EFFECTS OF AP PARTICLE SIZE IN COMPOSITE PROPELLANT COMBUSTION

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ABSTRACT

Composite propellant combustion is studied experimentally with systematic variation of particle sizes and mix ratios of coarse and fine APs. Considering the different modes of oxidizer-fuel flames in heterogeneous systems, the complex flame model is described to identify what combustion mechanisms are important under what conditions. The effects of AP particle size, ratio of coarse to fine AP, and pressure on burning rates are discussed in terms of qualitative theory of flame microstructure.

INTRODUCTION

Analyses of composite propellant combustion have sought to describe the details of the steady and unsteady burning characteristics. In composite propellants, a mixture of different AP (Ammonium Perchlorate) particle sizes was used to maximize the weight of AP per unit volume of propellants in order to enhance the burning rate, an effect resulting from increased AP particle perimeter and correspondingly increased the heat feedback from the flames above the propellant surface. Since the combustion processes differ over the range of AP particle size, mix ratio of coarse/fine AP, and pressure, it is necessary to understand the combustion microstructure in order to develop useful analytical models. The detailed processes in the combustion zone are not susceptible to rigorous analytical modeling, and reliable prediction of global combustion behavior as a function of formulation variables is only possible for a limited domains of formulation variables where extensive measurements of global combustion behavior are available.

One of the aspects of composite propellant combustion that has proven difficult to model is the coupling of the individual flames on adjoining AP particles, all of which share the surrounding fuel supply with their neighbors. However, better correlation between the measured combustion response and model prediction can't achieve until the multiflame modes in composite propellant combustion is characterized[1].

Several studies were reported to understand the interactive behavior between coarse and fine APs, and the effect of AP sizes on burning rates[2-7]. Some results indicated that the combustion behavior for a class of propellants containing both very fine and very coarse AP depart significantly from the theoretical predictions[5]. Recent studies of sandwich, edge burning of oxidizer-fuel laminates, also provided the details of the combustion behavior of coarse/fine AP particles and complex flame structure[2,3,8]. In the burning of different AP sizes, very fine AP might diffuse into the binder so quickly that normal AP self-deflagration would not occur on the particle. If there are many fine APs, they may burn with a premixed flame. If the particles are large enough, they may burn as individual particles. When coarse AP particles are near enough to each other, the interactive behavior will occur[3]. The details depend on AP size, pressure, and coarse/fine mix ratio in propellants.

In the present study, the focus has been on clarification of the details of the flame complex, and the resulting effects on the global burning rate of bimodal propellant samples. To address these issues, a series of bimodal propellants with systematic variation of oxidizer particle size and ratio of coarse/fine AP was manufactured and studied.

BACKGROUND

Recent analytical models of composite propellants embody the idea that the heat release responsible for propagation of burning occurs in three different kinds of flamlets with the relative importance of each depending on AP size and pressure.[5,6,9,10] 1) Oxidizer self-deflagration, probably involving also exothermic surface reactions. 2) A leading edge of the oxidizer-fuel diffusion flame variously called the "phalanx flame[9]," the "primary flame[11], and, here, "leading edge flame (LEF)[8]". 3) Diffusion-limited flames between mixing oxidizer and fuel vapors. The LEF region is pictured as a very small part of the overall flame, but is very important to the overall combustion process because of its proximity to the pyrolyzing surface. It is also found that the LEF is a region of very high heat release as compared to the rest of the diffusion flame, and contributes most of the heat transfer back to the propellant surface.[2]

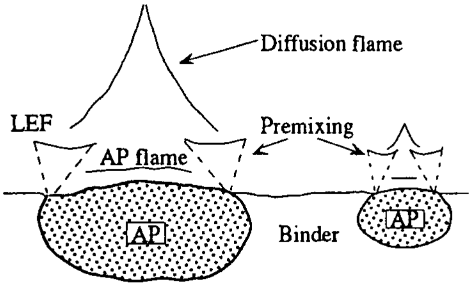

Fig. 1. Flames over AP particles; both coarse and fine particles have attached particle flames.

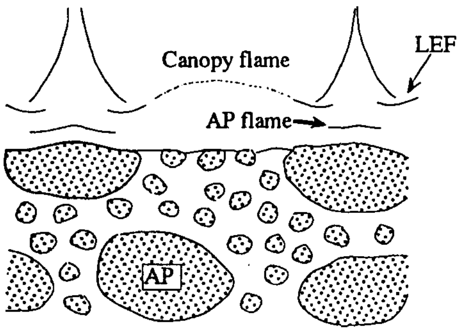

Fig. 2. Flame microstructure with canopy flame[3]; At low pressure, the O/F flame for the fine AP is a relatively cool, fuel rich premixed canopy flame anchored in the LEFs for the coarse AP. At higher pressure, each AP has its own O/F flame.

The nature of the flame complex on each AP particle would differ depending on the size of AP exposed surface and the width of the adjoining binder. Referring to the microflame stability[2,3,8](see Fig.1) for relatively large particle and/or high pressure, the AP particle flame will be established on the stoichiometric surfaces, the location of which is pressure dependent. For fine particle and/or low pressure, the establishment of individual oxidizer-fuel flame does not occur, and the AP particle is pyrolyzed without either exothermic surface decomposition or attached diffusion flame. If the AP particle pyrolyzes without an attached LEF, oxidizer and fuel continue to mix, and the reaction of the mixtures is delayed to a location more distant from the surface where a fuel-rich canopy flame anchored in the LEFs (as-yet-undetermined) exists[2,3,8] (see Fig. 2). Features of these complex flame behavior should affect the steady state burning of propellants with changing the mix ratio and different sizes of AP particles, because the measurement of the macroscopic burning rate effectively averages out the microscopoic combustion processes.

In this study, a series of bimodal propellants is manufactured with the earlier experimental results of microflame stability over AP particle sizes[3,8]; no particle flames over 6 µm AP; whereas there is a flame over 45 µm AP at higher pressure; whereas more chance to have particle flames over 90 µm AP. Because the normal location of a premixed flame is pressure dependent, the oxidizer-fuel (O/F) particle flame becomes more prevalent on a broad range of particle sizes with increasing pressure. Nominally 400 µm AP is used here as coarse APs, which is large enough to hold the LEF over the pressure range of this study.

EXPERIMENTAL PROCEDURES

The propellants in the present study consist of 12.5 % HTPB binder and 87.5 % AP. A systematic variations of bimodal propellants are formulated as shown Table 1. The AP is a bimodal blend of coarse and fine APs. Mix mass ratios of coarse/fine AP are 7/3, 5/5, and 3/7. The amounts and particle size of AP in the binder have a significant effect on the rheological properties, and the 3/7 mix ratio with 6 µm AP is not processable.

The coarse AP was of nominal diameter 400 µm which was as-received lots of Kerr-McGee. The nominal sizes used for the fine APs were 6, 45, and 90 µm. The 6 µm AP was a high purity material supplied by SNPE. Both 45 and 90 µm APs were ground and screened by sieve shaker. The 45 and 90 µm nominal sizes refer to the median of the sieve sizes; 37 and 53 mesh for nominal 45 µm; 75 and 106 mesh for nominal 90 µm. No attempt was made to quantify the size distributions within these sized particles. All samples used the particular size particles from the same batch. The consistent IPDI cured HTPB binder composition was used throughout these studies (see Table 2). The propellants were prepared by 1 gal. mixer. They were vacuum mixed, and the mix procedure was held constant for all mixes. After mixing, the mixture was placed under vacuum at room temperature for 20 min. After curing 7 days at 160^0 F, the samples for burning rates were prepared in the size of 6mm (dia.) x 120mm. The samples were coated, dried for 2 days, and fired in duplicate or triplicate in the strand burner at the pressure range of 300 to 2000 psi. The 77^0F strand burning rates of each samples with a burn distance of 88.9 mm was measured in a bomb pressurized with nitrogen.

The average burning rate of these experiments are calculated to obtain a data.

Table 1. Summary of Propellant Formulations:

Coarse AP	Fine AP	Mix Ratio of Coarse to Fine
400 μm	6 μm	7 : 3
		5 : 5
		3 : 7 (Unprocessable)
400 μm	45 μm	7 : 3
		5 : 5
		3 : 7
400 μm	90 μm	7 : 3
		5 : 5
		3 : 7

Table 2. Formulation of Binder Composition:

AP: 87.5 % (coarse and fine APs)
HTPB: 9.263 %
IDP: 2.13 %
HX-7523: 0.3 %
AO 2246: 0.12 %
IPDI: 0.667 %
TPB: 0.01 %

RESULTS AND DISCUSSION

The qualitative arguments are evaluated to discuss the experimental results of this study as shown Fig. 3-11. The burning rates for each propellants are presented in Fig.3-5 as burning rate vs. fine AP particle size. Figure 3 is for bimodal propellant with a 7/3 mix ratio of coarse to fine AP. Figure 4 and 5 are the corresponding results for 5/5 and 3/7 mix ratios of coarse to fine AP. At 7/3 (coarse/fine) ratio, the burning rate is nearly insensitive to the particle sizes of fine AP, except at 2000 psi. At 5/5 coarse/fine ratio, the burning rate is sensitive to fine APs. At 3/7 coarse/fine ratio, the burning rate is very sensitive to the particle sizes of fine AP.

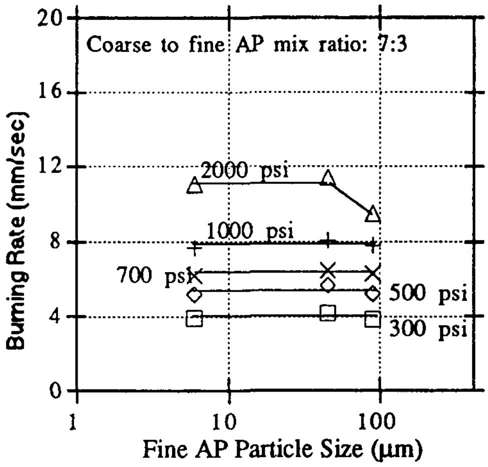

Fig. 3. Burning Rate vs. Fine AP size
Coarse to fine AP mix ratio is 7:3

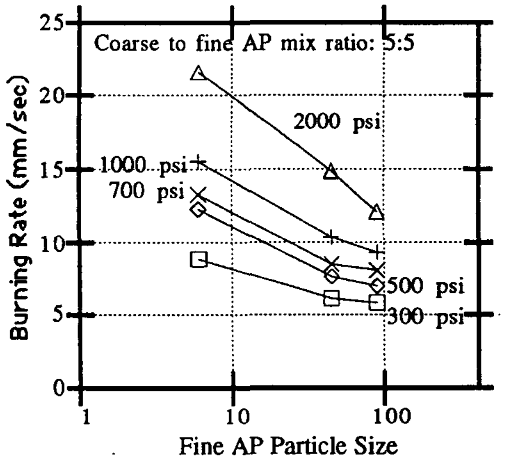

Fig. 4. Burning Rate vs. Fine AP particle Size
Coarse to fine AP mix ratio is 5:5

Before interpret the effect of fine AP on burning rates, consider the flame structure to be expected in bimodal propellants. In bimodal configurations, the 400 μm APs are packed with intervening volumes filled with fine APs and HTPB binder. The flame complex associated with 400 μm AP consists of an AP monopropellant flame over most of its surface area. A mixing fan of AP vapors and binder vapors extends outward from the periphery of 400 μm AP. In this mixing fan (see Fig. 1), the premixing of

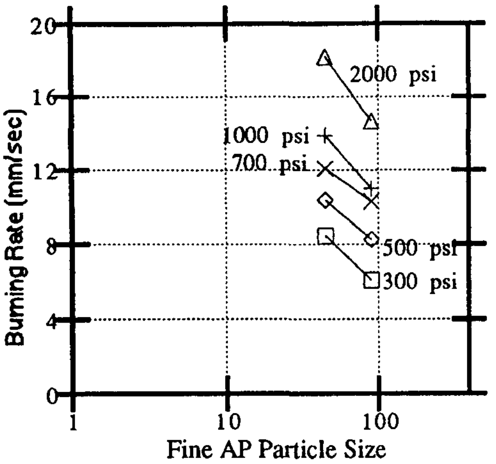

Fig. 5. Burning Rate vs. Fine AP size
Coarse to fine AP mix ratio is 3:7

oxidizer and fuel occurs before a LEF is established, and the LEF is a 3-D ring around the 400 μm AP and dominates the AP vaporization and binder pyrolysis near the outer periphery of the 400 μm AP. The LEF is presumed to be centered almost at the stoichiometric surface in the mixing fan, and extended outward laterally to an extent limit by flammability limits.[8] As previously noted, the oxidizer and fuel that are not reacted in the LEF mix and burn in a diffusion flame.

The behavior of fine APs between 400 μm APs are[2,3] (see Fig.6);

1) If the fine APs are small enough and pressure is low, the array of fine APs, fine AP-binder matrix, burn with a premixed flame.

2) If the fine APs are large enough and pressure is high, the array of fine APs burn with particle O/F flames.

3) The fine APs neighboring the 400 μm AP give a dilute fuel supply to the LEFs of 400 μm AP, and the LEFs of 400 μm AP may extend and shift further over the region of fine APs, correspondingly more energetic heat source to the array of fine APs as compared with the LEFs of 400 μm without the dilute fuel supply (see Fig. 6).

4) Because the diffusional distance increase with increasing AP particle size, it is proposed that the degree of O/F mixing is dependent on the AP particle size.

5) With or without particle flames over fine APs, the effect of the array of fine APs on burning rate is strongly dependent on the condition of neighboring 400 μm APs since the LEF of 400 μm AP extended over the nearby fine APs dominates the fine AP vaporization and the binder pyrolysis. Moreover, the fine APs nearby the 400 μm AP are oxidizer enriched by the 400 μm AP, and there are more chances to have particle O/F flames.

In order to interpret the experimental results, the strategy is to compare the burning rate results, and construct the qualitative arguments based on as listed above.

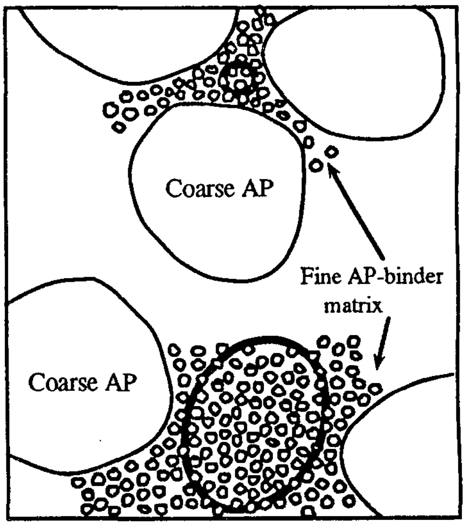

Fig. 6. Small and large fine AP-binder matrix areas according to the coarse/fine AP ratio; the solid region are the area which are not affected from the coarse AP (upper is higher coarse AP concentration, whereas the lower is higher fine AP concentration); the dilution effect of fine AP shifts and extends the LEF of coarse AP toward the matrix side.

If the distances between 400 μm APs are relatively small enough, for example 7/3 mix ratio, the 3-D LEFs of neighboring 400 μm AP close over the most area of the array of fine APs (see Fig. 6). In this situations, the burning rates are nearly insensitive to the fine AP sizes since the fine APs continue pyrolysis and act as the oxidizer supply mixed with fuel-rich vapors from adjoining binder to the LEFs of 400 μm AP and/or relatively cool canopy flame which located between the LEFs of 400 μm AP (see Fig. 2). Because the 3-D LEFs of 400 μm APs over the array of fine APs are dominant as well as AP

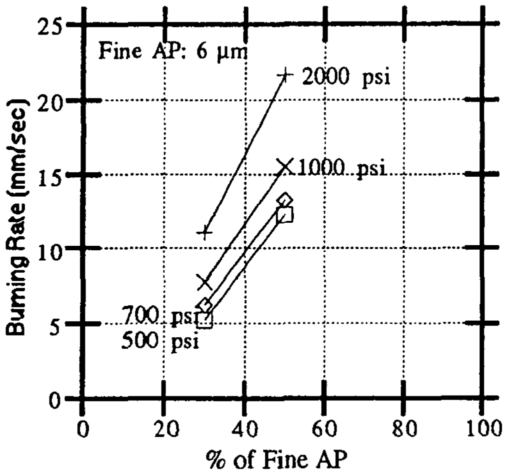

Fig. 7. Burning Rate vs. % of fine AP

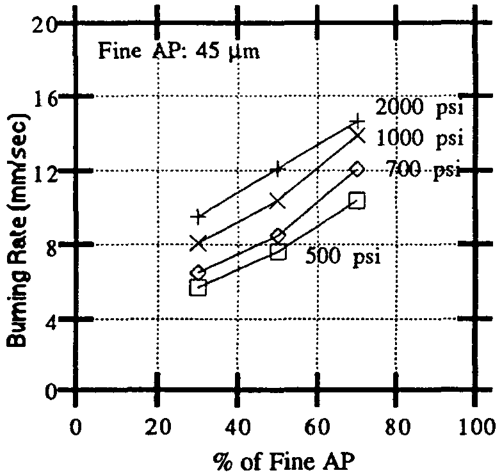

Fig. 8. Burning Rate vs. % of fine AP

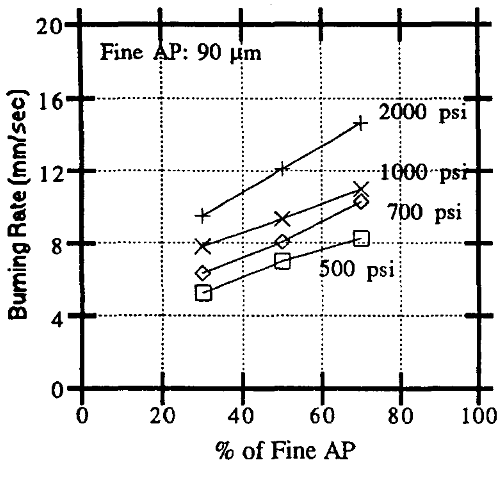

Fig. 9. Burning Rate vs. % of fine AP

monopropellant flames, burning rate is nearly insensitive to the particle sizes of fine AP when the coarse AP content is high enough, which is shown as Fig. 3. Both AP monopropellant flame and the LEFs are pressure dependent, the burning rates increase as pressure increase.

However, at 2000 psi, the width of the 400 µm LEF is relatively small; the LEF would move close to the surface and contract laterally as pressure is increased, and the 400 µm LEF may not cover the whole areas of the array of fine APs, correspondingly the effects of fine AP on burning rate occurs. According to the experimental results, the effect of 45 µm O/F flame compensate the incomplete mixing of dilute fuel supply with 45 µm AP (# 4), and the burning rate with 45 µm approaches the burning rate with 6 µm. Whereas the effect of 90 µm AP flame does not compensate the incomplete mixing effect, correspondingly the rates with 90 µm AP are lower than that with 45 µm AP.

The withholding effects of the 400 µm to fine APs are also shown in Fig. 7-9. In burning rate vs. % of fine AP graph, 0% fine AP corresponds to the monomodal propellant consist of all 400 µm particles, and 100% fine AP corresponds to the monomodal propellant consist of all fine particles, but the experimental burning rates of these monomodal propellants are not processable. Because of the withholding effects of the 400 µm to fine APs, the dr/d% (d(burning rate)/d(% of fine AP)) in the range of 0-30% fine AP is relatively very small as compared to that of dr/d% in the range of 30-50% fine AP. Referring to the calculated value of monomodal propellant with 400 µm at 1000 psi[6,7], the dr/d% in the range (0-30% fine AP) is about 0.03-0.05 mm/sec per 1% increase of fine AP, which value is only 10% of dr/d% with 6 µm AP. This approach also support that the fine APs don't contribute to enhance burning rate until coarse AP concentration decreases enough. Therefore, at higher coarse/fine ratio, the effect of fine AP on burning rate can be ignored.

In Fig. 10, % of fine AP vs. burning rate at 1000 psi, burning rates of all samples with different fine APs must approach the rate of 400 µm AP monomodal propellant at 0 % of fine AP as well as the rates of each fine AP monomodal propellants at 100 % of fine AP. To approach a both limits, the "S" shaped curves for % of fine AP are proposed, and the shape of this curve changes strongly with the variations of fine AP fractions as shown Fig. 11. In a region, "A", where coarse AP fraction is very high, the role of

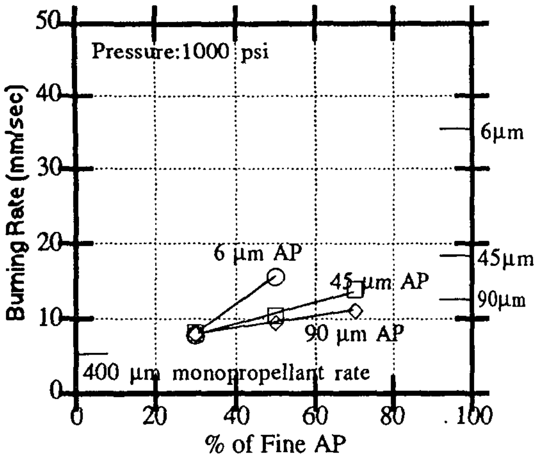

Fig. 10. Burning Rate vs. % of fine AP at 1000 psi: solid line on the left is the burning rate for 400 μm AP monopropellant[6], and solid lines on the right are the burning rates for each fine AP monopropellants.[6]

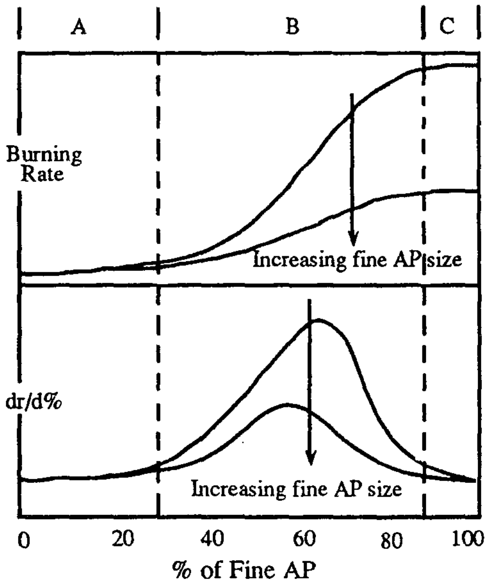

Fig. 11. Proposed effect of fine AP in bimodal distribution; as increasing fine AP sizes, the shape of dr/d% in region B becomes smaller and finally to be a line.

fine APs acts as a secondary effect, whereas in a region, "C"; where the fine AP fractions is very high, the role of coarse APs also acts as a secondary effect. Between the both regions, "B", an interactive effect of both coarse and fine APs occurs, which is less dominant at both extreme regions. With increasing the fine AP sizes, the region of interactive effect becomes narrow since the burning rate is less sensitive to the effect of 400 μm AP variations in a region where the fine AP fraction is very high, and the shape of dr/d% in region B becomes smaller and finally to be a line. Because of an insufficient experimental data, a detailed study is not accomplished yet.

As the coarse AP concentration decrease, the distance between the LEFs 400 μm AP increases and most of 400 μm LEFs may not cover the array of fine APs located around the outer periphery of 400 μm AP. In this circumstance, burning rate is sensitive to the role of fine AP since the area of fine AP-binder matrix increase further (see Fig. 6);

1) When the very small AP (6 μm AP) are used, fine AP cannot support individual O/F flamelets; AP/binder fuel-rich mixture forms a premixed canopy flame anchored the LEFs on 400 μm APs but easily vaporization of the very small AP contributes the nearby the LEFs, more effectively heating the propellant surface.

2) When the intermediate fine AP (45 μm AP) are used, individual O/F flamelets are sustained to intermediate pressure because individual stoichiometric surfaces further from the surface as compared to very small fine components are used.

3) When the relatively large AP (90 μm AP) are used, O/F flamelet holding on the individual particles continues to quite low pressure.

4) At this less coarse AP concentration, the contribution of the O/F vapors in the matrix to the LEFs of 400 μm AP is qualitatively lessened since a relatively large amount of fuel is consumed in the fine AP flames as compared to 7/3 mix ratio (the population of the AP flames in 5/5 ratio is higher than 7/3 ratio).

In Fig. 4 and 5, as the particle sizes decrease, it is easy to mix the oxidizer vapors with the surrounding fuel vapor, and the LEF of 400 μm AP with finer AP is more energetic that of 400 μm AP with relatively large fine AP, correspondingly the rate is higher as the fine AP sizes decrease.

At higher pressure, the area of fine APs with individual particle flame, which has more energetic portions of particle flame with stoichiometric regions of relatively high temperature and surface proximity, increase, but also lessens the LEFs of 400 μm AP. Because of this counteraction, it is argued that the amount of increase in burning rate between 90 and 45 μm is smaller than that in between 45 and 6 μm. As shown Fig. 8 and 9, the dr/d% with 45 μm in this region is higher value than with 90 μm since the propellant with 45 μm heat the surface more effectively (more dense population of 45 μm flame in between 400 μm APs). As coarse AP concentration decrease further, the withholding effect of 400 μm to fine AP disappear, and the role of fine APs is a dominant factor to the burning rate, leading to higher enhancement as shown Fig. 9.

To study the effectiveness of fine AP on burning rates in the range between 30 and 70% fine AP at each pressure, the dr/d% is calculated from the experimental results as shown Fig. 12. The dr/d% with 6 μm shows a different behavior as compared with 45 and 90 μm. This parametric study is useful in the evaluation of composite propellants and aid in propellant development. As pressure increases, the d(rate)/d(% of fine AP) increases, and the slope is dependent on fine particle sizes. Because the premixed effect is well developed with 6 μm AP, so the slope is very steep. As the fine AP sizes increase, the slope is less dependent on the pressure.

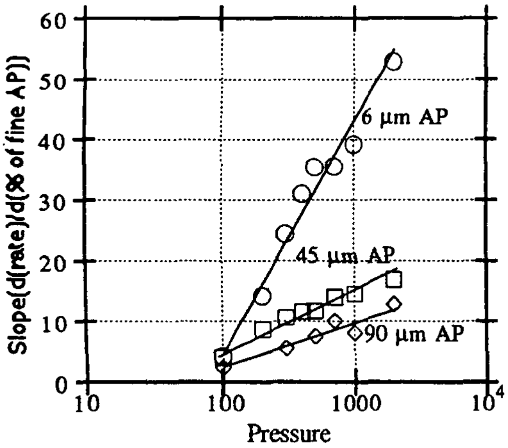

Fig. 12. Pressure vs. Slope
(% of fine AP is between 30-70 % with 45 and 90 μm, and between 30-50 % with 6 μm)

CONCLUSIONS

In order to develop the useful analytical models, it is necessary to understand the combustion microstructure, and determine what features dominate the complex processes. The present study provide the mechanistic insights in propellant combustion to accomplish the task of tailoring combustion characteristics. It shows that the contribution of fine APs to burning rate is significantly dependent on the features of coarse APs. Experimental results of the flame interactions and the characteristics of the array of fine APs are important to the combustion details to improve the modern burning rate and combustion response models.

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