propellants to FI and ESD. Thermal decomposition reactions played an important role in the mechanisms of these two tests.

Comparison between the motor case materials used in 5.56mm bullet impact test indicated that CFRP was effective in improving the IM characteristics of the solid rocket motors.

REFERENCES

1) H. B. Frankel et al., Final Report to Office of Naval Research, Arlington, VA, NTIS AD-110292 (1982).

2) H. A. H. Talukder et al., J. Polymer Soc. Part A Polym. Chem., 28, 2393 (1990).

3) Y. Oyumi et al., Propellants Explosives Pyrotech., 17, 226 (1992).

4) B. Xu et al., J. Applied Polym. Soc., 46, 1603 (1992).

5) G. H. Hiue et al., J. Polymer. Soc. Part A Polym. Chem., 32, 2155 (1994).

6) E. Kimura et al., Propellants Explosives Pyrotech., 19, 270 (1994).

7) M. Farber et al. Combust. Flame, 55, 203 (1994).

8) Y. Oyumi et al., ibid, 65, 127 (1986).

9) DOD-MIL-STD-2105B (1992).

10) Standard of the Industrial Explosives Society of Japan, 3rd ed. (1988).

11) F. Hosoya et al., Propellants Explosives Pyrotech., 16, 119 (1991).

12) R. W. Milton et. al., Proc. Insensitive Munitions Technol. Sympo., pp. 309 (1994).

13) Y. Oyumi et. al., Propellants Explosives Pyrotech., 18, 195 (1993).

14) Y. Oyumi et. al., ibid, 20, 150 (1995).

15) Y. Oyumi et. al., ibid, 19, 180 (1994).

16) K. Kato et. al., J. Industrial Explosives Soc. of Japan, 43, 323 (1982).

17) Y. Oyumi et. al., Propellants Explosives Pyrotech., 17, 226 (1992).

18) Y. Oyumi et al., J. Explos. Soc. of Japan, 55, 194 (1994).