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Effect of Oxidizer Particle Size on Burning Rate and Thermal Decomposition of Composite Solid Propellants

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Abstract. Studies on Thermal decomposition of ammonium perchlorate (AP)—polystyrene (PS) propellant and burning rate of PS/AP propellant have been carried out as a function of oxidizer particle size. Thermal decomposition of AP and AP/PS propellant as a function of AP particle size shows a maximum rate around 100 micron particle size which has been explained on the basis of Mample's theory. No such maxima is observed in the case of PS/AP propellant burning rate.

1. Introduction

Quite a good deal of studies have been carried out on the effect of oxidizer particle size on the combustion behaviour of condensed mixtures like ammonium perchlorate (AP)—polymethylmethacrylate (PMMA) and AP—polystyrene (PS)[1,2]. The burning rate ($\dot{r}$) increases by decreasing the particle size. Derr & Boggs[3] studied the effect of particle size on the combustion of polyurethane—AP or $KClO_4$ or HMX propellants. They also observed that $\dot{r}$ increases by decreasing the oxidizer particle size.

Bastress[4] studied the effect of particle size of AP on the combustion of polysulphide based propellants. Particle size of AP was varied from 9 to 265 microns mean diameter. The $\dot{r}$ increased in the pressure range of 15–1500 psi with decreasing particle size. The author concluded that the mono-propellant burning may be the rate controlling step.

Cohen Nir[5] finds that a CTPB propellant containing a bimodel mixture of 100/10 microns has a higher burning velocity with respect to the unimodel (100 microns) propellant. However, he finds that the pressure exponents are identical.

Attempts have also been made in the past to predict the effect of particle size from the analytical models. Hermance[6] developed the combustion model for composite propellants which is based on surface heterogenity and condensed phase reactions and found that the model adequately explains the experimental observations on the effect of particle size on $\dot{r}$. Beckstead *et al.*[7] based on their triple flame model, predicted that $\dot{r}$

should increase as the particle size decreases, they compared their predictions with the experimental data of Bastress[1] and found that the predicted change in $\dot{r}$ was somewhat greater than that observed experimentally.

The objective of the present investigation is to understand the effect of oxidizer particle size on the $\dot{r}$ of the propellant from the view point of the thermal decomposition behaviour of the propellant.

2. Experimental

Preparation of the polystyrene/ammonium perchlorate propellant[8], burning rate measurements[9], and isothermal TG studies[10] were done as described earlier.

3. Results and Discussion

$\dot{r}$ data as a function of the average oxidizer particle size are given in Table 1 and the plot is shown in Fig. 1. An increase in the $\dot{r}$ with decrease in the particle size is observed. In order to verify the present trend of $\dot{r}$ vs. the AP particle size, the data available in literature were analysed. Adams *et al.*[11] have also studied the effect of particle size on the combustion of condensed mixture of polystyrene. The particle size was found to have little or no effect at pressures upto 60 kg/cm^2 till the particle size exceeds 100 microns diameter. At higher pressures, however, there is a significant difference. His data was analysed to obtain a plot of $\dot{r}$ vs. particle size and the same is given in Fig. 2. A drastic increase in $\dot{r}$ with decrease of particle size is evident. Here also the dependence is non-linear in nature. Similar analysis of the data of Waesche & Wenograd[12] is also shown in Fig. 3. Here again the increase in the $\dot{r}$ with the decrease in the oxidizer particle size is seen and also the non-linear dependence is observed.

Table 1. Burning rate data of PS/AP (75 per cent) propellants as a function of particle size of AP at ambient pressure

Particle size range of AP (microns)	$\dot{r}$ (cm/sec)
40–53	0.095±0.002
75–100	0.088±0.002
100–150	0.078±0.001
150–212	0.075±0.001
200–300	0.068±0.0025

In composite propellants the particle size effect has been explained by Bastress[4]. According to him the mono-propellant AP deflagration controls the combustion.

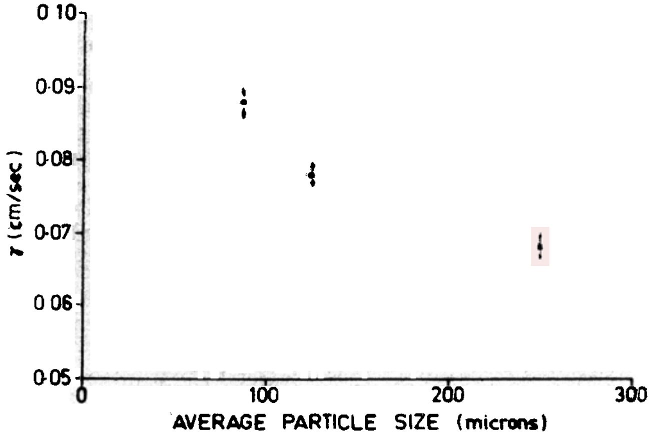

Figure 1. Plot of burning rate of AP/PS (75 per cent) propellant vs. average oxidizer (AP) particle size.

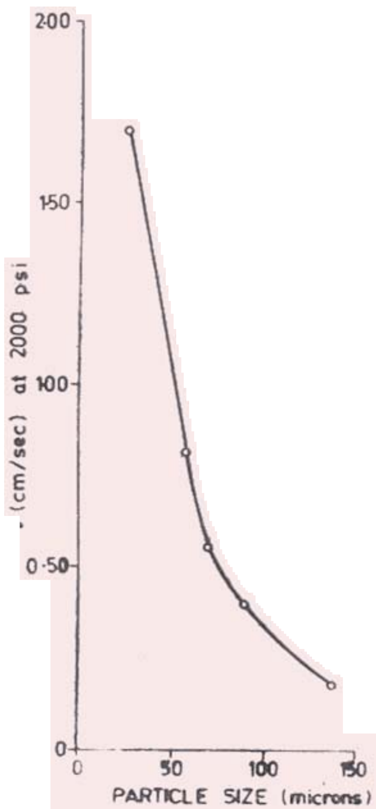

Figure 2. Plot of $\dot{r}$ vs. particle size for stoichiometric mixtures of AP/PS (Analysis of the data of Adams *et al.* 1960).

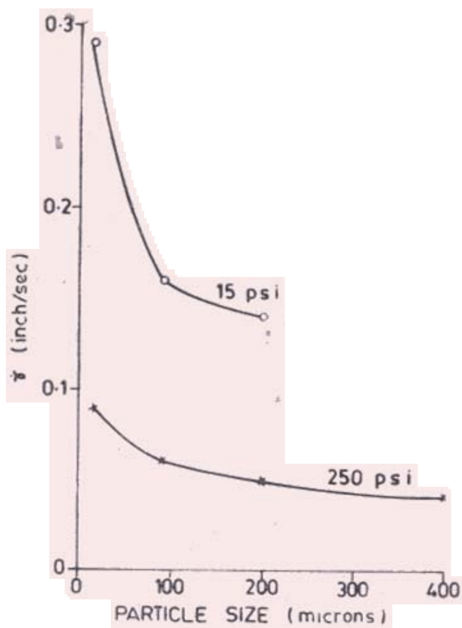

Figure 3. Effect of oxidizer particle size on the $\dot{r}$ of PBAA/AP (75 per cent) propellant. (Analysis of the data from Waesche and Wenograd, 1967).

Waesche *et al.*[12] explained the particle size effect based on the condensed phase theory. They studied the thermal decomposition (TD) and combustion of copolymer of polybutadiene and acrylic acid (PBAA)/AP (75 per cent) propellants as a function of particle size both at ambient pressure and at 250 psi[12]. TD was studied by Differential Scanning Calorimetry (DSC). From their thermograms the end temperature has been calculated and the data are plotted in Fig. 4, where it is evident that TD gets sensitized as the particle size is decreased both at ambient as well as higher pressures. To further clarify the effect of particle size, TD of the propellant and oxidizer was studied as a function of the AP particle size. TD data of the propellant and AP decomposition are given in Figs. 5 and 6. From the weight loss vs. time plots the average rate for 25 per cent decomposition was calculated and the same has been plotted in Fig. 7 both for propellant and AP. Fig. 7 shows that as the particle size decreases, the decomposition rate increases both for the propellant and AP and then falls off. However, the particle size at the maximum rate is different in the two cases which may be due to the difference in the physical state.

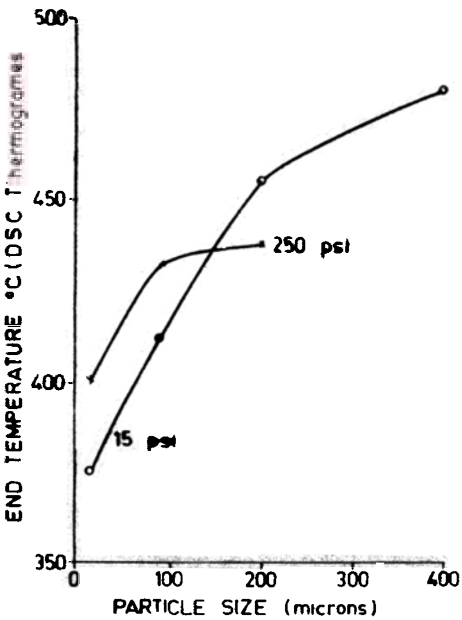

Figure 4. Plot of end temperature vs. particle size of AP. (Data from Waesche and Wenograd, 1967, PBAA/AP (75 per cent) propellant).

In AP decomposition, the effect of particle size has been explained on the basis of Mample's theory[13] according to which the fall in the rate after the maximum is due to the overlap of the growing nuclei. A similar explanation can also be given for the propellant (which contains high proportions of AP) decomposition.

The difference in the particle size behaviour of $\dot{r}$ from the TD of the propellant and the oxidizer may be due to the following reasons :—

(i) It has been recently[14] shown that change in $\dot{r}$ is one-fold when there is a three-

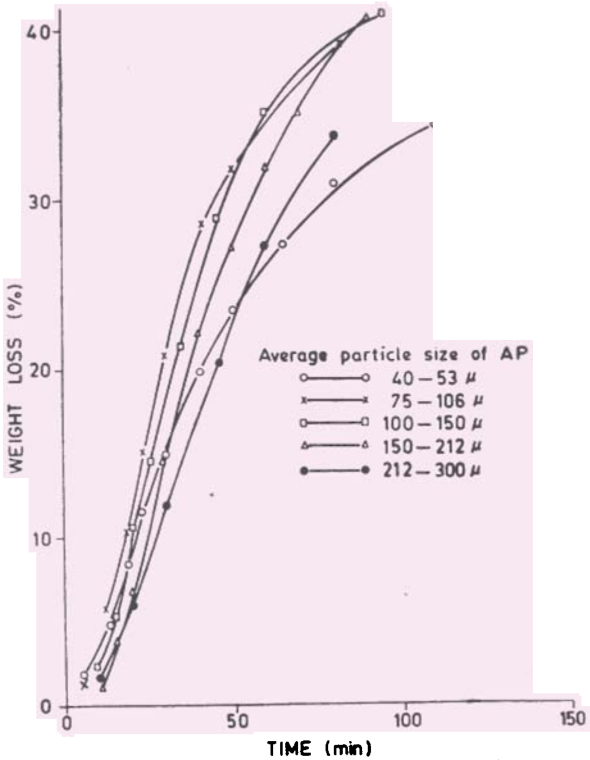

Figure 5. Plot of percentage weight loss vs. time for PS/AP (75 per cent) propellant.

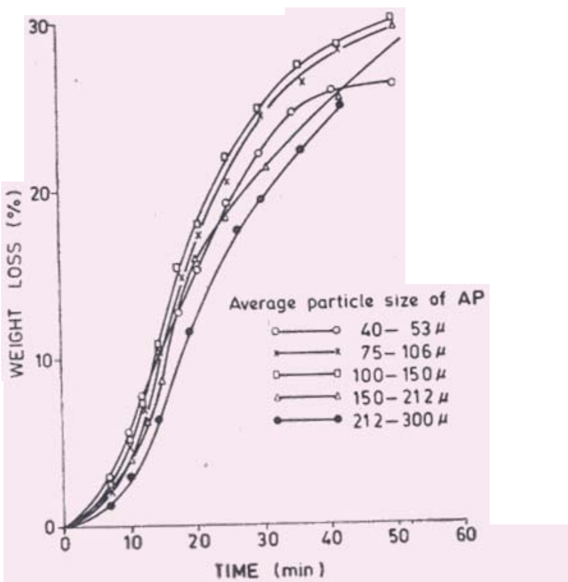

Figure 6. Plot of percentage weight loss vs. time for AP.

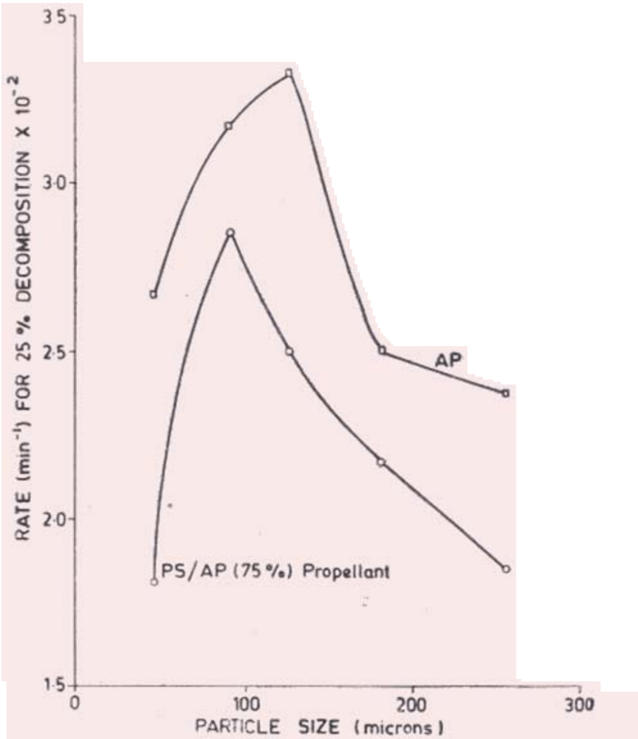

Figure 7. Plot of rate of decomposition vs. average particle size.

fold change in TD. Thus, to observe a reversal in the $\dot{r}$ plot one needs a very drastic change in the TD characteristics.

(ii) The effect of particle size may not be observed in those formulations which burn at a very high rate. Such compositions do not give sufficient time for the particles to decompose. Bakhman[2] has observed a reversal in the $\dot{r}$ of condensed mixture for the composition which are oxidizer deficient and burn at a slow rate. Waesche *et al.*[12] have also pointed out that condensed phase reactions become more and more pronounced with low $\dot{r}$ compositions. This is because in compositions which have a low $\dot{r}$ (as in the case of fuel rich composition), the combustion of the propellant may be considered to be akin to the TD and hence a reversal is observed.

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