Influence of Isopropyl Nitrate on the Performance of Propellants

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***Abstract* — Isopropyl nitrate in the fuel air explosive mixture leaks into the ammunition. In this paper we determine the influence of isopropyl nitrate on the performance of the propellants, we test the thermal decomposition of propellants with an acceleration rate calorimeter. Thermal decomposition characteristic parameters and kinetic parameters are obtained by analyzing temperature-time curves and pressure-time curves. It is found that isopropyl nitrate can affect the storage stability of CMDB propellant and SG-2 double-base propellant, but do no harm to YB single-base propellant. The combustion of propellant was tested. It is shown that combustion time of YB and CMDB propellant are shorter. Combustion time of QJ and SF-2 propellant are longer.**

Keywords - thermal decomposition; combustion; isopropyl nitrate; propellant; accelerating rate calorimeter; closed bomb

I. INTRODUCTION

Fuel Air Explosive(FAE) is a new surface damage weapon[1]. Military targets can be attacked by aerosol cloud formed by the explosion. The current commonly used FAE components are magnesium powder and isopropyl nitrate. Isopropyl nitrate that is a kind of volatile liquid at normal temperature can leak into the ammunition from the joint of warhead and fuze chamber. Due to the strong oxidation property and solubility of isopropyl nitrate, the stability and combustion performance of propellants will be affected by the leakage of isopropyl nitrate.

ZENG[2] studied the thermal stability of isopropyl nitrate with accelerating rate calorimeter(ARC) and differential scanning calorimetry(DSC). XUAN[3] proposed a chemical stability test method of FAE with gas chromatography(GC) and atomic absorption spectroscopy(AAS). KAN[4] used FT-IR to study the thermal decomposition mechanism of isopropyl nitrate. However, there is still no relative study about the influence of isopropyl nitrate on performance of propellants.

In order to determine the influence, thermal analysis experiments are done with ARC[5] to test the stability. Closed bomb[6] is used to test the combustion performance of propellants.

II. EXPERIMENT PART

A. Thermal analysis experiments

The experimental propellant samples are three propellants which are used by ammunition with FAE warhead, YB single-base propellant, composite modified double-base(CMDB) propellant and SG-2 double-base propellant. The main component of YB single-base propellant is nitrocellulose(NC). The main components of composite modified double-base propellant are NC, nitroglycerin(NG), ammonium perchlorate(AP) and aluminum. The main components of SG-2 double-base propellant are NC, NG and cobalticoxide.

The experimental instrument is accelerating rate calorimeter produced by British thermal hazard technology company. Sample containers are thick titanium alloy ball. The mass of ball m_b is 7.1254g. The mean heat capacity $\overline{C_{v,b}}$ is 0.42J•(g•℃)$^{-1}$. In order to study the influence, isopropyl nitrate is mixed with propellant in the ball. Each propellant test has 6 groups which differ in the volume of isopropyl nitrate. The leakage of isopropyl nitrate in ammunition is about 200-300mg/L. The experimental volume of isopropyl nitrate is determined by the practical leakage to reveal the actual influences. The mass of samples and test conditions are in Table 1.

B. Combustion performance experiments

The experimental instrument is CBS100-700 closed bomb detection system produced by Nanjing University of Science and Technology. The volume of closed bomb body is 106.1mL.

YB single-base propellant and CMDB propellant are tested to study the influence. SG-2 double-base propellant is not chosen because its shape is not suitable for testing. Three commonly used propellant, QJ single-base propellant, SF-3 double-base propellant and SF-2 triple-base propellant are also tested to be compared with those propellants. The main component of QJ single-base propellant is NC. The main components of SF-3 double-base propellant are NC

and NG. The main components of SF-2 triple-base propellant are NC, NG and nitroguanidine(NQ).

Isopropyl nitrate is mixed with propellant in the closed bomb body. Because isopropyl nitrate is a kind of energetic material, charge densities[7] are lowered to Δ_1=0.10g•cm^{-3} and Δ_2=0.16g•cm^{-3} to insure safety. In addition, the charge densities of CMDB propellant experiment are lowered to Δ_1=0.08g·cm^{-3} and Δ_2=0.12g·cm^{-3} since CMDB propellant is a new propellant with higher energy.

Each propellant test has 5 groups which differ in the volume of isopropyl nitrate mixed with propellant. Table 2 is the isopropyl nitrate volume V_{IPN} of each group.

TABLE 1 MASS OF SAMPLES AND TEST CONDITIONS

Group	*m*			*V*	T_{start}	T_{step}	t_{wai}	*s*
	YB	CM DB	SG -2					
1#	0.180	0.197	0.244	0	50	5	15	0.02
2#	0.177	0.198	0.245	0.5	50	5	15	0.02
3#	0.175	0.192	0.244	1	50	5	15	0.02
4#	0.181	0.199	0.246	2	50	5	15	0.02
5#	0.181	0.192	0.241	4	50	5	15	0.02
6#	0.183	0.194	0.242	6	50	5	15	0.02

m is propellant mass, g. *V* is isopropyl nitrate volume, μL. T_{start} is the initial temperature, ℃. T_{step} is the heating step, ℃. t_{wait} is the waiting time, min. *s* is the sensitivity of heating rate, ℃•min^{-1}.

TABLE 2 THE VOLUME OF ISOPROPYL NITRATE

Group	1#	2#	3#	4#	5#
V_{IPN}[mL]	0	0.2	0.4	0.6	0.8

III. RESULTS AND DISCUSSION

A. Thermal analysis experiments

Figure 1 to 3 are the experiment results of three kinds of propellants including temperature-time curves, pressure-time curves and temperature rate-temperature curves.

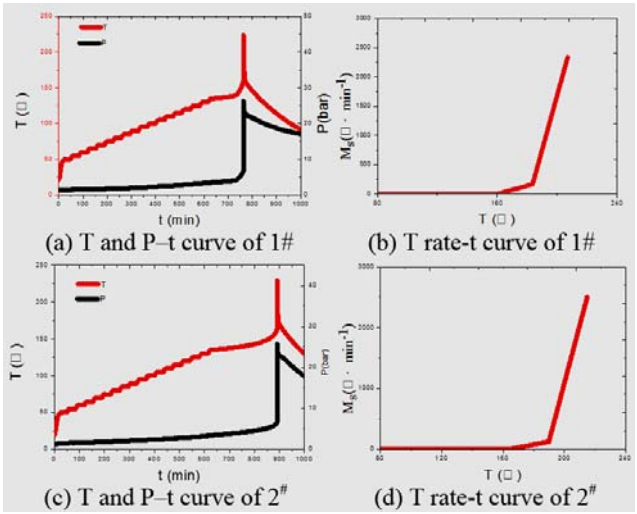


Fig.1 Decomposition curves of YB

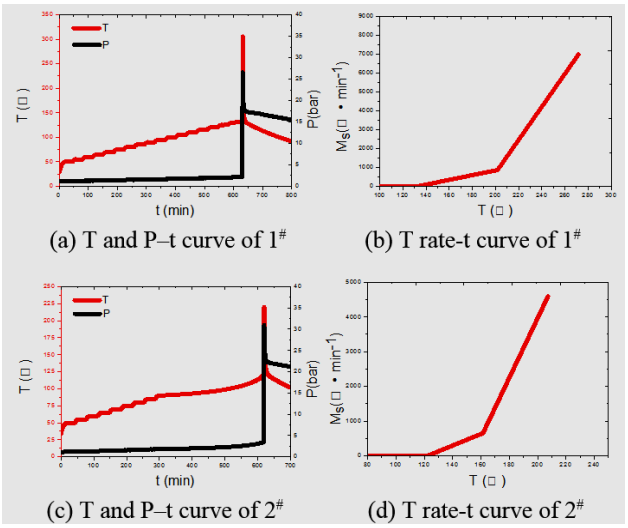


Fig.2 Decomposition curves of CMDB.

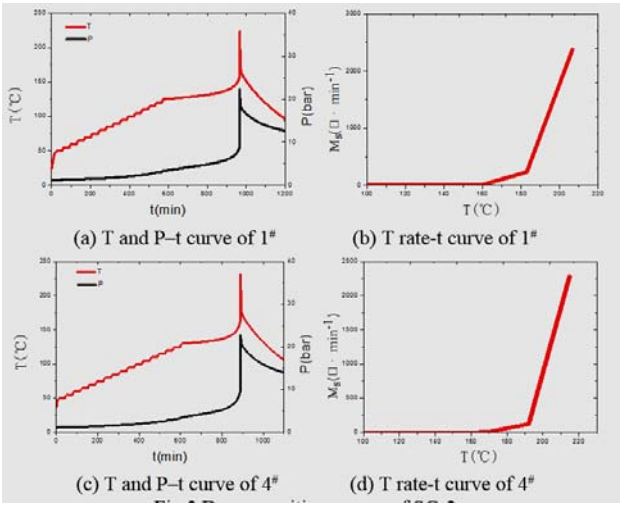


Fig.3 Decomposition curves of SG-2

According to the thermal decomposition curves, the thermal decomposition characteristic parameters of 3 kinds of propellants can be determined. The results are in Table 3.

From Figure 1 to 3 and Table 3, it can be found that isopropyl nitrate causes different influences on propellants. The initial decomposition temperature of YB single-base propellant does not change significantly. But the initial decomposition temperature of CMDB propellant drops from 128.5 ℃ to about 100 ℃. The initial decomposition temperature of SG-2 double-base propellant rises from 125.3℃ to about 135℃.

The heat produced by samples in the decomposition process is not fully used for heating itself. Part of the heat is absorbed by the container ball. The temperature measured in the test is not the temperature of the sample but the system including the container ball and the sample. So the thermal

inertia factor[8] Φ is needed to make the experiment results accurate.

TABLE 3 THERMAL DECOMPOSITION CHARACTERISTIC PARAMETERS

Prop -llant	*Gro -up*	$T_{0,s}$	$T_{f,s}$	$\Delta T_{ad,s}$	$P_{m,s}$	$M_{0,s}$	$M_{m,s}$
YB	1#	142.4	217.0	74.6	26.31	0.038	2340.4
	2#	145.5	216.2	70.7	25.72	0.024	2506.9
	3#	145.6	220.6	74.9	24.52	0.034	2703.1
	4#	145.6	219.2	73.7	25.24	0.026	2830.7
	5#	142.6	222.0	69.5	25.88	0.033	2979.7
	6#	140.7	222.6	75.3	25.93	0.026	2411.3
CM DB	1#	130.6	271.7	141.1	26.65	0.033	6994.1
	2#	105.4	218.7	113.4	24.90	0.036	3765.0
	3#	105.5	213.7	108.2	22.64	0.027	5087.4
	4#	102.4	200.8	98.3	30.94	0.023	4593.6
	5#	100.6	210.0	109.4	24.13	0.020	5766.1
	6#	100.4	218.3	118.0	22.53	0.044	6318.4
SG-2	1#	125.3	211.0	85.7	21.30	0.024	2157.6
	2#	134.3	192.5	58.2	18.68	0.022	2021.9
	3#	135.6	217.8	82.3	25.12	0.039	2562.3
	4#	136.3	221.8	85.6	22.73	0.022	2276.6
	5#	140.4	193.8	53.4	20.23	0.031	1093.7
	6#	133.4	205.4	72.0	20.25	0.031	2946.4

$T_{0,s}$ is the initial system decomposition temperature, ℃. $T_{f,s}$ is the terminating system temperature, ℃. $\Delta T_{ad,s}$ is the adiabatic system temperature rise, ℃. $P_{m,s}$ is the largest reaction pressure, bar. $M_{0,s}$ is the initial system temperature rate, ℃•min^{-1}. $M_{m,s}$ is the maximum system temperature rate, ℃•min^{-1}.

$$\phi = \frac{(m\overline{C_v} + m_b\overline{C_{v,b}})}{m\overline{C_v}} \tag{1}$$

Adiabatic temperature rise of sample ΔT_{ad} :

$$\Delta T_{ad} = \phi \Delta T_{ad,s} \tag{2}$$

Sample decomposition temperature rate m_T :

$$m_T = \phi m_{T,s} \tag{3}$$

The initial exothermic temperature of sample T_0 :

$$T_0 = \left(\frac{1}{T_{0,s}} + \frac{R}{E} \ln \phi \right)^{-1} \tag{4}$$

The terminating reaction temperature of the sample T_f :

$$T_f = T_0 + \Delta T_{ad} \tag{5}$$

$\overline{C_v}$ is the mean system capacity. $m_{T,s}$ is system temperature rate. E is activation energy. R is universal gas constant.

The experiment results of 3 kinds of propellants modified by Φ are in Table 4.

The initial decomposition temperature is lower after correction, which means the results are reasonable. The adiabatic temperature rise and temperature rate are higher. The differences among initial decomposition temperature of each propellant are consistent with previous conclusions. Based on the adiabatic temperature rise equation and Arrhenius equation[9-12]:

$$m_{T,s} = \frac{dT}{dt} = k\left(\frac{T_{f,s} - T_s}{\Delta T_{ad,s}}\right)^n \Delta T_{ad,s} \tag{6}$$

Formula (7) is obtained:

$$\ln k = \ln \left(\frac{m_{T,s}}{\left(\frac{T_{f,s} - T_s}{\Delta T_{ad,s}}\right)^n \Delta T_{ad,s}} \right) \tag{7}$$

The natural logarithm of Arrhenius formula is[13-15]:

$$\ln k = \ln A - \frac{E}{R} \cdot \frac{1}{T} \tag{8}$$

$m_{T,s}$, $T_{f,s}$ and $\Delta T_{ad,s}$ can be obtained through the ARC test. When the reaction series is suitable, Ink is obtained through formula(7). In this way, thermal dynamic parameters in formula(8) can be calculated by data fitting. Take $1/T$ as the abscissa axis, Ink as the ordinate axis for linear fitting. The activation energy is calculated by the slope, the Arrhenius factor is calculated by the intercept. The calculation results are in Table 5.

As shown in Table 5, the activation energy of propellants change differently. E of CMDB propellant decreases by about 20kJ • mol^{-1}. E of YB single-base propellant is about 220kJ • mol^{-1}, which does not change significantly. E of SG-2 double-base propellant rises from 194.86kJ • mol^{-1} to about 210kJ • mol^{-1}.

The results mean that isopropyl nitrate can affect the storage stability of CMDB propellant and SG-2 double-base propellant, but do no harm to the storage stability of YB single-base propellant.

TABLE 4 THERMAL DECOMPOSITION CHARACTERISTIC PARAMETERS MODIFIED BY Φ

Prop -llant	*Gro -up*	*Φ*	T_0	T_f	ΔT_{ad}	M_0	M_m
YB	1#	9.31	140.7	601.9	742.6	0.35	21805.4
	2#	9.45	144.0	762.8	896.8	0.22	23708.5
	3#	9.60	144.6	719.6	864.2	0.28	25970.5
	4#	9.28	144.4	683.9	828.3	0.23	26269.7
	5#	9.29	141.1	645.7	796.8	0.27	27681.4
	6#	9.19	139.3	692.7	832.0	0.18	22181.4
CM DB	1#	8.61	128.5	1212.1	1340.6	0.28	60149.6
	2#	8.59	103.3	970.6	1054.9	0.31	32379.1
	3#	8.81	103.9	950.4	1054.3	0.24	44765.6
	4#	8.55	91.8	837.9	929.7	0.20	39270.1
	5#	8.81	99.3	959.2	1058.5	0.17	50740.8
	6#	8.75	98.9	1026.3	1125.2	0.38	55282.5
SG-2	1#	7.15	124.0	613.2	738.5	0.17	15437.6
	2#	7.14	133.1	515.7	640.0	0.15	14442.4
	3#	7.15	134.2	588.9	724.5	0.27	18335.8
	4#	7.11	134.8	609.1	745.2	0.15	16200.2
	5#	7.22	138.9	385.9	526.3	0.22	7904.1
	6#	7.21	132.0	519.4	652.8	0.22	21253.1

M_0 is the initial sample temperature rate, ℃•min^{-1}. M_m is the maximum sample temperature rate, ℃•min^{-1}. The unit of T_0, T_f, ΔT_{ad} is ℃.

TABLE 5 KINETIC CALCULATION

Group	E[kJ•mol^{-1}]			A[s$^{-1}\times10^{15}$]		
	YB	CMDB	SG-2	YB	CMDB	SG-2
1#	218.8	145.6	194.8	15.6	8.6	7.8
2#	218.9	128.3	207.5	16.3	3.4	8.4
3#	219.0	127.7	217.7	14.7	4.2	11.5
4#	218.1	138.0	203.3	16.6	8.1	7.6
5#	220.2	138.7	214.9	13.5	9.6	10.4
6#	216.1	120.4	209.1	17.3	2.3	10.6

One of the CMDB propellant components is aluminum. Isopropyl nitrate that is a strong oxidizer is easy to react with aluminum, which promotes the decomposition of propellant. In a result, isopropyl nitrate harms the storage stability of CMDB propellant. The initial thermal decomposition temperature of isopropyl nitrate is 156℃, which is higher than that of SG-2 double-base propellant. It leads to the rise of initial thermal decomposition temperature and activation energy. The initial thermal decomposition temperature of YB single-base propellant is close to isopropyl nitrate. Therefore the thermal decomposition of YB single-base propellant is not affected by isopropyl nitrate.

B. Combustion performance experiments

Figure 4 is the Pressure-time curves and d*P*/d*t*-*t* curves.

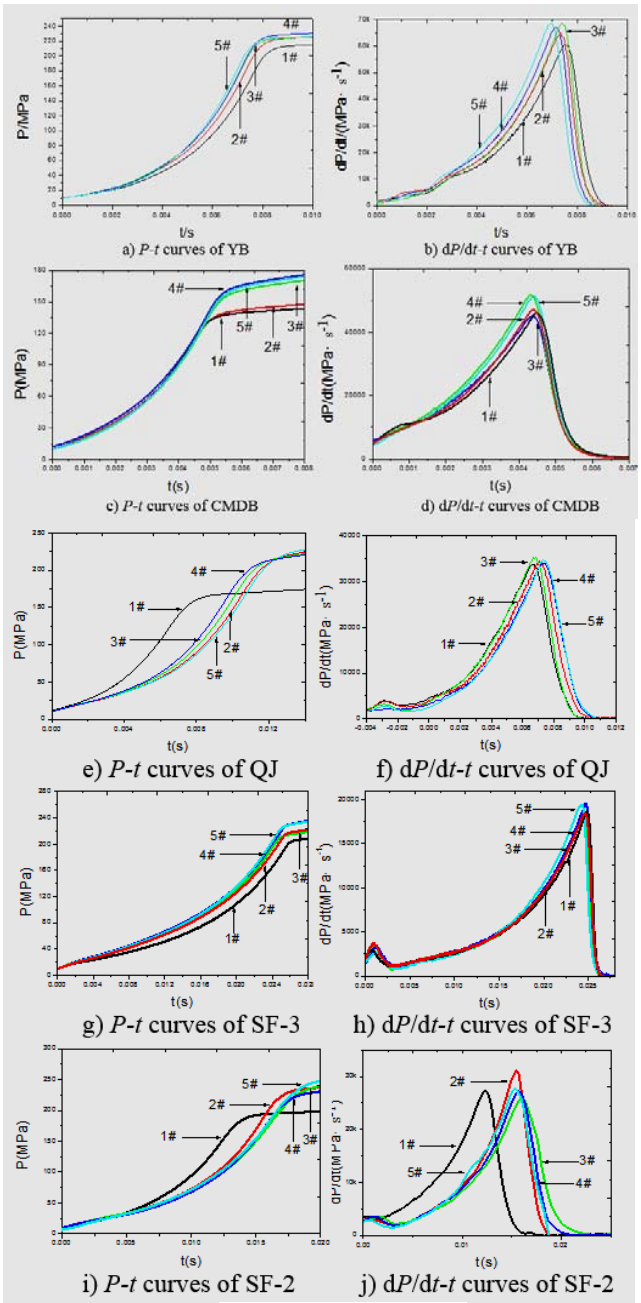


Fig.4 *P*-*t* curves and d*P*/d*t*-*t* curves.

The experiment results are calculated in Table 6.

As shown in the Figure 4 and Table 6, maximum pressure of 5 kinds of propellants all increase after mixed with isopropyl nitrate because of the combustion of isopropyl nitrate.

Combustion time of YB single-base propellant and CMDB propellant reduce after adding isopropyl nitrate. Combustion time of QJ single-base propellant and SF-2 triple-base propellant increases after adding isopropyl nitrate. Combustion time of SF-3 double-base propellant with isopropyl nitrate does not change significantly.

As for CMDB propellant, the reaction of isopropyl nitrate and aluminum promotes the combustion of propellant. As a result, the combustion time is shorter.

TABLE 6 MAXIMUN PRESSURE AND COMBUSTION TIME

Propellant	group	Δ_1		Δ_2	
		P_m[MPa]	t[ms]	P_m[MPa]	t[ms]
YB	1#	108.33	10.17	187.20	8.23
	2#	108.63	10.06	190.00	7.90
	3#	113.39	9.80	193.84	7.67
	4#	114.97	9.66	193.02	7.63
	5#	118.32	9.67	197.69	7.83
CMDB	1#	76.83	8.30	121.46	7.67
	2#	79.95	8.27	122.74	7.60
	3#	81.62	8.03	127.49	7.45
	4#	82.64	8.23	127.57	7.05
	5#	85.89	8.10	130.67	7.55
QJ	1#	74.46	13.73	150.36	12.57
	2#	78.23	15.83	153.44	12.60
	3#	86.67	16.70	158.06	13.33
	4#	83.48	16.53	157.94	13.50
	5#	92.61	18.77	160.73	14.33
SF-3	1#	83.32	36.9	148.13	26.70
	2#	83.56	37.0	149.45	26.07
	3#	85.27	36.2	150.03	26.06
	4#	85.29	34.1	152.09	26.17
	5#	88.08	37.0	155.00	26.17
SF-2	1#	80.63	19.34	165.79	16.51
	2#	91.79	24.13	167.56	17.08
	3#	92.36	25.12	169.34	19.41
	4#	93.04	25.17	165.88	19.36
	5#	92.99	23.85	168.99	17.34

P_m is maximum pressure. t is combustion time.

Impetus f and covolume α[16] can be calculated through:

$$\alpha=\frac{P_{m2}/\Delta_2-P_{m1}/\Delta_1}{P_{m2}-P_{m1}} \tag{9}$$

$$f=\frac{P_{m2}}{\Delta_2}-\alpha\cdot P_{m2} \tag{10}$$

P_{m1} is the average maximum pressure of low charge density Δ_1. P_{m2} is the average maximum pressure of high charge density Δ_2.

The calculation results are shown in Table 7.

As shown in the table, the impetus increase and the covolume reduce after mixed with isopropyl nitrate. The reason is that the combustion of isopropyl nitrate creates energy and gases.

Burned propellant percentage Ψ_e, pressure impulse I_e and gas generation brisance Γ_e at potential balance point are calculated. The parameters of CMDB propellant are listed in Table 8.

TABLE 7 IMPETUS AND COVOLUME

Prope-llant	Param-eter	1#	2#	3#	4#	5#
YB	f	880.51	955.137	965.54	1017.73	1055.28
	α	1.11	1.06	0.97	0.73	0.67
CMDB	f	974.29	1010.90	1035.29	1078.00	1116.74
	α	1.17	0.93	0.55	0.34	0.32
QJ	f	558.93	604.764	671.028	726.878	827.954
	α	2.60	2.36	2.07	1.72	1.16
SF-3	f	752.39	768.20	784.94	795.81	803.09
	α	1.13	1.01	0.98	0.87	0.76
SF-2	f	596.20	759.29	769.88	776.12	783.46
	α	2.72	1.84	1.77	1.70	1.68

The unit of f is J•g^{-1}. The unit of α is cm^3·g^{-1}.

TABLE 8 CHARACTERISTIC PARAMETERS OF CMDB PROPELLANT

group	Δ_1			Δ_2		
	Γ_e	I_e	Ψ_e	Γ_e	I_e	Ψ_e
1#	4.042	0.157	0.815	3.709	0.162	0.791
2#	4.046	0.159	0.817	3.382	0.166	0.784
3#	3.957	0.157	0.803	3.502	0.176	0.816
4#	4.083	0.154	0.798	3.730	0.173	0.798
5#	3.956	0.156	0.788	3.694	0.173	0.789

The unit of Γ_e is (MPa·s)$^{-1}$. The unit of I_e is MPa·s.

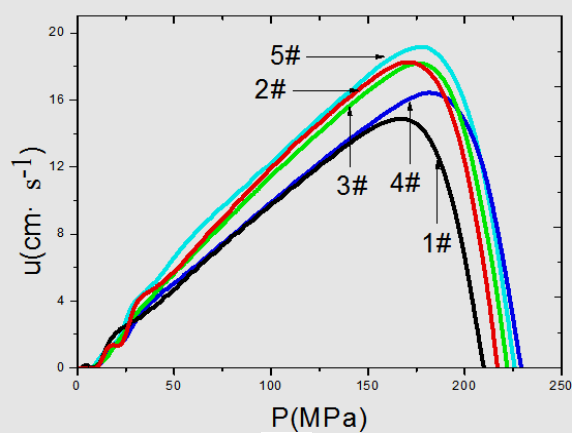
Three kinds of parameters do not change significantly by comparing data in Table 8. Other propellants experiments are the same results. It means that isopropyl nitrate does not affect these characteristics of propellants.

The combustion rate law[17] is a formula describing the combustion rate u and pressure P.

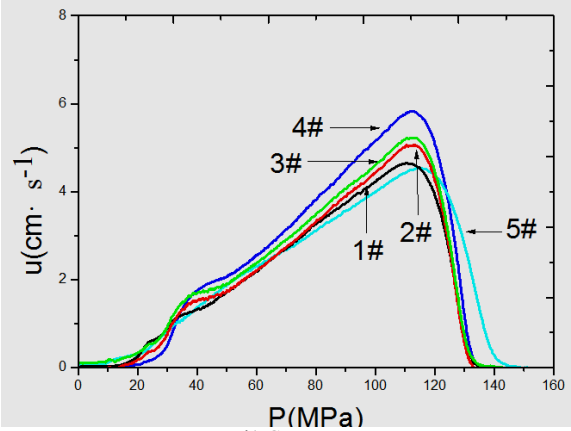
$$u=AP^v \tag{11}$$

A is combustion rate coefficient, v is pressure index.

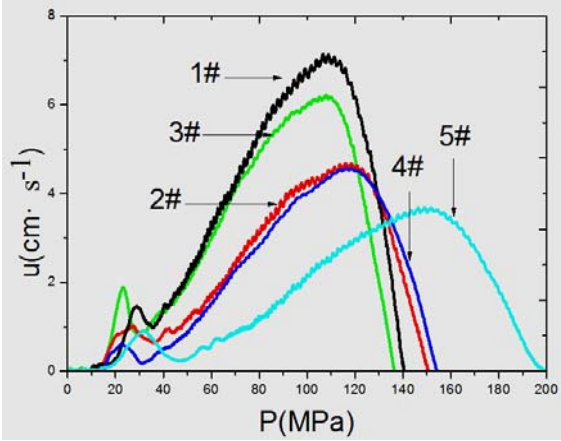
Figure 5 is the u-P curves of propellants.



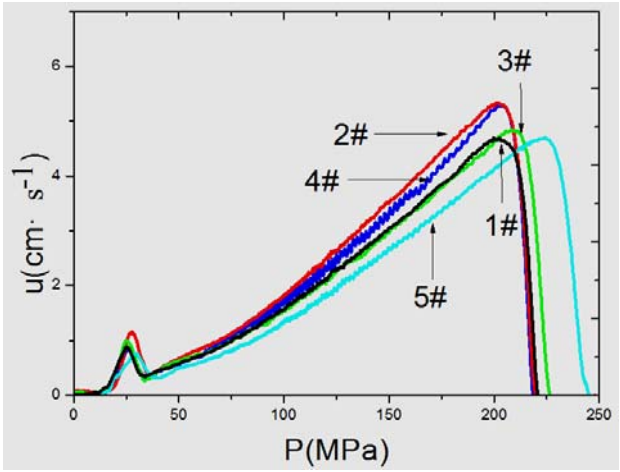
a) YB



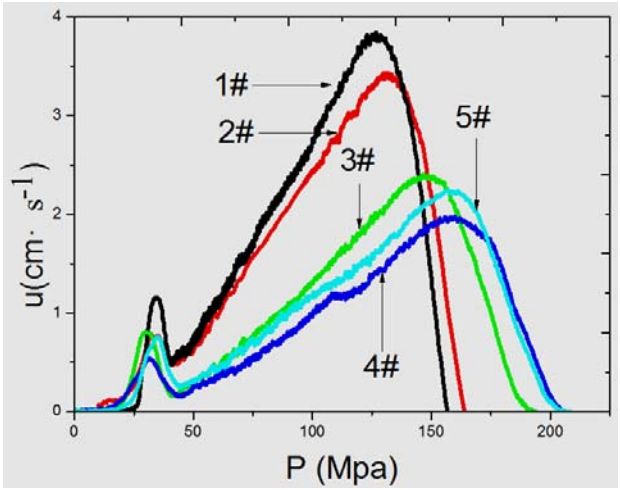
b) CMDB



c) QJ



d) SF-3



e) SF-2

Fig.5 *u-P* curves of propellants.

Table 9 is the calculation results.

As shown in Table 9 and Figure 5, combustion rate coefficients of YB single-base propellant and CMDB propellant are higher and pressure indexes become lower with isopropyl nitrate. Combustion rate coefficients of QJ single-base propellant and SF-2 triple-base propellant are lower and pressure indexes become higher. Combustion rate coefficients and pressure indexes of SF-3 double-base propellant with isopropyl nitrate do not change significantly.

The change of combustion rate coefficient reflects the change of combustion rate. When the combustion rate is slower, the combustion time is longer and the combustion rate coefficient drops.

TABLE 9 COMBUSTION RATE LAW CALCULATION RESULTS

propellant	group	Δ_1		Δ_2	
		A	*v*	*A*	*v*
YB	1#	4.793	0.82	3.967	0.86
	2#	5.082	0.79	5.030	0.81
	3#	5.736	0.78	4.386	0.84
	4#	6.067	0.77	4.144	0.86
	5#	6.275	0.75	4.400	0.84
CMDB	1#	9.40	0.78	8.27	0.87
	2#	9.53	0.76	8.44	0.85
	3#	9.88	0.78	8.27	0.83
	4#	10.40	0.72	8.38	0.86
	5#	9.89	0.78	8.24	0.86
QJ	1#	9.976	0.415	4.235	0.596
	2#	6.193	0.519	3.886	0.612
	3#	5.997	0.525	3.433	0.638
	4#	3.643	0.664	2.834	0.681
	5#	2.545	0.698	2.364	0.715
SF-3	1#	7.347	1.04	7.767	1.11
	2#	9.238	0.95	8.783	0.98
	3#	8.996	0.97	7.519	1.06
	4#	7.602	1.03	9.302	0.97
	5#	7.310	0.98	7.913	1.03
SF-2	1#	8.573	0.60	6.327	0.61
	2#	5.776	0.73	5.736	0.67
	3#	2.162	0.89	2.276	0.84
	4#	2.512	0.86	3.082	0.80
	5#	2.772	0.83	3.828	0.74

The unit of *A* is $m \cdot s^{-1} \cdot MPa^{-1} \times 10^{-4}$.

IV. CONCLUSIONS

The thermal analysis experiment and combustion performance experiment are done to test the influences on performance of propellants. It is found that isopropyl nitrate causes different influences on different propellants by reacting with propellant component or its own combustion.

In the future, the technology should be improved to prevent isopropyl nitrate from leaking out in the production and reform process. The propellant used in ammunition with FAE warhead should not contain components that react with isopropyl nitrate.

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