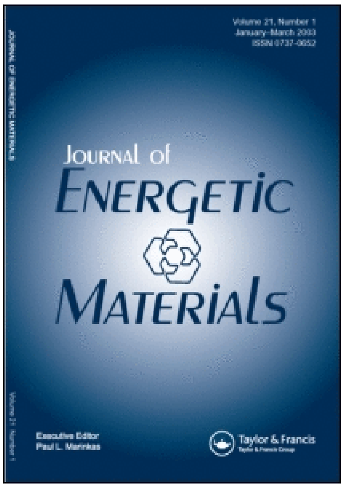

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SENSITIVITIES OF AZIDE POLYMER PROPELLANTS IN FAST COOK-OFF, CARD GAP AND BULLET IMPACT TESTS

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ABSTRACT

Sensitivities of GAP propellants and BAMO/NMMO propellants were evaluated. The fast cook-off test, card gap test and bullet impact test were employed to characterize the propellant samples. All the samples tested here showed no reaction other than burning. In the fast cook-off test, ignition time was dependent on the confinement and propellant composition. In the card gap test, the double base propellant was found to have a higher sensitivity than AP-based composite propellant. In the bullet impact test, the case material played an important role in the sensitivity. The case made of carbon fiber-reinforced plastics (CFRP) was effective in mitigating the sensitivity to the bullet impact. As a whole, AN-based composite propellants had relatively lower sensitivity.

INTRODUCTION

Insensitivity of propellant is one of the important requirements in advanced solid

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rocket propellants. For minimum signature, ammonium nitrate, nitramines and nitric ester as oxidizer or co-oxidizer are preferred. These oxidizers, however, show relatively low performance and ballistic characteristics compared to ammonium perchlorate, which has been commonly used as a high performance oxidizer. Therefore, azide polymer binder has become important to the improvement of combustion characteristics of minimum smoke propellants. Relatively few studies have been reported on azide polymer propellants, though sensitivities, including initiation mechanisms, of solid rocket propellants have been summerized[1, 2]. Many assessment methods have been recommended to evaluate the propellant sensitivities[3, 4], but card gap tests, fast cook-off (FCO) tests and bullet impact (BI) tests were conducted to screen for insensitive munitions (IM) characteristics.

EXPERIMENTAL

Samples

Table 1 shows the GAP sample compositions tested here. The compositions of

Table 1 Sample compositions in GAP series

No.	GAP	TN	HMX	AP	AN	NC	NG	DEP	UT	CuC	PbC	CB	B	Al	FeO
1	29.5	-	14.8	-	54.1	-	-	-	-	-	-	0.6	1.0	-	-
2	20.0	20.0	-	-	60.0	-	-	-	-	-	-	-	-	-	-
3	14.5	14.5	-	-	48.2	19.3	-	-	-	1.0	1.9	0.6	-	-	-
4	17.4	-	-	79.2	-	-	-	-	-	-	-	-	-	2.0	1.0
5	-	-	-	-	-	45.9	41.0	4.8	4.8	-	2.9	0.6	-	-	-

GAP: GAP binder, TN: trimethylolethane trinitrate (TMETN), HMX: tetramethylene tetranitramine, AP: ammonium perchlorate, AN: ammonium nitrate, NC: nitrocellulose DEP: diethyl phthalate, UT: urethane binder, CuC: copper chromite, PbC: lead citrate, CB: carbon black, FeO: iron oxide.

Table 2 Sample composition in BAMO/NMMO series

No.	BR1	BR2	HMX	AP	AN	NC	NG	PL	CuC	Pb	Al	FeO	FeB	ZrC
6	23.8	-	14.3	-	57.1	-	-	-	2.9	-	-	-	1.9	-
7	-	23.8	14.3	-	57.1	-	-	-	2.9	-	-	-	1.9	-
8	21.9	-	-	73.3	-	-	-	-	-	-	-	2.9	-	1.9
9	-	11.5	-	70.5	-	-	-	-	-	-	16.4	1.6	-	-
10	-	-	14.1	-	-	36.7	32.4	11.6	-	5.2	-	-	-	-

BR1: BAMO/NMMO binder, BR2: hydroxyl-terminated polybutadiene (HTPB), PL: polyol binder, Pb: catalyst based on lead, FeB: butacene

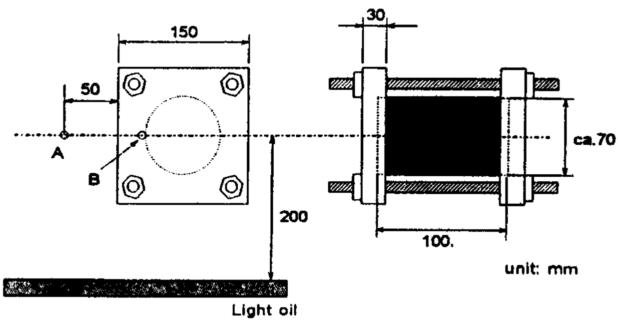
BAMO/NMMO propellants are listed in Table 2. In both the GAP and BAMO/NMMO series, AN- and AP-based composite propellants and double based propellant were provided.

Fast cook-off test

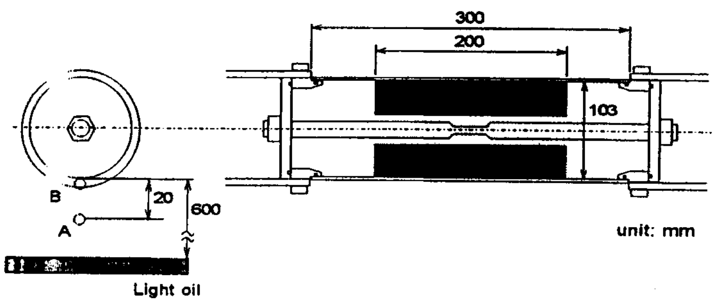
Test conditions were based on the IM Military Standard, except for the sample height from the fuel pan[4]. Sample height was adjusted to the temperature requirements and flame coverage area. The time until the sample surface temperature reached 540°C was more than 30 seconds, and the average flame temperature was greater than 870°C in all the tests. Schematic representations of the test setups for the GAP and BAMO/NMMO series are shown in Figure 1(a) and 1(b), respectively.

For the GAP series, grains were 100 mm in length with a 32 mm bore diameter, and were cast 66 mm in inner diameter with 1.5 mm insulator in thickness. It was difficult for inner gases to escape away because of the 2-mm urethane sheet placed between the case and steel holder. Two different case materials, one of carbon/epoxy composite, and one of steel, were used in Samples 1 and 6 respectively to characterize the case effect. Relatively large propellant samples were used in the BAMO/NMMO series. To address safety concerns, a central shaft, designed to cut off below an inside pressure of 18 MPa, was applied.

Four igniters at each corner of the fuel pan were simultaneously used for the



a) GAP series



b) BAMO/NMMO series

Figure 1 Schematic arrangements of FCO test ignition of fuel (light oil), the amount of fuel was controlled such as to keep the test time above 15 minutes. As shown in Figure 1, two thermocouples labelled A and B were used to monitor the flame and the sample surface temperature, respectively. Video tape recorder was used to observe remotely the reaction behaviors during the tests. Ignition time was defined as the time between the fuel ignition and the flame observed.

<u>Card gap test</u>

This test was conducted based on the standards of the Japan Explosives Society[3] except for the gap material and the sample holder material in order to increase the shock energy and the confinement, respectively. Polymethylmethacrylate gap material and polyvinyl chloride sample holder material were replaced with aluminum and steel, respectively. The test setup was shown in Figure 2. The shock wave, generated by the pentolite detonator, was transferred into the propellant sample through the solid aluminum gap plate. Pentolite was cast in a polyvinyl chloride tube, whose size was 31 mm in diameter and 30 mm in length. The propellant sample was cast in a tube made of 32A carbon steel with a 37 mm inner diameter, and 50 mm length. The gap plate was made of aluminum with a diameter of 80 mm, and different thickness at 5 mm intervals. A witness plate under the sample was used to decide whether or not "detonation" had occurred. "Detonation" was determined when the plate had a crack

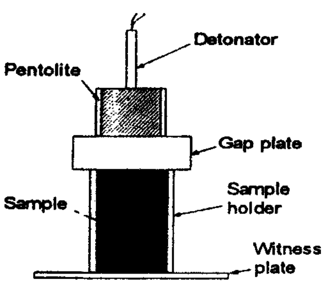


Figure 2 Experimental setup of the card gap test

or hole. "Critical gap length" was defined as the minimum gap length at which no detonation was observed in three trials, and "critical shock pressure" was defined as the pressure at the critical gap length[5].

<u>Bullet impact test</u>

Schematic arrangement of the BI test is shown in Figure 3. Two different distances were used because of facility limitations, but the bullet velocities in both series were almost the same. Although a 12.7 mm bullet was used in the standard[4], a 5.56 mm projectile was applied here because the bullet with 5.56 mm caliber was reported to be sufficient and effective on small size propellant grains[6]. This test was conducted with a three-round burst.

Dimensions of the propellant grain are shown in Figure 4. The velocity of the first

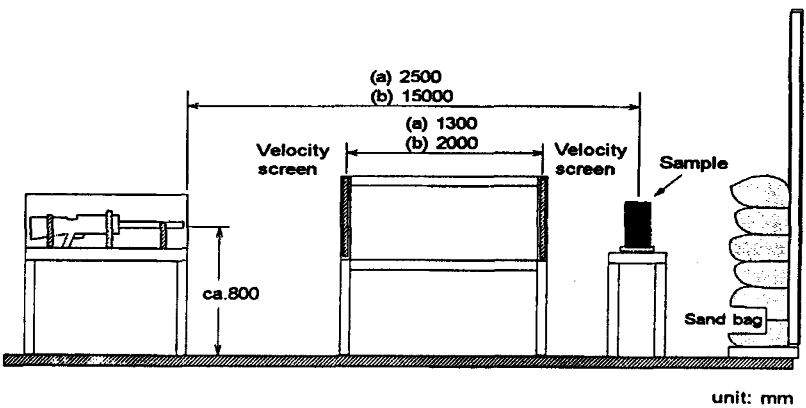


Figure 3 Schematic arrangement of the BI test for GAP series (a) and BAMO/NMMO series (b)

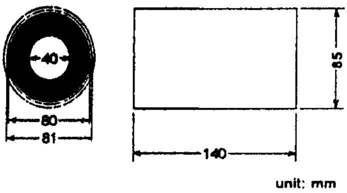


Figure 4 Sample configuration of the BI test

bullet was measured by two electronic velocity screens. Three bullets passed horizontally through the center of the sample with a velocity of more than 920 m/s. The firing interval was 75 ms. The case materials were a steel of SS41 with 2 mm thickness, and a carbon/polyimide compo-site with 2 mm thickness. Each case was tested twice and monitored remotely with a high speed video camera.

RESULT AND DISCUSSION

1. Fast cook-off

Ignition times are listed in Table 3. For the GAP series, the bottom of the case material which faced the fuel pan was severely damaged in all tests. The steel case used in Sample 1 broke in the axial direction because of the pressure generated by the propellant decomposition. Relatively moderate burning was observed in the CFRP case

Table 3 Ignition time in FCO test [s]

No.	1	2	3	4	5	6	7	8	9	10
steel	210	-	-	-	-	110	138	64	123	79
CFRP	178	133	140	196	150	75	152	44	138	89
	193	158	155	206	144	61	193	48	117	90
Ave.*	186	144	148	201	147	78	173	46	128	90

*: Average ignition time of composite case tests

samples. This indicated that the combustible gases could escape through the decomposed resin and the carbon fiber and relatively low pressure was kept in the motor case. In Samples 1 and 2, the replacement of HMX with TMETN shortened the ignition time by 42 seconds. AN-based composite propellant containing 20% TMETN, Sample 2 acted as did the double-base propellant, Sample 5. Although the ignition time of Sample 4, an AP-based propellant, was relatively long, the burning was severe because of its high burn rate. These results indicated that the decomposition temperature of the propellant ingredients and endo/exothermic heat balance played an important role in the ignition time of FCO test.

From a comparison of Sample 6 with 7, and also of Sample 8 with 9, it appears that the azide polymer binder shortened the ignition time because of its exothermic decomposition, which occurs at around 150° C[7,8]. For Samples 6 and 10, both of which contain butacene, a relatively short ignition time was observed. This indicates that the catalytic effect of butacene influences the ignition time, as well as combustion characteristics.

In general, burning conditions depended on burn rates. High burn rate propellants, such as Samples 4, 8 and 9, showed relatively severe burning. Burn rates are shown in Table 4.

Table 4 Burn rate of samples at 50 kgf/cm^2 [mm/s]

1	2	3	4	5	6	7	8	9	10
5.2	-	6.8	18.8	9.4	5.2	1.7	27.4	16.7	11.3

- : no data

Table 5 Results of the card gap test

No.	G/L [mm]	judgment	critical G/L [mm]	critical shock press. [GPa]
1	5	×××	5	18.4
	0	○○○		
2	-	no data	-	-
3	20	×××	20	10.8
	15	○○○		
4	5	×××	0	>23.4
	0	×××		
5	25	×××	25	8.73
	20	○○○		
6	10	×××	5	18.4
	5	×××		
	0	○○○		
7	10	×××	5	18.4
	5	×××		
	0	○○○		
8	10	×××	5	18.4
	5	×××		
	0	××○		
9	10	×××	0	>23.4
	5	×××		
	0	×××		
10	25	×××	20	10.8
	20	×××		
	15	○○○		

G/L: gap length
×: No Go, ○: Go

2. Card gap

Table 5 lists results of the card gap tests. In comparison with Samples 1 and 3, use of nitrate ester and removal of HMX gave greater sensitivity to the shock wave. Sample 5, a double-base propellant, was more sensitive to the shock than Sample 3 because of an increase of the nitrate ester amounts. Sample 4, an AP-based propellant, had an insensitive characteristic for the shock stimuli, yet detonation was observed even at 0 mm gap length. But Sample 4 burnt out during the test because it was easy to ignite.

In comparison between Samples 6 and 7, no difference between the azide polymer and HTPB binder was observed in this test. Binder decomposition had little effect on the sensitivity to the shock wave. Samples 8 and 9, AP-based composite propellants, were relatively insensitive for the shock wave, though the samples did burn when testing. This was also the case for GAP-binder propellants. Nitrate ester based propellants were the most sensitive to the shock.

3. Bullet impact

Both metal and carbon/polyimide composite cases were used for two trials of each propellant sample. The average velocity in the GAP series was 936 m/s with the two extremes of 922 and 942 m/s. A value of 931 m/s was observed in the BAMO/NMMO series with the variance between 926 and 934 m/s. Three bullets penetrated the center of each cases with very little scattering. Test results are summarized in Table 6. Both steel and CFRP cases of Sample 1 showed fumes for a few minutes, and then stopped. Smoking indicated that local thermal decomposition of the propellant occurred when 5.56 mm projectiles passed through. The exotherm generated by the thermal decomposition was consumed by AN melting at the initial stage; the heat balance gradually became negative.

The steel case #1 of Sample 2, complete substitution of HMX and partial substitution of GAP with TMETN, smoked for 7 seconds and then ignited, while that of #2 smoked for 30 seconds and then quenched. The sensitivity of Sample 2 towards bullet impact was worse than that of Sample 1 because of the addition of TMETN.

In Samples 3 and 5, bullet impact stimuli was just sufficient to ignite the metal case samples; no reactions were observed for the composite case. These results indicate that the CFRP case played an effective role for an improvement of the sensitivity. The friction between CFRP and the bullet was less than that of the steel and the bullet, judging from the conditions of the 5.56 mm projectiles after testing.

Sample 4, whose main oxidizer was AP, immediately ignited on impact. The reactions for the steel case were especially vigorous, and the case moved off the test

Table 6 Results of BI test

No.	case	velocity [m/s]	phenomenon
1	metal #1	935	Smoked for 16 s and the quenched.
	metal #2	935	Smoked for 60 s and the quenched.
	CFRP #1	929	Smoked for 25 s and the quenched.
	CFRP #2	922	Smoked for 60 s and the quenched.
2	metal #1	935	Smoked for 4 s and then burnt.
	metal #2	943	Smoked for 30 s and then burnt.
	CFRP #1	935	Smoked for 20 s and then burnt.
	CFRP #2	942	Smoked for 20 s and then burnt.
3	metal #1	922	Ignited after 3 s of the bullet impacts.
	metal #2	935	Ignited after 1 s of the bullet impacts.
	CFRP #1	942	Smoked for 45 s and then quenched.
	CFRP #2	942	Smokes for 15 s and then quenched.
4	metal #1	942	Ignited at the bullet impacts.
	metal #2	942	Ignited at the bullet impacts.
	CFRP #1	942	Ignited at the bullet impacts.
	CFRP #2	923	Ignited at the bullet impacts.
5	metal #1	935	Ignited at the bullet impacts.
	metal #2	942	Ignited at the bullet impacts.
	CFRP #1	942	Smoked for 28 s and then quenched.
	CFRP #2	942	Smoked for 23 s and then quenched.
6	metal #1	930	Smoked for 5 s and then burnt.
	metal #2	926	Smoked for 3 s and then burnt.
	CFRP #1	930	No reaction.
	CFRP #2	926	No reaction.
7	metal #1	934	Smoked for 69 s and then burnt.
	metal #2	934	Smoked for 150 s and then quenched.
	CFRP #1	926	No reaction.
	CFRP #2	930	No reaction.
8	metal #1	930	Ignited at the bullet impacts.
	metal #2	934	Ignited at the bullet impacts.
	CFRP #1	930	Ignited at the bullet impacts.
	CFRP #2	934	No reaction.
9	metal #1	930	Ignited at the bullet impacts.
	metal #2	930	Ignited at the bullet impacts.
	CFRP #1	934	Ignited at the bullet impacts.
	CFRP #2	926	Ignited at the bullet impacts.
10	metal #1	934	Ignited after 1 s of the bullet impacts.
	metal #2	934	Ignited after 1 s of the bullet impacts.
	CFRP #1	930	Smoked for 8 s and then burnt.
	CFRP #2	930	No reaction.

stand. Therefore, the order of the sensitivity to the bullet impact test was Samples 4, 5, 3, 2 and 1 according to the reaction behavior. The most sensitive, Sample 4, was due to the high combustibility of AP.

Sample 6 showed no reaction in the CFRP case, while in the steel case it burnt during both tests. Sparks of fire from passing bullets passing were not direct origins of ignition, since the sample started to burn with a few seconds delay.

Sample 7, the same composition as Sample 6 except for the substitution of HTPB for the azide polymer, was less sensitive than Sample 6. The ignition time was longer than that of Sample 6, and one of the steel cases did not ignite despite the fact that they smoked for 150 seconds. The other steel case probably ignited because the bullet(s) passed through the side of center perforation, which induced a more severe friction exotherm.

Samples 8 and 9, mainly composed AP oxidizer, showed vigorous reaction in both steel and CFRP cases because of a high burning rate. In both cases, the samples ignited on the first bullet shot. One or two bullets of three did not pass through the sample because the sample moved off the test stand resulting from the ignition shock.

One of CFRP cases in Sample 10 ignited and flame was observed 8 seconds after the shot. The flame forming on the top of the case was unstable, and chaffing combustion was observed at the beginning. The burning of double-base propellant is unstable at a low pressure.

Cross-sectioned samples revealing the penetration tunnel were observed for the non-reacted samples in the CFRP case. Photo 1 shows the cross-section near the penetration tunnel of Sample 6. Bullets penetrated the sample from left to right. White-shining particles are AN and HMX (upper half); no such particles were shown

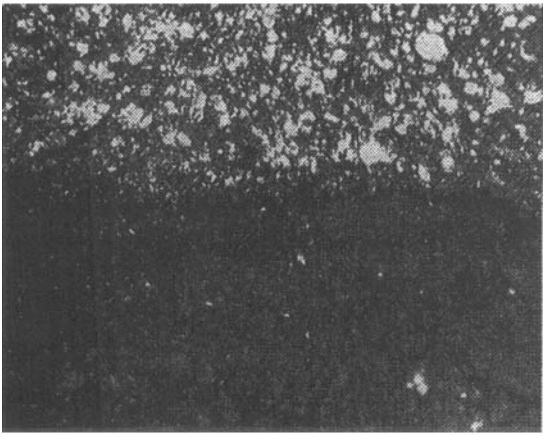


Photo 1 Cross section near penetration tunnel in the BI test.

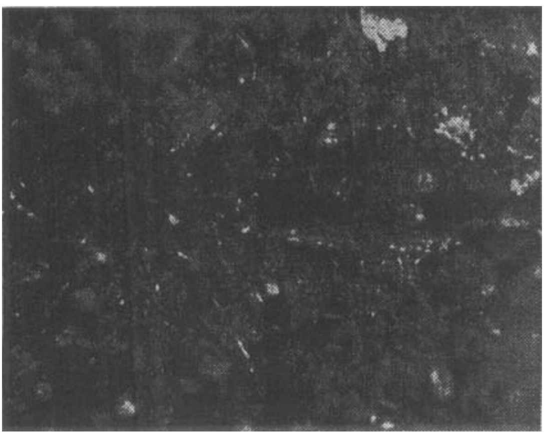


Photo 2 Surface of the penetration tunnel

along the penetration tunnel. Photo 2 shows a magnified view of penetration tunnel surface. Many small voids and crystalline needles appeared; some fine particle of HMX were also observed on the surface. In contrast with Photo 3, a virgin surface, relatively large particles of both AN and HMX were found in the binder without voids. In Photos 1 and 2, it may be seen that AN and HMX were scratched by bullet and melted. Some or all of them re-crystallized gradually after the heating. Propellant melted. Some or all of them re-crystallized gradually after the heating. Propellant containing AN was difficult to ignite because of consumption of the heat by AN melting. Although it was difficult to judge from this photo whether or not the binder decomposed thermally, it might be expected that an azide polymer binder might not decompose since HMX, which has a melting point of 273° C[9], is left intact.

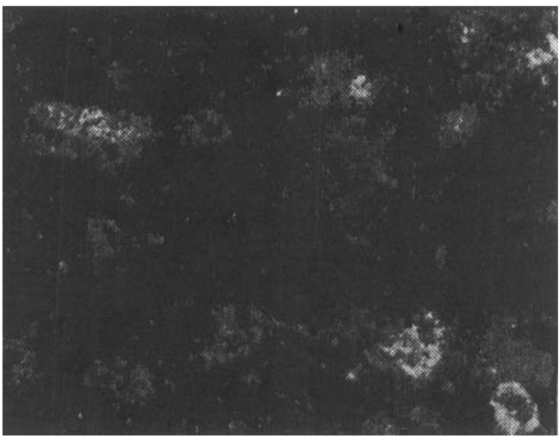


Photo 3 Virgin surface of Sample 6

CONCLUSIONS

In the FCO test, no detonation occurred on the samples tested. AP composite propellant took a longer time to ignite, though reaction was severe because of a relatively high burn rate. Double-base propellant and composite propellants containing nitrate ester compounds showed relatively shorter ignition time. Although the ignition time of the composite case was shorter than that of steel case, organic resin of the composite case was observed to have been decomposed by exposure to the flame, some combustible gases could have leaked through the fibers resulting in a more moderate reaction. Mechanical properties of the composite case became quite low at temperatures above 150°C[10)] and the case could hold pressure for approximately 70 seconds according to the temperature measurement at the surface[11)]. Ignition time depended not only on the strength of the case but on leakage and combustibility of gaseous products.

AN composite propellants were generally insensitive to the sensitivity assessments conducted here.

AP composite propellants were very sensitive to the BI test, and less sensitive to the card gap test. In the FCO test, their reaction behavior was more violent than the others.

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