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Effects of Oxidizer Particle Size on Propellants Based on Modified Polyvinyl Chloride

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The effects of the oxidizer particle size and size distribution on the burning rate of composite solid-rocket-propellant series known as Flexolite have been presented in this paper. All Flexolite-series propellants are based on modified polyvinyl chloride as binder and ammonium perchlorate as oxidizer. Different compositions of nonaluminized and aluminized propellants have been studied experimentally, and burning rates were reported in this paper. Results were obtained for propellants compositions using different ammonium perchlorate particle sizes from fine (20 μ) to coarse (200 μ). It was shown that the oxidizer size has a substantial effect upon the burning rate. As would be expected, it was determined that the burning rate was higher for the smaller oxidizer size. Also, effect of catalyst (Fe_2O_3) is examined on aluminized propellants with a fixed fraction of aluminum mass. All burning rates were measured in a special test motor at different pressures, using small-motor measurement method.

Introduction

KNOWLEDGE of the combustion properties of a solid propellant is a prerequisite in the design of new solid-propellant rocket motors. The combustion properties comprise burning rate, pressure exponent, and temperature sensitivity. Among them, the propellant burning rate is probably the governing factor that is used in the calculation of grain ballistic properties. The combustion mechanism for a solid propellant is very complex and involves a large number of chemical and physical processes. The solid is transformed into combustion gasses at the grain-burning surface. The burning surface regresses normal to itself in parallel layers. The rate of regression is called the burning rate.

The influence of oxidizer particle size on combustion properties of composite propellants has been known for some time.[1–3] It has been reported that the combustion properties for composite solid propellants are highly dependent upon the physical nature of the oxidizer, that is, the size and size distribution of each of the individual oxidizer size fractions. In general, burning rate increases with decreasing particle size.

The purpose of this work was to study the effect of ammonium perchlorate particle size on the burning rate of solid composite propellants. To study the effect of oxidizer size distribution on burning rate, a series of Flexolite propellants was manufactured and tested. In many ways the Flexolite series of polyvinyl chloride propellants are similar to the many composite propellants that have binders made of polyesters, acrylates, epoxies, polysufides, polyurethanes, or polybutadiene-acrylicacid. 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, while 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.

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Experimental Procedures

Presented here are the results of an experimental investigation of the effect of ammonium perchlorate particle size on the burning rate of solid composite propellant Flexolite series. Beside the effect on viscosity of uncured propellant and strength of cured propellant, particle size of solids has an important effect on burning rate of composite solid propellants. The ballistic properties of composite propellants are determined primarily by its calorific value because the latter determines the combustion temperature and the composition of the propulsive gas at the entrance cross section of the rocket nozzle. If the Flexolite series of propellants is viewed as simple two-component systems comprising PVC binder and oxidizer, the ballistic properties are related to the weight fraction of oxidizer in the formulation. Combustion properties are dependent not only upon the binder material and its weight fraction, but also on the particle size distribution of oxidizer. Series of composite propellants (both nonaluminized and aluminized) were formulated to examine the effect of AP size distribution on combustion properties. The binder type and technology were always the same, whereas oxidizer grinds were changed. Single lots of each AP size fraction were employed throughout. All propellants used a constant binder composition and were produced using the same processing cycles.

Five ammonium perchlorate grinds with nominal particle size 20, 60, 90, 100, and 200 μ were used in experimental propellants. All of the propellant grade ingredients used in this investigation were commercially available or obtained on the standard hammer mill. AP particle size fractions of nominal 90 and 200 μ were received as lots of Keer-McGee materials. Size fractions of nominal 100, 60, and 20 μ were prepared from nominal 200 μ by conventional grinding techniques appropriate to the specific nominal size. The size distribution of individual size fractions was measured using one of existing standard techniques. For size fraction of 90 μ nominal size or greater, standard screen analysis was employed. For size fractions of nominal size 20 and 60 μ, the Micromerograph was employed. Propellant size distribution was constructed analytically from the data on individual size fractions. Figure 1 shows particle-size analysis for these AP grinds.

The compositions of the five thermoplastic propellants examined in this study are shown in Table 1. Basic low-energy propellant formulation is A. Medium-energy propellant formulation B has increased oxidizer content from 69 to 75% in comparison with propellant formulation A. Increase in oxidizer content is obtained by decreasing binder content. High-energy propellant formulation C has increased aluminum content in comparison with propellant A, which is obtained at the expense of binder content. In comparison with two other formulations, low-energy propellant A has 1% of burning-rate modifier in its composition (Sicomin-Rot K-3130 S

Table 1 Composition of experimental propellants

Composition, weight %	A	B	C	D	E
Oxidizer	69.00	75.00	69.75	69.75	69.55
Metallic fuel	0.50	0.50	10.00	10.00	9.70
Binder	28.45	23.40	19.40	19.40	19.40
Stabilizer	0.50	0.55	0.50	0.50	0.50
Processing additive	0.25	0.25	0.25	0.25	0.25
Carbon black	0.30	0.30	0.10	0.10	0.10
Catalyst	1.00	—	—	—	0.50

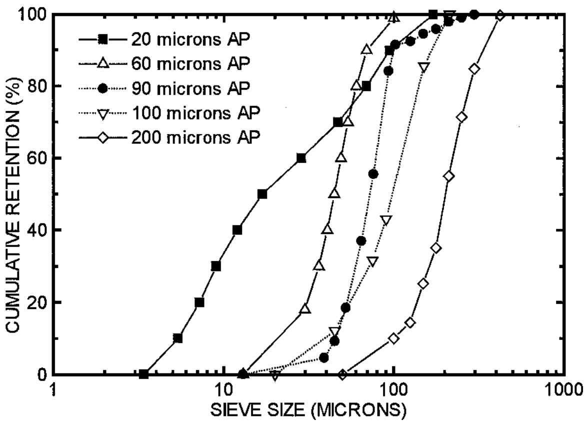

Fig. 1 Ammonium perchlorate particle size distribution data.

manufactured by BASF) to improve ignition and stable burning at low pressure. Propellant formulation D has the same composition as C. The only difference is in type of plasticizer, which is used as ingredient. Dioctyl phthalate, which is used in the preceding formulations, is substituted by dioctyl adipate. Propellant formulation E has 0.5% of ferric oxide (Fe_2O_3) added as burning-rate modifier, in comparison with the formulation D. Burning-rate modifier is added and the content of AP decreased for 0.2% and aluminum for 0.3% in comparison with the formulation D.

The propellant grains were prepared using standard procedure for these propellants known as the TEPVAC process.[4] 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 the 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.[5] A small-motor measurement method is used for determination of the instantaneous burning rate of solid rocket propellants at different instantaneous pressures during one test. The method is based on the pressure vs time trace obtained by burning a small cylindrical grain with known development of burning surface. Propellant grain has a progressive surface spread because of its cylindrical shape with concentric bore and is inhibited from both heads and laterally. Analysis of this trace permits the calculation of the burning rate.

Measurements have been performed in a special test motor developed for that purpose. 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 microwave reflection interferometry method.[6] Results of burning rates from these two methods show good agreement.

Results and Discussion

The experimental results summarized in Figs. 2–6 have been presented as effects of AP particle size on the burning rate of various propellant formulations in dependence of pressure. Figure 2 represents the influence of AP particle size on burning rate of formulations A, Fig. 3 represents this influence on formulation B, and Fig. 4 shows this influence on formulation C. Figures 5 and 6 represent this influence on formulations D and E, respectively.

All of the burning rates on those figures were correlated with empirical equation (Saint-Robert's or Vieilles law):

$$r = b \cdot P_c^n \tag{1}$$

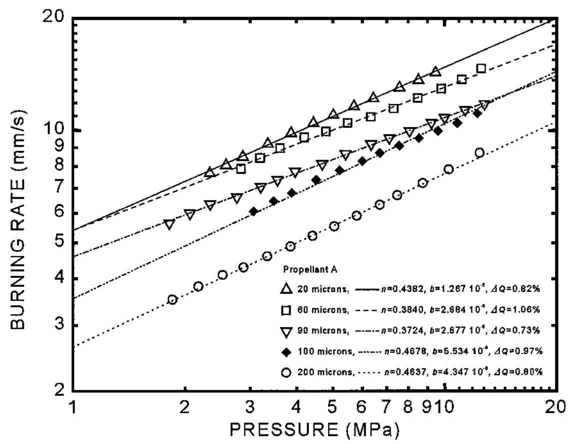

Fig. 2 Burning rate of propellant A.

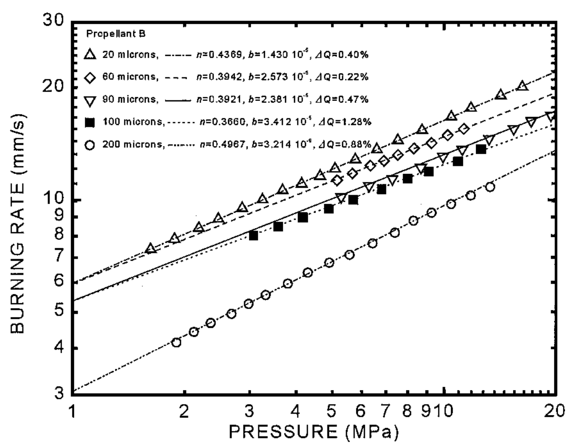

Fig. 3 Burning rate of propellant B.

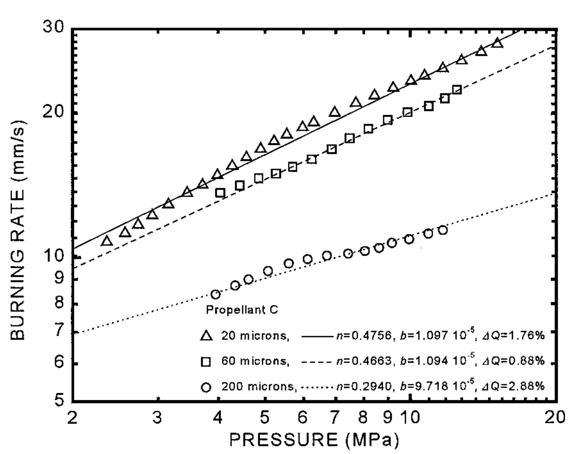

Fig. 4 Burning rate of propellant C.

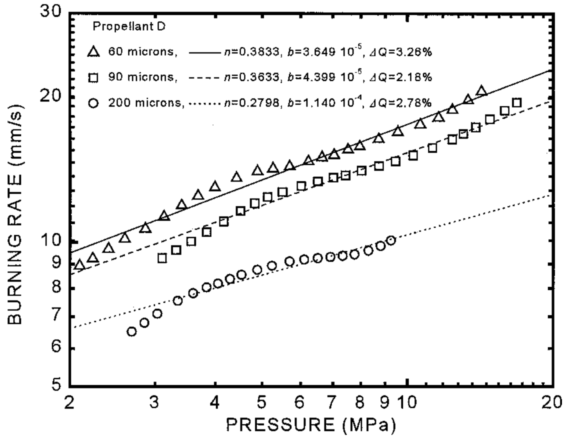

Fig. 5 Burning rate of propellant D.

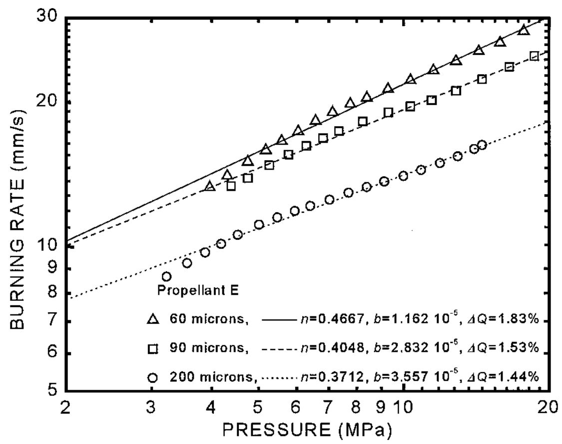

Fig. 6 Burning rate of propellant E.

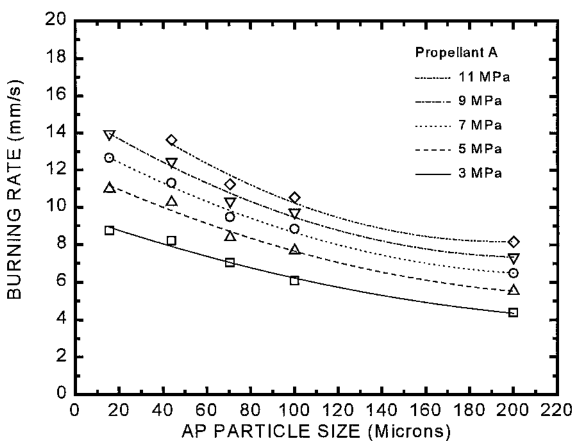

Fig. 7 Burning rate vs AP particle size diagram of propellant A.

where r is burning rate, P_c is pressure in combustion chamber, b is coefficient of pressure, and n is pressure exponent in burning rate law. Parameter ΔQ represents standard deviation of the burning rate in comparison with Saint-Robert's law.

Effects of AP particle size on the burning rates of various propellants are presented in Figs. 7–11, where the burning rate is plotted vs ammonium perchlorate grind mean diameter $\bar{D}$. The mean diameter is termed the 50% weight mean diameter, because half of the oxidizer's mass is composed of particles less than $\bar{D}$ (see Fig. 1).

The effects of oxidizer particle size on propellants Flexolite series based on modified polyvinylchloride are also shown on Figs. 12 and 13, where relative burning of each AP grinds is presented in dependence of pressure. Relative burning rate for any AP grind is obtained by dividing its burning rate with burning rate of 200 μ nominal particle size grind at the same pressure. Experimental results for all five propellant formulations show that the burning rate increased with decreasing AP particle size. The burning rate of propellant A increases about 95%, the burning rate of propellant B increases about 75%, and the burning rate of propellant C increases about 95% at 7 MPa as the particle size of the AP is reduced from nominal size 200 to 20 μ.

The burning rate of propellant C increases about 65%, the burning rate of propellant D increases about 60%, and the burning rate of propellant E increases about 45% at 7 MPa, as the particle size of the AP is reduced from nominal size 200 to 60 μ.

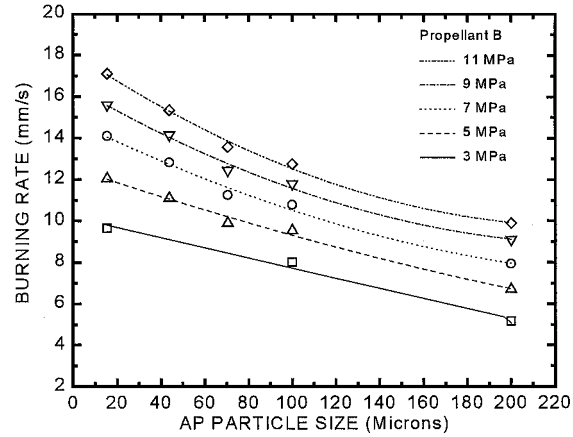

Fig. 8 Burning rate vs AP particle size diagram of propellant B.

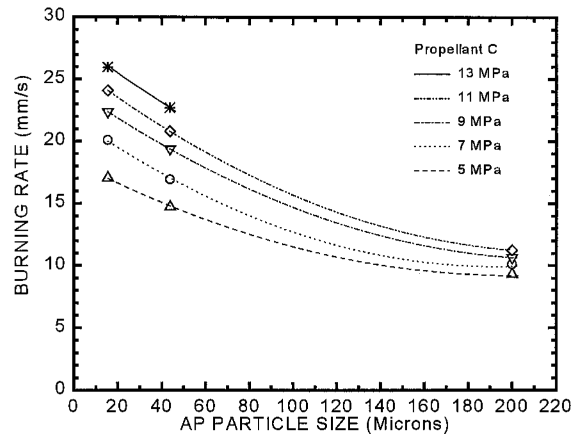

Fig. 9 Burning rate vs AP particle size diagram of propellant C.

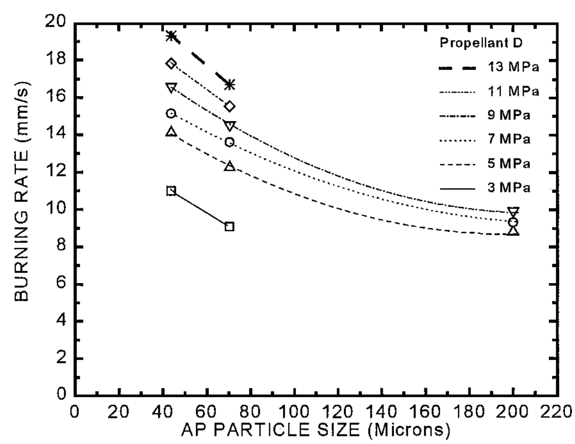

Fig. 10 Burning rate vs AP particle size diagram of propellant D.

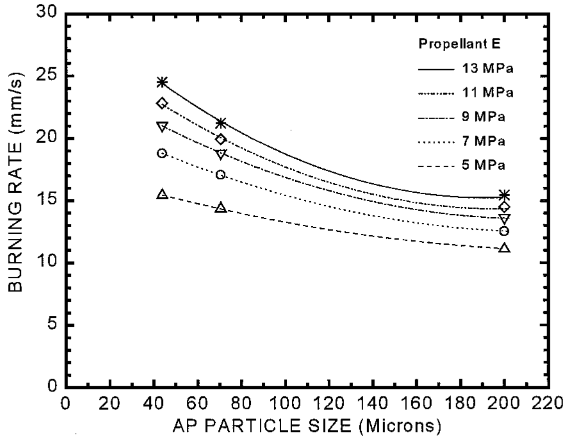

Fig. 11 Burning rate vs AP particle size diagram of propellant E.

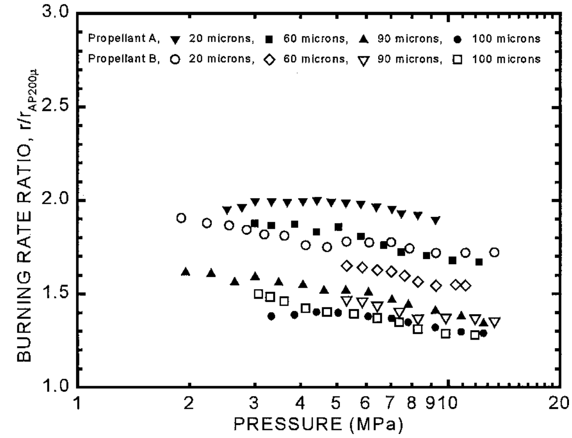

Fig. 12 Relative burning rates of different AP grinds, for propellants A and B.

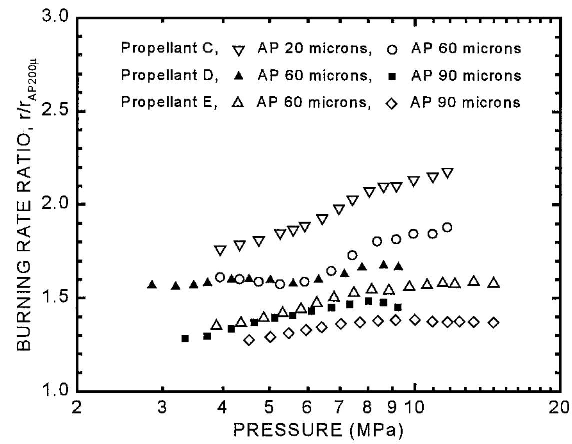

Fig. 13 Relative burning rates of different AP grinds, for propellants C, D, and E.

The explanation for this phenomenon is found in the following. On the microscale at which the combustion reactions take place, PVC propellants are heterogeneous. An examination of the details of the burning propellant surface reveals ammonium perchlorate (oxidizer) particles of various sizes surrounded by modified PVC binder. A very complicated reaction mechanism occurs during combustion. The oxygen-rich and fuel-rich gases, which evolve from the burning surface, must mix before the combustion reactions can be completed. The faster the reaction processes the higher the burning rate of the propellant. The reaction rate between the binder and oxidizer particles depends on the surface area of oxidizer. Finer particles, as a result of larger surface area per unit mass, are more rapidly gasified than coarse AP particles, and the reaction rate increases. Gas-phase mixing is therefore an important rate-controlling process in the propellant burning. From this it follows that the more intimately the binder and oxidizer are mixed in the solid phase (such as by decreasing oxidizer particle size at constant oxidizer percentage), the less the mixing resistance to combustion and the faster the burning rate.

From the experimental results it is obvious that the influence of oxidizer particle size on the burning rate of propellants is variable with pressure. This effect is the greatest for propellants A and C, and it is the lowest for propellant E, although all three propellant formulations have approximately the same level of oxidizer (about 69%). Propellant A is the composition without aluminum, which has the lowest burning rate and flame temperature in comparison with all five propellant formulations that are tested. Propellant C has 10% of aluminum, and propellant E, besides 10% of aluminum, has a catalyst, and this formulation has the greatest burning rate for all AP grinds. If we compare two nonaluminized propellants A and B with different AP level in composition (69 and 75%), influence of 100 μ AP grind is approximately the same for propellants A and B. Further decreasing in particle size of oxidizer has greater effects on propellant A (which has less energy and slower burning rate because of lower level of oxidizer). For aluminized propellants the influence is equal up to 7 MPa for propellants C and D (which have the same formulation and only differ in type of plasticizer). Substitution of dioctyl phthalate with dioctyl adipate in composition C reduced oxidizer particle size effects at pressure over 7 MPa. Presence of catalyst has increased burning rate of propellant E (in comparison with propellant D), but it has been decreased the oxidizer particle size effect.

Results from Figs. 12 and 13 have also shown that influence of oxidizer particle size on burning rate is different for aluminized and nonaluminized propellants. Oxidizer particle size effect decreased with pressure for propellants A and B (which have no aluminum in their compositions), whereas for aluminized propellants C, D, and E it increased with pressure. Obviously, the presence of small particles of aluminum during burning affects the reaction process of oxidizer particles with binder and intensifies the oxidizer particle size effects on burning rate with pressure. On the other side, presence of aluminum has no influence on the value of oxidizer particle size effect. The propellants A and C, nonaluminized and aluminized propellants with 69% of oxidizer, have approximately equal value of oxidizer size effect for all AP grinds, although character of change with pressure is different.

Influence of Solid Content

Influence of composition (solid content) on burning rate of Flexolite propellants can be determined if we compare burning-rate results of propellants A and B (presented in Fig. 2 for propellant A and Fig. 3 for propellant B). Composition B has increased oxidizer content in comparison with composition A, which affects flame temperature. As might be expected, the higher flame temperature results in a higher rate of heat transfer from the hot flame zone to the burning propellant surface. This, in turn, increases the rate of gasification of the unburned propellant. This theory is confirmed by the results of all five AP grinds for propellants A and B; burning rate is increased with increased oxidizer content in composition.

Influence of Aluminum as an Ingredient

The energy content of a solid propellant can be increased by including certain light metals in the propellant formulation. The addition of aluminum increases the combustion temperature and thus the specific impulse. In addition, loading density of propellant is increased with incorporation of aluminum into propellant formulation. Many investigators have studied the effects of aluminum powder on the burning rate of AP-based composite solid propellants. It has been reported that the net effect of the addition of powdered aluminum on the burning rate is usually not large and can be either positive or negative.[7,8] Also, it was previously shown that specific impulse of PVC propellant is substantially increased by incorporating aluminum in the formulation.[9]

An illustration of what can be accomplished with Flexolite series of propellants is indicated in Figs. 2 and 4. For propellant formulation C (Fig. 4) an increase in aluminum content is obtained at the expense of binder content in comparison with formulation A (Fig. 2), while aluminum perchlorate weight percentage is held constant. The addition of the aluminum in composition increases flame temperature. The higher flame temperature results in a higher rate of heat transfer from the hot flame zone to the burning propellant surface, which, in turn, intensifies the rate of gasification of the unburned propellant. Also, addition of spherical or spheroidal aluminum in contrast to the shape of ground AP also increase reactions of burning products. These processes lead to acceleration of propellant burning rate. From these figures we can see that burning rate of formulation C is increased by the addition of finely divided aluminum to Flexolite formulation A for all AP grinds.

Burning-Rate Modifier

Burning-rate modifiers in a propellant formulation are always of interest to the rocket designer as they meet various ballistic needs. The universal hope is for a selection of additives that can be used in small quantities, controllably to increase or decrease burning rate, to decrease the sensitivity of burning rate to pressure or temperature, or to accomplish some combination of these changes. The ideal additives would have negligible effect on the fluidity of the mixed propellant, physical properties of the cured propellant, thermal stability, storage stability, or safety characteristics. Influence of 0.5% of ferric oxide (Fe_2O_3) on aluminized propellant formulations is shown on Figs. 5 and 6. It is obvious from comparison of burning-rate data from these figures that addition of Fe_2O_3 as catalyst increases burning rate of composite propellant formulation D for all AP grinds.

Conclusions

An experimental ballistic database for Flexolite propellants has been presented. From the experimental results it is evident that the ammonium perchlorate particle size has a strong influence on burning rate. Decreasing the ammonium perchlorate particle size increases the burning rate of the Flexolite propellants. Also, size distribution of ammonium perchlorate particles has influence on burning rate. Comparison of presented results also shows influence of percent of solid and aluminum in propellant formulation on burning rate. As might be expected from its effects on flame temperature, increased oxidizer content increases the burning rate. Addition of aluminum in propellant formulation also increases the burning rate. It is concluded that the effect of ammonium perchlorate particle size on the burning rate of propellants depends on the burning-rate modifier contained in the propellant.

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