Influence of Carbon Black on Combustion Performance of RDX-CMDB Propellant

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Influence of carbon black (CB) on burning rate (u) and pressure index (n) of high-heat RDX-CMDB propellant are investigated. Eight kinds of CB with different specification and of different sources are used. It is observed that the addition of CB into the matrix plays a key role in reducing n, when the lead salt of aromatic acid and the copper salt of fatty acid are present in definite proportion. The results of experiments have shown that presence of heat-resisting aromatic acid lead, which begins to decompose above 750℃, is not a necessary precondition for decreasing n of a high-heat propellant. However, the particle diameter ($\bar{d}$) of CB may be an important control factor among various chemical and physical properties of CB. And neither very fine CB (~5 mμ) nor coarser CB (~63 mμ) can decrease the value of n obviously, while the CB with medium $\bar{d}$ (24-35mμ) can exert a better effect for improvement of n.

We have also observed that the influence of CB on burning performance of RDX-CMDB propellant is similar to that of low-heat DB propellant.

Some phenomena of experiments are explained qualitatively.

1. Introduction

It has been well-known since early times that carbon black (CB) plays a role of opacifier or radiation-resisting. Later, with the development of plateau DB propellants, while researching the effect of various lead salts as plateau ballistic modifier on reducing pressure index (n) of DB propellant, people found[1] that burning rate (u) of propellant could be raised greatly by CB and certain of dyes ; and plateau burning rate was highly increased when content of CB was lower (about 0.2%). But if CB was over 0.5% of amount, n became bigger, and plateau disappeared when more than 1%. It was also shown that burning rate of DB propellant with 4% β-resorcin lead and 0.4% Carbalac I CB, which heat of explosion equaled 1350 cal/g, was 28 mm/sec at 77.3 kg/cm² which was 38% higher than those without CB.

For the fact that burning rate can be increased by CB, A. П. Денисюк considered[2] that CB inhibits particles of lead catalyst on combustion surface from gathering and keeps them closing to combustion surface, so that catalytic activity of the lead salts is increased and u, as result, increased. D. T. Hewkin thought[3] that CB was a good catalyst for many reactions of gas phase and a good catalyst carrier as well and it seemed to be the active center when lead exists. Carbon, both produced by burning of DB propellant on combustion surface and added into the formulation beforehand, could accelerate the exothermal reaction in which NO was reduced to N_2 near the combustion surface, leading to the increase of u. With increase of pressure, carbon (or CB) was oxidated continuously by NO, so u was decreased gradually and n became smaller.

People are interested in the effect of CB and other catalysts on combustion performance of

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Table 1 Effect of CB types, chemical

test number NO.	CB symbol	Production process	use	arithmetic mean diameter (electron microscope method) mμ	chemical and physical pro-					
					specific surface (electron microscope method) M^2/g	iodine adsorption mg/g	oil absorption ml/g	PH	ash %	Volatiles %
1	T	furnace	rubber	63.3	—	29.9	0.59	9.6	0.23	0.4
2	E	thermal decomposition	bettery	34.9	85.9	87.5	3.42	5.6	0.05	0.1
3	ZG	furnace	rubber	26.6	101.1	142.6	1.34	9.2	0.25	0.6
4	Z1	〃	〃	28.5	97.5	125.1	1.15	8.7	0.14	0.7
5	Z2	〃	〃	27.1	95.5	128.1	0.99	7.4	0.32	0.7
6	Z3	〃	〃	24.4	108.0	136.1	1.26	7.9	0.12	0.7
7	H	fire room	〃	30.6	91.8	~90	0.99	3.2	0.01	3.8
8	X	rolling cylinaer	coating	~5	(BET) 440.6	—	1.65	3.1	0.17	6.4
0	Basic formulation (without CB) is an CMDB propellant containing RDX (19%), Al (9.5%) and lead-copper salts. The rate of lead-copper salts is 1 : 0.30									

Note : except sample NO. O without CB, each of samples (NO. 1 – 8) contains 0.4% CB.

CMDB propellant containing RDX and Al which is the subject of this paper. According to Kubota [6], because of the obvious differences between chemical and physical properties of nitramine and AP, the structures of combustion wave of CMDB propellants containing nitramine and AP are different accordingly. The former is similar to DB propellant. Therefore it may be estimated that effect of CB on combustion of CMDB propellant containing nitramine is similar to DB propellant, and can be explained by aforesaid theories.

2. Sample and method of test

The basic formulatin (without CB) is an CMDB propellant containing RDX (19%), Al (9.5%) and lead-copper salts. The rate of lead- copper salts is 1 : 0.30. A conventional method was used to prepare samples, i. e, slurry, rolling and screw extrusion. The strand was 4 millimeters diameter and 130-140 millimeters long, coating with inhibitor. Burning rates of strands were measured in a Crawford bomb and *n* was then reduced. The characteristics of some samples were examined by small test motors.

3. Effect of CB specification

Carbon black mainly is used in industrial productions such as rubber, printing inks, coating and plastics. There are more than twenty items of specification for CB according to different requirement of use. Since CB mainly is used as combustion catalyst in solid propellant, we put our emphasis only on the following properties of CB : particle-size, specific surface area, structure, PH, volatiles, hydrogen and oxygen content, conductivity, etc, and their effects on *u* and *n* so as to find the inner relation among them.

Carbon black principally is made from carbons which have nature of sub-graphitoid micro-crystal. Its particle-size is very small, varying from 5 to 500 mμ which can be represented by arithmetic mean diameter ($\bar{d}$). Though its specific surface can be measured by electron-microscope and BET, measurement will be done quickly by means of iodine adsorption with which the value obtained is approximately equal to that with BET. The structure of CB can be shown by oil absorption value, the bigger the oil absorption, the higher the structure.

Table 1 lists data of effect of eight kinds of CB and physical properties on u and n

perties of CB				$P=125kg/cm^2$		Pressure index n					
						Pressure range kg/cm^2					
C %	H %	S %	O %	burning rate u mm/sec	catalysis efficiency u/uo	$P=80-100$	$P=100-125$	$P=125-150$	$P=150-175$	$P=100-150$	$P=100-175$
98.6	0.37	0.30	0.33	15.17	1.06	0.33	0.49	0.63	—	0.56	—
99.6	0.14	0.13	0.06	20.08	1.40	0.39	0.24	0.22	0.24	0.23	0.23
98.2	0.41	0.46	0.60	19.61	1.37	0.35	0.22	0.28	0.43	0.25	0.31
98.0	0.47	0.27	0.98	20.62	1.44	0.40	0.34	0.22	0.36	0.28	0.31
97.4	0.28	0.33	1.55	20.92	1.46	0.41	0.39	0.31	0.34	0.35	0.35
97.8	0.36	0.50	1.09	22.22	1.55	0.40	0.37	0.38	0.30	0.38	0.35
93.4	0.97	0.20	5.32	21.69	1.52	0.39	0.26	0.18	0.41	0.22	0.28
—	—	—	—	23.58	1.65	0.47	0.32	0.56	—	0.44	—
and lead - copper				14.31	1.00	0.34	0.45	0.65	0.88	0.55	0.66

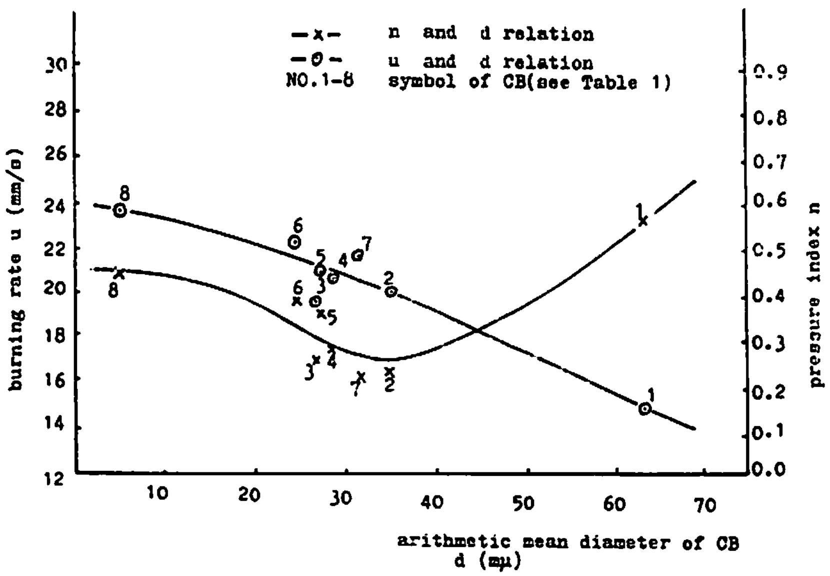

Fig. 1 Effect of CB particle size on u and n

with different specification and sources on u and n of nitramine propellant.

Range of the CB specification in Table 1 are as follows ;

PH——from 3.2 to 9.6 ;

structure (shown by oil adsorption) ——from 0.99 to 3.4 ;

volitiles——from 0.09 to 6.41 ;

oxygen content——from 0.06 to 5.32 ;

hydrogen content——from 0.14 to 0.97.

It can be seen that the effect of CB of different specification on u and n of propellant is irregu-

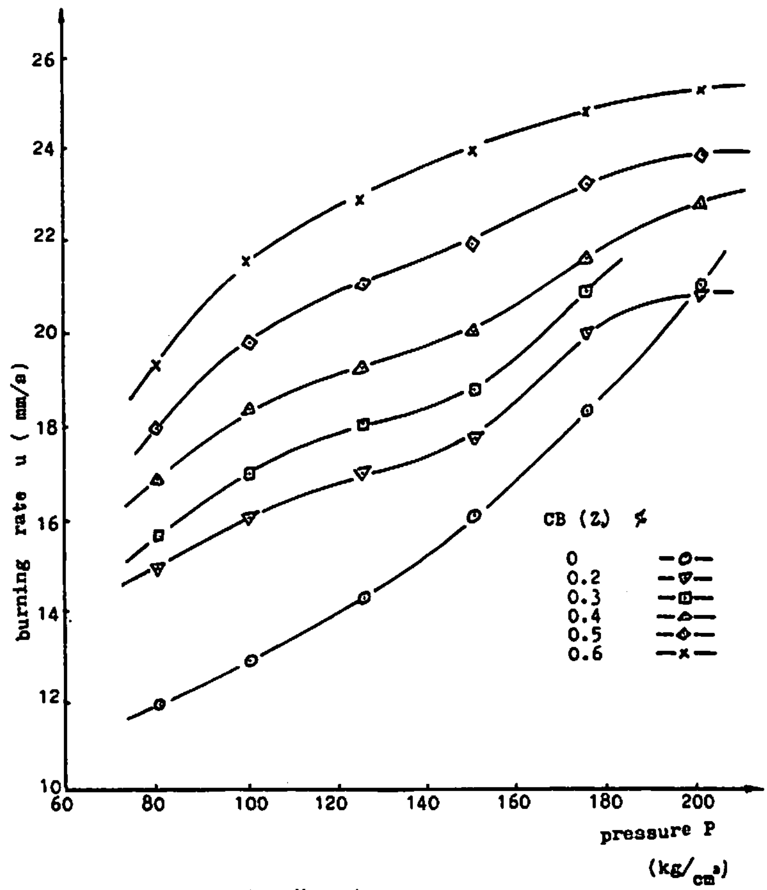

Fig. 2 Effect of CB content on u and n

lar. However, in raising u, d and specific surface of CB play an important role which is similar to that in low-heat DB propellants. As shown in Fig. 1 and Table 1, $\bar{d}$ is inversely proportional to u and the relationship of $\bar{d}$ and u is approximately linear in the range of $\bar{d}=63\text{-}25\,\mathrm{m}\mu$, that is, the slope of the curve is bigger. For example, when $\bar{d}$ decreases from 63 mμ to 24-34 mμ (1/2~1/3 of the original), u increases by 1.37-1.55 times, while $\bar{d}$ decreases from 25 to 5 mμ (1/5 of the original), u just increases by 1.12 times, i.e, the curve slopes gently. Moreover, in respect to improvement of n from Fig. 1 it also can be seen that except CB (T) and CB (X) the other six kinds of CB (H, $Z1\sim3$, ZG and E) which have different specifications and come from different manufacturers can reduce n less than 0.35 over the pressure range of 100 to 175 kg/cm², the optimum n being 0.23 by using CB (E). Perhaps, a good conductivity of CB (E) is one of the reasons that lowers n. Among the six kinds of CB, there are four kinds to have n less than 0.3 over the pressure range of 100-150 kg/cm². The order of CB can be arranged as follows according to n value from small to big:

$E<H<ZG,\ Z_1<Z_2, Z_3<T<X.$

Neither fine CB (~5 mμ) nor coarser CB (~63 mμ) can decrease the value of n obviously, while the CB with medium $\bar{d}$ (24-35mμ) can exert a better effect on improving n. The facts have therefore shown that among many chemical and physical properties of CB, the influence of $\bar{d}$ and specific surface of CB on improving n and u may be important control indexes.

It is special interesting that CB is efficiency not only to increase u of RDX-CMDB propellant of high-heat, but also to decrease n clearly while CB is used in combination with some aromatic

Table 2 Effect of CB content on u and n

test number	CB content (weight) %	$P=100$ kg/cm²		Pressure index n				
				Pressure range				
		burning rate mm/s	catalysis efficiency (u/u_0)	$P=80-100$ kg/cm²	$P=100-125$ kg/cm²	$P=125-150$ kg/cm²	$P=150-175$ kg/cm²	$P=175-200$ kg/cm²
1	0	12.95	1.00	0.34	0.45	0.65	0.88	>1
2	0.2	16.10	1.24	0.31	0.27	0.23	0.80	0.28
3	0.3	17.06	1.31	0.37	0.27	0.22	0.70	—
4	0.4	18.48	1.43	0.39	0.20	0.23	0.48	0.40
5	0.5	19.88	1.54	0.44	0.27	0.24	0.38	0.18
6	0.6	21.65	1.67	0.49	0.28	0.23	0.19	0.13

Note : a. Basic fomulation is the same with Table 1.
b. Used CB (Z_1)

acid lead and fatty acid copper salts in proper proportion. The detail mechanism of such a "Synergism" among CB-lead salt-copper salt has been unclear, and needs to investigate deeply in future.

4. Effect of CB content

The relation of CB content against n or u in low-heat propellants was reported long ago[1]. The effect of CB content on u and n in nitramine propellant is obvious in this paper (see Table 2). The burning rate of propellant increases gradually with the increase of CB content. When the content of CB is over 0.6%, u tends to increase continuously. In this case, the catalysis efficiency of increasing burning rate (u/u_0) is up to 1.67 and u increases from 12.9 (without CB) to 21.65 mm/sec (CB=0.6%). This rule is similar to that of low-heat DB propellant. Clearly, CB is most effective catalyst in increasing u among three catalysts, playing a main part in adjusting u. In addition, the n of propellant gradually decreases with the increase of CB content. At first, the curve of u against p takes the shope of S which disappeares by degrees with the rising of CB content ; pressure area of low n tends to high pressure and n is less than 0.2 (at 150-200 kg/cm², 0.6% CB). This tendency is also similar to that of low-heat DB propellant.

5. Discussion

Preckel[1] once showed that plateau burning could only occur in high-heat propellant in which heat-resisting aromatic acid lead (decomposing temperature is over 750℃) was added instead of lead stearate. We use a sort of aromatic acid lead as catalyst, which thermal decomposition at just 240℃. When the lead salt was alone or combined with either fatty acid copper or CB added into nitramine propellant, the effect of improving n was not remarkable. while three kinds of combustion catalysts (lead salt-copper salt-CB) were added together in definite proportion, n decreased considerably. It can therefore be seen that the heat-resisting of aromatic acid lead is not the precondition for plateau burning, while the existance of CB with definite $\bar{d}$ is its important condition. We can imagine that because of the high temperature of burning surface (T_s) of high-heat propellant containing aromatic acid lead and fatty acid copper salts which makes less carbon exist on the burning surface, the super-burning can not be formed. If a proper amount of CB is added, the carbon content on burning surface will be increased and which can accelerate the reducing reaction of NO, leading to super-burning and plateau.

For the fact that CB (X) with super-fine particle and CB (T) with coarser particle have unremarkable effect on improving n, we try to explain as follows : Since T_s of high-heat propellant is high up to 400℃ and the kindling temperature of CB is just 290-380℃, super-fine CB ($\bar{d}=5\text{m}\mu$) is oxidized rapidly in the vicinity of burning surface, and then disapears. As for the coarse CB ($\bar{d}$ = 63 mμ), it can not prevent lead catalyst from gathering together on the burn-surface. In view of above two reasons, catalysis effects of both CB (X) and CB (T) are not satisfactory.

The explaination, however, is nothing but a deduction based on the previous plateau theories. In fact, the surface properties of CB is very complex. For example, on the periphery of its aromatic nucleus there are many surface functional groups, such as carbonyl, phenol, lactone and quinone which probably also participate the mechanism of combustion catalytic reaction. Consequently, the combustion catalysis of CB is very complex, too. We need to use some more advanced and accurate means to investigate it.

6. References

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RDX-CMDB 推進薬の燃焼特性に対するカーボンブラックの影響

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高エネルギーRDX－CMDB推進薬の燃焼速度（u）と圧力指数（n）に対するカーボンブラック（CB）の影響を求めた。異なった8種の CB を用いて推進薬を試製した。芳香族系の鉛塩と脂肪族系の銅塩が最適比で混合され，これに CB が添加されることが，n を低減させるための最重要なポイントであることが明らかになった。750℃以上で分解する耐熱性芳香族系の鉛塩は高エネルギ推進薬の n 低域のための必要条件にはなっていない。CB の粒径（$\bar{d}$）は CB の有する数多くの物理化学的特性のうち重要な因子となっている。ただし，微粒（～5μm）であっても大粒（～63μm）であっても n 低減には十分な効果を示さず，中粒（24～35μm）の CB が効率良く n を低減させる。

本研究では RDX－CMDB 推進薬の燃焼速度に対する CB の効果が低エネルギ・ダブルベース推進薬に対する CB の効果と同様であることを確認した。

実験で観察したいくつかの現象については定性的ではあるが検討を加えた。

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