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Burning-Rate Modifier Effects on a Modified Polyvinyl Chloride-Based Propellants

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Combustion of the composite solid rocket propellants series known as Flexolite and various additives were studied. All of the Flexolite series of propellants are based on ammonium perchlorate as oxidizer and modified polyvinyl chloride as binder. Several burning-rate modifiers were utilized separately in basic propellant formulations, to determine their effects on propellant burning rate. It was shown that burning-rate modifiers have a substantial effect on the burning rate, increasing it in dependence of their amount in propellant formulation. Influence of one new burning-rate modifier is shown on both nonaluminized and aluminized formulations and is compared with other standard modifiers. Also, the influence of plasticizers on propellant burning rate of nonaluminized propellant with a new burning-rate modifier is shown. All burning rates were measured in a special test motor at different pressures, using small-motor measurement method.

Introduction

It is well known that the addition of small quantities of inorganic and organic substances to a solid rocket propellant can drastically alter the burning rate. These materials are normally used at the 1–3% level to regulate the propellant burning rate beyond that achievable by particle size adjustment. Increasing amounts of catalyst reduce the specific impulse because they are normally nonenergetic diluents.

The purpose of this work is to study effects of various modifiers on the burning rate of composite solid rocket propellants from the Flexolite series. Also, effects of changes of level of plasticizer in propellant compositions on burning rate of propellant have been investigated. The Flexolite series of propellant consist of 70–80% by weight of finely divided inorganic solids uniformly dispersed in a continuous matrix of organic elastomeric binder. Solids (also known as fillers) comprise ammonium perchlorate (AP) as oxidizer and sometimes aluminum as powdered metal, whereas the binder consists of modified polyvinyl chloride (PVC) polymers and plasticizer. Minor ingredients, normally less than 2% of the total, consist of stabilizer, processing additives, opacifier, and burning-rate modifier. Selection of components in Flexolite compositions is limited to those that are produced in large quantities by the chemical industry. All ingredients are standard materials and are commercially available. An originally developed process for producing grains is presented briefly.

Experimental Procedures

The whole Flexolite series of propellants can be divided into three groups on the basis of their energy properties: low-energy, medium-energy, and high-energy propellants. Totally 21 propellant formulations, shown in Tables 1–3, with different catalysts were prepared for measurements in medium-energy and high-energy propellants. All propellants were produced using the same processing cycles, with constant binder type and composition.

Four ammonium perchlorate grinds with nominal particle size 200, 100, 60, and 20 μm were used in experimental propellants. The first grind was commercially supplied, whereas the other three grinds have been obtained by milling on the standard hammer mill. The size distribution of individual size fractions was measured using one of the existing standard techniques. For size fraction of 90- and 200-μm nominal size, standard screen analysis was employed. For size fractions of nominal size 20 and 60 μm, the micromerograph was employed. Particle-size analysis for these four AP grinds is shown in Fig. 1. The particle size of burning-rate modifiers added to the propellant formulations were not measured, and therefore, specific areas of the additives were not determined.

Sicomin-Rot K 3130 S manufactured by BASF, copper chromite ($CuO\ Cr_2O_3$) manufactured by Aldrich, iron oxide (Fe_2O_3), and aerosil (SiO_2) manufactured by Alkaloid, Skoplje, are used as catalysts. It appears from the literature that this is the very first attempt of using Sicomin-Rot K 3130 S as catalyst for burning-rate measurement. This catalyst is a mixed crystal consisting of lead chromate, lead molybdate, and lead sulphate, which is stabilized by coating with silicate and antimony compounds. Its general formula is $Pb(Cr,S,Mo)O_4$, density is $\rho = 5777$ kg/m^3, and mean diameter is below 1 μm.

Processing technique known as TEPVAC procedures[1] were employed to prepare the propellant grains. All ingredients, oxidizer, polymers, plasticizer, and additives, were weighed and mixed. The slurry of mixed material was poured on the two-roll mill, where the propellant is obtained in the form of sheet. The piece of sheet with defined dimension is rolled into cylindrical form to obtain the preblock form. The preblock form was covered with insulated sheet laterally and from both heads and placed into the appropriate tool. This preblock in the tool was heated, evacuated, and later pressed at defined temperature and pressure. Finally, a grain 63 mm in outside diameter was formed.

All burning rates reported in this paper were measured using the small-motor measurement method.[2] The method is based on a pressure vs time trace (Fig. 2), obtained by burning a small cylindrical grain with known development of burning surface. Analysis of this trace with an internal ballistic model, based on nozzle as a mass flowmeter, permits direct computation of the instantaneous burning rate of solid rocket propellants at different instantaneous pressures during one test. The grain has cylindrical shape with concentric bore and is inhibited from both heads and laterally. This form enables the propellant grain to have a progressive surface spread during burning.

Measurements have been performed in a special test motor developed for that purpose (Fig. 3). Grains were ingnited by electric igniter. The burning rate was measured at different pressures from 2 to 20 MPa at ambient temperature (288 K). All measurements were checked at least twice at each pressure, and average values were used. In a few tests, burning-rate data from this method were correlated with burning rates obtained by the microwave reflection

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interferometry method.[3] Results of burning rates from these two methods show good agreement.

Results and Discussion

The burning rate of solid propellants depends on a number of parameters: on the pressure and on the initial propellant temperature, crossflow velocity, propellant type, fuel-to-oxidizer ratio, and oxidizer particle size in the case of composite propellants. Generally, the burning rates of solid propellants may be described by the linear empirical equation (Saint–Robert's or Vielle's law):

$$r = b \cdot P_c^n \quad (1)$$

where P_c is combustion chamber pressure, b is the coefficient of pressure, and n is pressure exponent. The experimental results summarized in Figs. 4–19 have been presented as effects of burning-rate modifiers on the burning rate of various propellant formulations in dependence of pressure. All of the data were correlated with Saint–Robert's law, where ΔQ is standard deviation of the burning rate in comparison with Saint–Robert's law. Figures 4–13 show the influence of catalysts on medium-energy propellant formulations, whereas Figs. 14–19 show this influence on high-energy propellant formulations.

Medium-Energy Propellants

Different ingredients such as copper chromite, iron oxide, and other transition metal compounds have long been known to increase the burning rate of pure AP as well as AP-based composite propellants. The particle size and state of aggregation of each catalyst, which have great influence on burning rate of propellants, are different. This is why the quantitative comparison of the relative catalyst effectiveness in mechanistic terms is difficult when dealing with solid catalysts.

Copper chromite is a nonstoichiometric material, whose properties depend on the method of manufacture. There are many papers that are deal with the catalytic effect of copper chromite. Copper chromite catalyzes the decomposition of AP (Refs. 4 and 5), and the catalysis takes place in the solid phase.[6] The copper chromite catalyst enhances high-temperature decomposition.[5,7,8] In the area of combustion of AP and copper chromite, it was found that small amounts of the catalysts increased the low-pressure deflagration limit, whereas large amounts, 10%, decreased this limit.[9,10] It was also found that copper chromite enhanced the burning rate over that of AP alone.[10]

Numerous investigators have also extensively studied iron oxide. Ferrous ions are formed at the burning temperature of the propellant, whereas a very complicated reaction mechanism occurs at high temperature. Burning rate was found to be a function of both the catalyst area as well as the oxidizer area.[11] On the other hand it was found, on the basis of the results on AP/polymethyl methacrylate (PMMA)/Fe_2O_3 mixtures, that the dependence of burning rate on the catalyst area was very small.[12,13] The catalysts action was explained by that only the outside exposed surface affects the rate. Correlation between burning rate and thermal decomposition by the addition of various metal oxides was not found,[7] which suggested that the gas-phase processes rather than the solid phase are critical in controlling the burning rate. It appears from sandwich studies that iron oxide acts in the interface between the oxidizer and binder. The experimental results on the effects of transient metal oxides on the propellant combustion[6] indicate that the catalysts influence reactions in both the solid and gaseous phases. Catalysts also influence gas-phase and condensed-phase reactions[14] in combustion of condensed mixtures containing polystyrene or PMMA and AP with iron oxide as catalyst. A diffusion-controlled mechanism taking into account the competition of the catalytic and homogeneous reaction was also proposed.[10]

It appears that in PVC plastisol propellants[15] the addition of 2% of iron oxide or 1% of chromic oxide increase burning rate 10%. Copper chromite (Cu-0202P from Harshaw Chemical Company) is more effective: 0.2% increases the burning rate for 25%. Copper chromite has proved to be the most useful additive for increasing the burning rate, and in addition, it has a persistent tendency to lower the pressure exponent.

Three different solid catalysts were investigated with the Flexolite series medium-energy propellants: copper chromite (CC), iron oxide (IO), and Sicomin-Rot K 3130 S. Their compositions are shown in Tables 1 and 2. The basic medium-energy formulation is labled A. The addition of catalyst to formulation A is accompanied with a reduction in aluminum, oxidizer, and binder level. In the pressure intervals of the study, the burning rate of the catalyzed materials was above that for the pure formulation A (without catalysts).

Influence of CC and IO on burning rate of propellant A is shown in Fig. 4 for AP 20-μm grind. Because Flexolite propellants do not have rheologic problems with greater percent of CC, CC was added at levels of 0.5, 3, and 5%. The addition of IO was 3%. It can be seen from Figs. 4 and 5 that CC is a better catalyst that IO for 3% below 9 MPa, and that 5% of CC has no significant effect on burning rate

Table 1 Compositions of medium-energy propellants with catalysts

Composition, weight %	A	B	C	D	E
Oxidizer	75.00	74.50	75.00	73.50	75.00
Aluminium	0.50	0.50	0.50	——	0.50
Binder	23.40	23.65	20.60	20.60	20.60
Stabilizer	0.55	0.50	0.50	0.50	0.50
Processing additive	0.25	0.25	0.25	0.25	0.25
Carbon black	0.30	0.10	0.15	0.15	0.15
CC	——	0.50	3.00	5.00	——
IO	——	——	——	——	3.00
Density, kg/m^3	1680	1690	1735	1750	1740

Table 3 Compositions of high-energy propellants

Composition, weight %	O	P	Q	R	S	T
Oxidizer	69.75	69.55	69.70	69.70	69.55	69.55
Aluminium	10.00	10.00	10.00	10.00	10.00	9.70
Binder	19.40	19.40	18.80	18.30	19.40	19.40
Stabilizer	0.50	0.50	0.50	0.50	0.50	0.50
Processing additive	0.25	0.35	0.40	0.50	0.25	0.25
Carbon black	0.10	——	0.10	——	0.10	0.10
Aerosil		0.20	0.50	1.00	——	——
Sicomin-Rot K3130 S	——	——	——	——	0.20	——
IO	——	——	——	——	——	0.50
Density, kg/m^3	1765	1770	1770	1770	1762	1762

Table 2 Compositions of medium-energy propellants with Sicomin-Rot K 3130 S catalyst

Composition, weight %	A	F	G	H	I	J	K	L	M	N
Oxidizer	75.00	74.50	74.00	75.00	75.00	75.00	74.50	73.50	73.50	73.00
Aluminium	0.50	0.50	0.50	0.50	0.50	0.50	0.50	——	——	——
Binder	23.40	23.65	23.65	20.60	20.60	20.60	20.60	20.60	20.60	20.60
Stabilizer	0.55	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Processing additive	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Carbon black	0.30	0.10	0.10	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Sicomin-Rot K3130 S	——	0.50	1.00	3.00	3.00	3.00	3.50	5.00	5.00	5.50
Density, kg/m^3	1680	1685	1695	1745	1740	1735	1753	1770	1755	1776

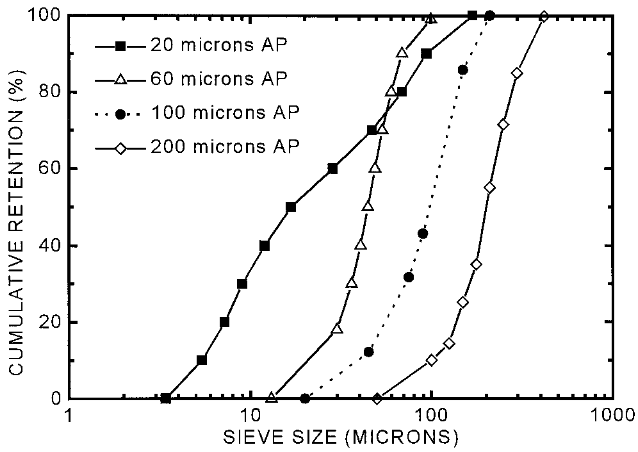

Fig. 1 AP particle size distribution data.

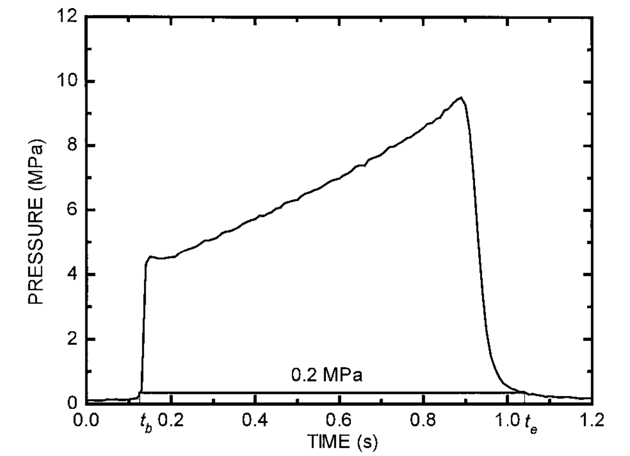

Fig. 2 Typical pressure vs time trace obtained from one static firing test.

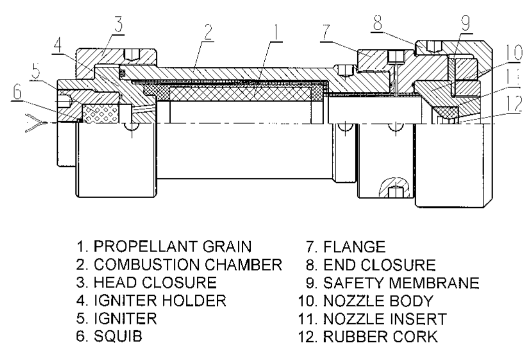

Fig. 3 Experimental motor.

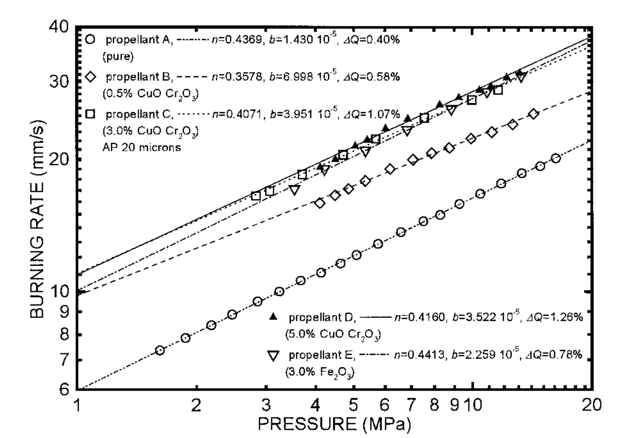

Fig. 4 Influence of CC and IO on medium-energy propellants (AP 20 μm).

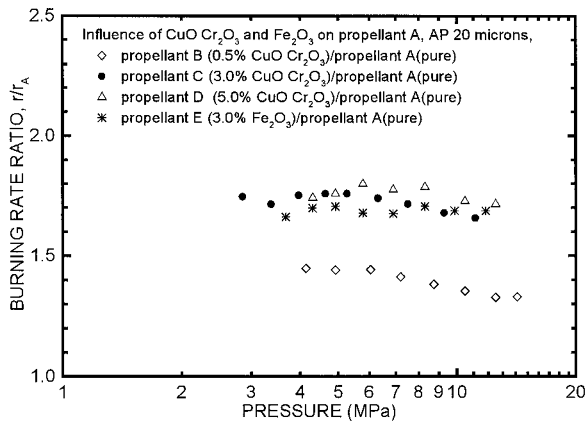

Fig. 5 Influence of CC and IO on basic propellant A (AP 20 μm).

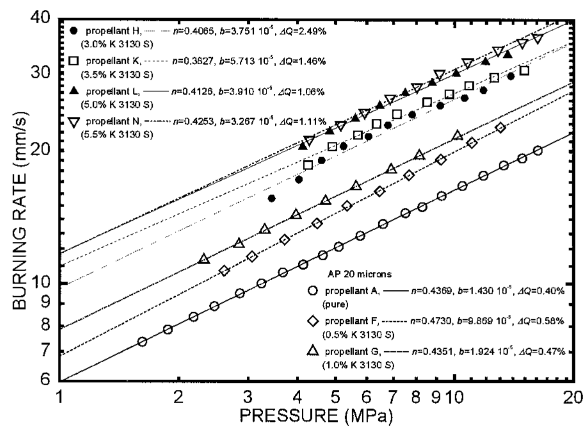

Fig. 6 Influence of catalyst Sicomin-Rot K 3130 S on medium-energy propellants (AP 20 μm).

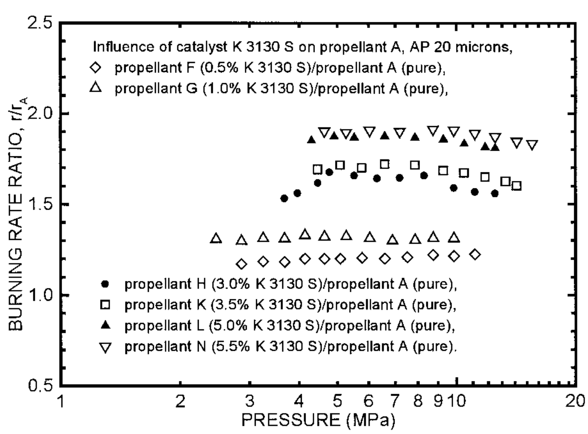

Fig. 7 Influence of catalyst Sicomin-Rot K 3130 S on basic propellant A (AP 20 μm).

in comparison with 3% of CC. As the concentration of the CC was increased, the burning rate exponent was also increased.

Influence of Sicomin-Rot K 3130 S on Flexolite series medium-energy propellants for AP 20-μm grind is shown in Figs. 6 and 7. The catalyst level is 0.5, 1, 3, 3.5, 5, and 5.5%. The burning rate is significantly changed when the level is increased from 3 to 5%. Also, the exponent in the burning-rate law is changed with addition of 3% or more of this catalyst. The addition of 3% of all of these catalysts has shown that CC is the most effective single catalyst (Fig. 8), whereas comparison of 5% of catalysts has shown that Sicomin-Rot K 3130 S is the most effective single catalyst at this percentage (see Fig. 9). We can conclude from these results that CC is the best catalyst if the amount added is up to 3%. Further

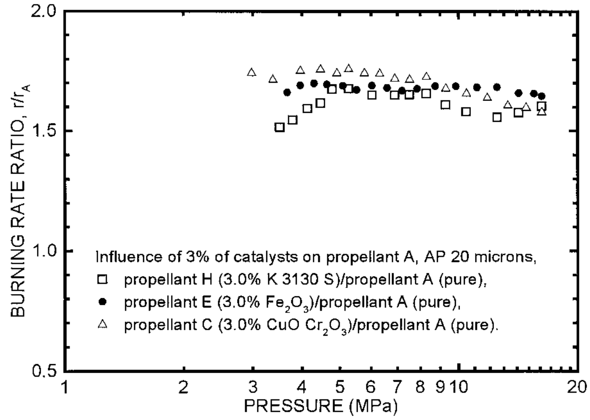

Fig. 8 Influence of 3% of different catalysts on basic propellant A (AP 20 μm).

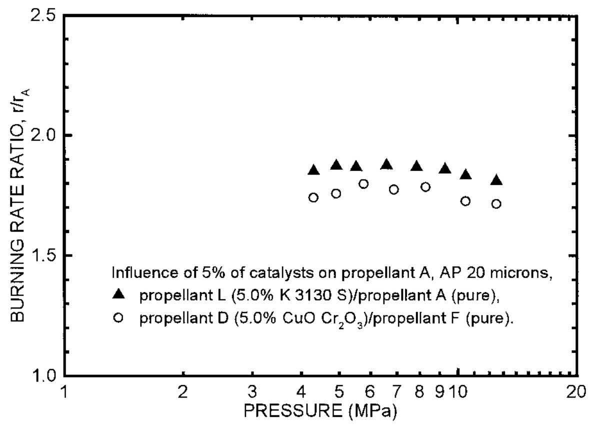

Fig. 9 Influence of 5% of different catalysts on basic propellant A (AP 20 μm).

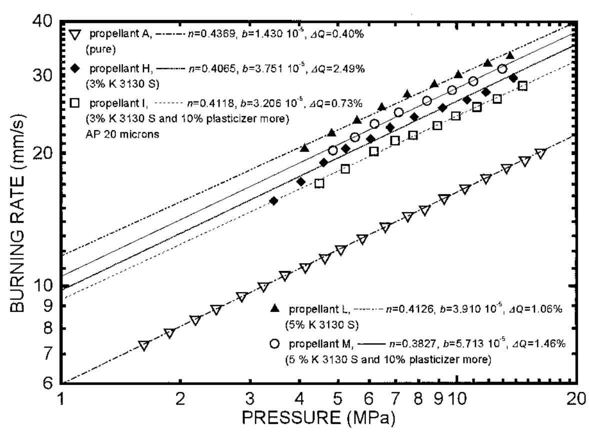

Fig. 10 Influence of plasticizer and Sicomin-Rot K 3130 S on medium-energy propellants (AP 20 μm).

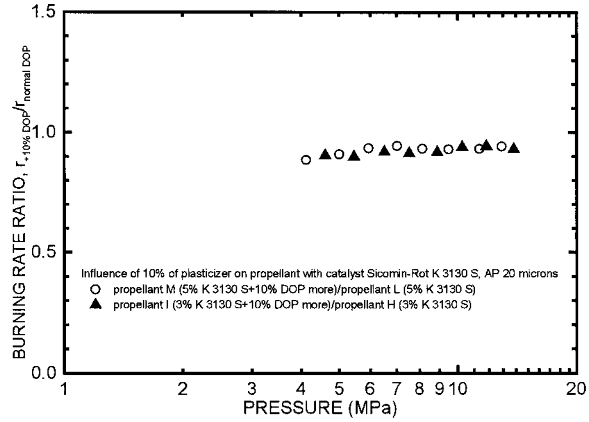

Fig. 11 Influence of increasing level of plasticizer for 10% on basic propellants (AP 20 μm).

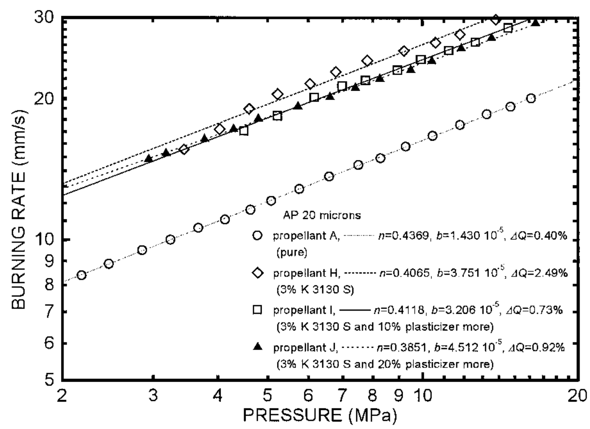

Fig. 12 Influence of plasticizer on medium-energy propellants (AP 20 μm) with 3% of catalyst (K 3130 S).

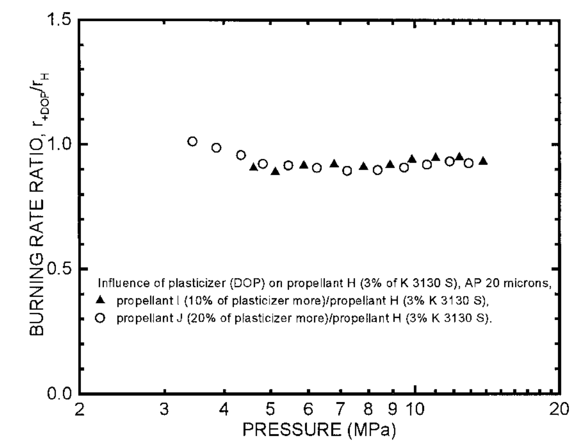

Fig. 13 Influence of level of plasticizer on basic propellant H (AP 20 μm).

increase of burning rate requires the use of Sicomin-Rot K 3130 S. This catalyst is much cheaper than CC.

The influence of plasticizer level has been examined on Flexolite series medium-energy propellants with AP ground to 20 μm using Sicomin-Rot K 3130 S as catalyst. Results are shown in Figs. 10–13. Dioctyl phthalate is used as plasticizer in all Flexolite series medium-energy propellants. In propellants with 3 and 5% of catalyst (propellant formulations H and L), the level of plasticizer in the binder is increased to 10% (propellant formulations I and M). The results are shown in Fig. 10. Addition of 10% of plasticizer for both propellant formulations (3 and 5% of catalyst Sicomin-Rot K 3130 S) decreases burning rate for the same percent (see Fig. 11). In compositions with 3% of catalyst, where the level of plasticizer in binder was increased to 20% (formulation J in Fig. 12), the burning rate decreased approximately to the same level as with the formulation in which level of plasticizer in binder is increased to 10% (see Fig. 13).

High-Energy Propellants

Including certain light metals in the propellant formulation can increase the energy content of a solid propellant. The addition of aluminum increases the combustion temperature and, thus, thereby the specific impulse. In addition, loading density of propellant is

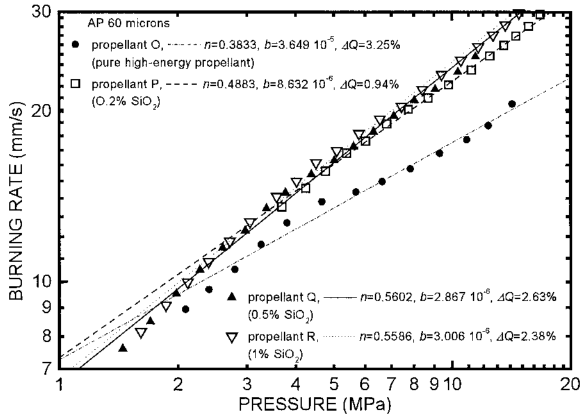

Fig. 14 Influence of aerosil on high-energy propellants (AP 60 μm).

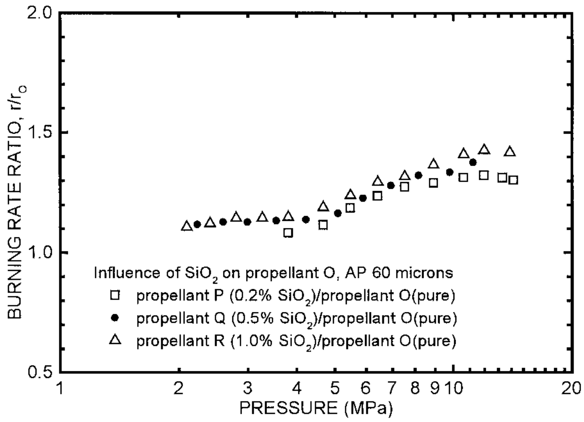

Fig. 15 Influence of aerosil on basic propellant O (AP 60 μm).

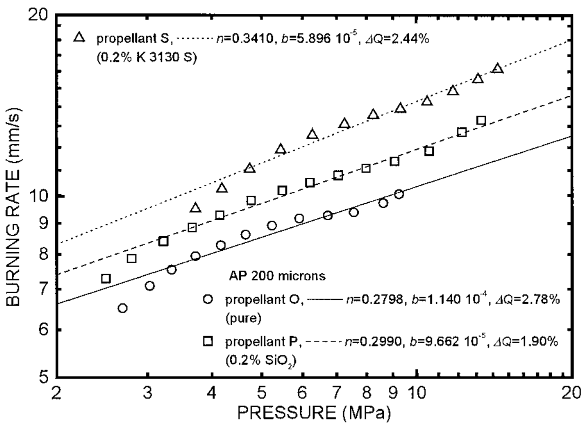

Fig. 16 Influence of aerosil and Sicomin-Rot K 3130 S on high-energy propellants (AP 200 μm).

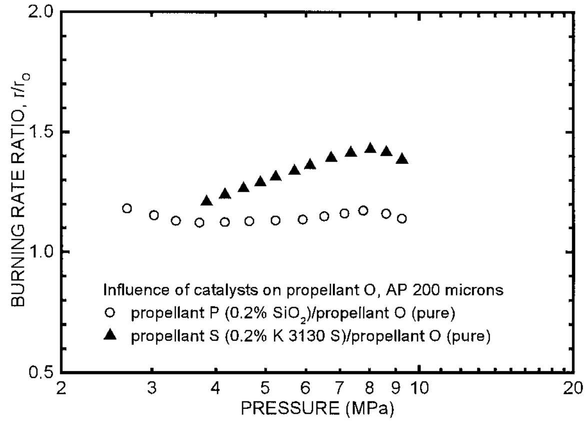

Fig. 17 Influence of aerosil and Sicomin-Rot K 3130 S on basic propellant O (AP 200 μm).

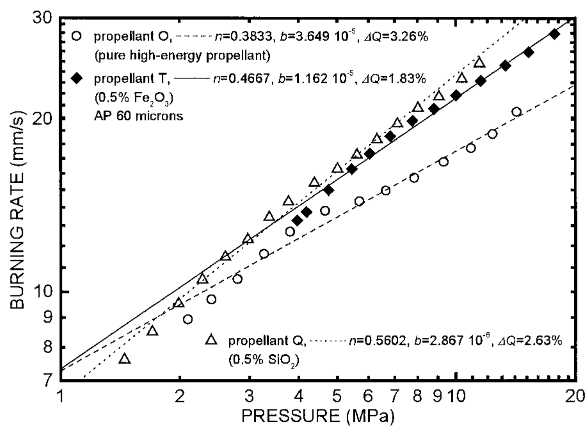

Fig. 18 Influence of aerosil and IO on high-energy propellants (AP 60 μm).

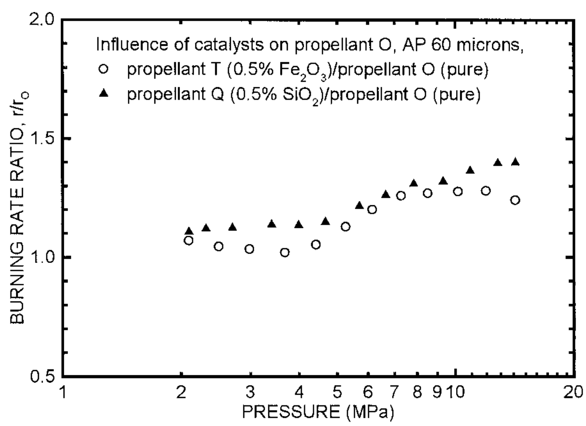

Fig. 19 Influence of aerosil and IO on basic propellant O (AP 60 μm).

also increased. Flexolite series high-energy propellants have 10% of aluminum in the propellant formulation.

The influence of different catalysts such as aerosil, IO, and Sicomin-Rot K 3130 S was investigated in the Flexolite series high-energy propellants. Their compositions are shown in Table 3. Burning rates are shown in Figs. 14–19. Dioctyl adipate has been used as the main plasticizer in these series of propellants. Basic high-energy propellant formulation is formulation O. The influence of 0.2, 0.5, and 1% of aerosil on burning rate of high-energy propellant formulation with 60-μm AP grind is shown in Fig. 14. We can conclude from Figs. 14 and 15 that aerosil has an influence as a catalyst at pressures higher than 4 MPa and that an addition of 0.5 or 1% of aerosil does not significantly increase burning rate in comparison with 0.2% of aerosil. The influence of 0.2% of Sicomin-Rot K 3130 S and aerosil on the basic high-energy formulation O with 200-μm AP grind is shown in Fig. 16. Sicomin-Rot K 3130 S has been shown to be a better catalyst than aerosil in these formulations (see Fig. 17). The influence of 0.5% of IO on basic formulation O with 60-μm AP grade is shown in Fig. 18, and it has been shown as a slightly worse catalyst than aerosil (see Fig. 19).

Conclusions

This paper presents results of measurements elucidating the influence of different catalysts on burning rate of a Flexolite series of modified PVC-based propellants. From the experimental results, it can be seen that CC is the best catalyst used in the experiments with medium-energy propellants up to 9 MPa. CC is effective up to

3%; above this, it does not affect the burning rate. Sicomin-Rot K 3130 S is a little less effective in comparison with the same amount of CC and IO, but its effectiveness on the burning rate exists up to 5.5%. Therefore, larger increases in burning rate of basic propellant formulations can be achieved with this catalyst. Also this catalyst is much cheaper than CC. Sicomin-Rot K 3130 S has been shown as the best catalyst in high-energy propellant formulations. Then follows aerosil, which is a slightly better catalyst than IO. Aerosil has shown its influence as a catalyst in propellant formulations at pressures greater than 4 MPa, but its effectiveness is poor above 0.2%. Fine regulation of burning rate can be achieved by modifying the level of plasticizer in propellant formulation. Results of experiments have shown that increasing the plasticizer level in propellant formulations up to 10% decreases burning rate for a lesser amount.

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