

Technical Notes

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Effect of Preheating on the Burning Rate of Solid Propellants

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Introduction

ALTHOUGH the effect of initial temperature of solid propellants on the burning rate (i.e., temperature sensitivity) is well known, the change of burning rate due to the preheating of the propellant has not received any attention. The temperature sensitivity $(\pi_r)_P$ and $(\pi_r)_K$ of the burning rate is expressed by the following two equations which represent the relative variation of burning rate (\bar{r}) per degree centigrade of the initial temperature (T_i) at constant pressure (P) and at constant motor geometry (K), respectively

$$(\pi_r)_P = (1/\bar{r}) (d\bar{r}/dT_i)_P = (d \ln \bar{r}/dT_i)_P$$

$$(\pi_r)_K = (1/\bar{r}) (d\bar{r}/dT_i)_K = (d \ln \bar{r}/dT_i)_K$$

Temperature sensitivity may be obtained by determining the burning rate (at constant pressure) at different initial temperatures of the propellant. In preheating, on the other hand, the propellant is heated at a particular temperature for a particular time and then it is cooled down to room temperature. The burning rate then is determined at ambient temperature and at constant pressure.

Recently, it has been shown by Pai Verneker and Rajeshwar that the thermal decomposition of preheated ammonium perchlorate (AP) is sensitized.¹ It has also been shown recently by us that the thermal decomposition of AP and of the propellant are correlated with its burning rate.² This implies that the thermal decomposition and the burning rate of preheated propellant also should be sensitized. The objective of the present Note, therefore, is to see 1) whether the burning rate and the thermal decomposition of the preheated propellants increase and 2) if there exists any correlation between them.

Experimental

The polystyrene PS/AP propellants were prepared as described earlier.³ Recrystallized commercial AP of the particle size 172-204 μ was used in the propellant formulation. Fractionally distilled styrene monomer was used for preparing the binder. The propellant composition contained 25% PS and 75% AP by weight. The preheating studies were carried out in air at 63, 100, 120, 150, and 200°C. The temperature

was maintained constant up to an accuracy of $\pm 2^\circ\text{C}$. The propellant sample of length 8 cm and diameter 1.3 cm were used for preheating studies. The burning rate was determined at ambient temperature and pressure. The percentage change in burning rate was calculated with respect to the unheated propellant.

Isothermal decomposition of the propellant at 270°C was studied on a TGA assembly, as described elsewhere.⁴ The propellant piece of definite shape and weight (50 mg) was used in all the runs.

The changes in weight loss and in the density during the preheating also were measured. For these studies propellant samples in the shape of a flat spherical disk of diameter 1.3 cm and width 0.65 cm were used. The percentage changes in the density and weight loss were calculated as a function of time and temperature of preheating.

Results and Discussion

Figure 1 shows the percentage change of the burning rate as a function of temperature and time of preheating. It is evident that the burning rate increases with the time of preheating of the propellant. For a given time of preheating it can also be seen that the percentage change in burning rate increases with the temperature of preheating. A similar trend in thermal decomposition is evident from Fig. 2. This confirms our earlier observation² that there is a correlation between the burning rate of the propellant and its thermal decomposition. Together with our prior observation,¹ one can show further a correlation between the thermal decomposition and burning rate of propellant and the thermal decomposition of AP. Although it is difficult to speculate on the exact mechanism of sensitization, it seems likely that the interpretation for the sensitization of preheated AP¹ should hold good in the case of propellant as well, i.e., the cause of the sensitization lies in an increased strain resulting from preheating.

To probe the possibility of the role of porosity of the propellant, developed during preheating, on its burning rate, we have made some measurements of the weight loss and density change during preheating. During the preheating, the

Table 1 Comparison of the percentage change in weight loss and burning rate during preheating

Temperature, °C	Time, hr	% Weight loss	% Change in burning rate
150	24	0.420	7.5
	48	0.500	17.5
	72	0.640	27.5
	96	0.740	41.0
	120	0.750	48.0
120	48	0.320	6.0
	96	0.350	12.6
	144	0.370	18.5
	192	0.390	25.0
	240	0.420	31.5
100	48	0.260	2.0
	96	0.270	3.5
	144	0.280	5.0
	192	0.285	6.5
	240	0.350	8.0
63	360	0.44	4.0
	480	0.50	5.5
	600	0.54	7.5
	960	0.58	9.5

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Index categories: Fuels and Propellants, Properties of; Solid and Hybrid Rocket Engines.

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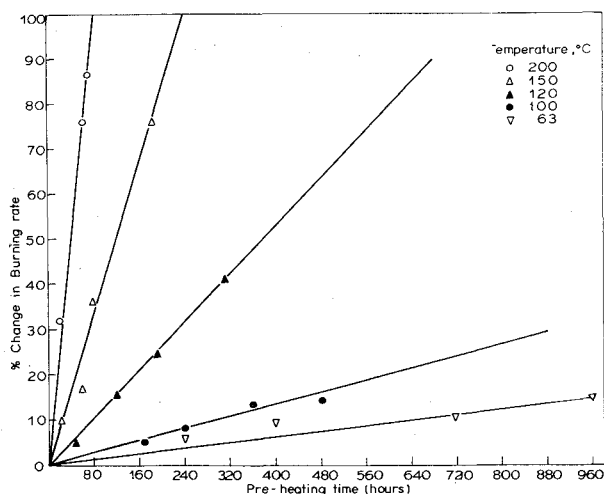


Fig. 1 Dependence of burning rate of PS/AP (75%) propellant at ambient pressure as a function of time and temperature of preheating.

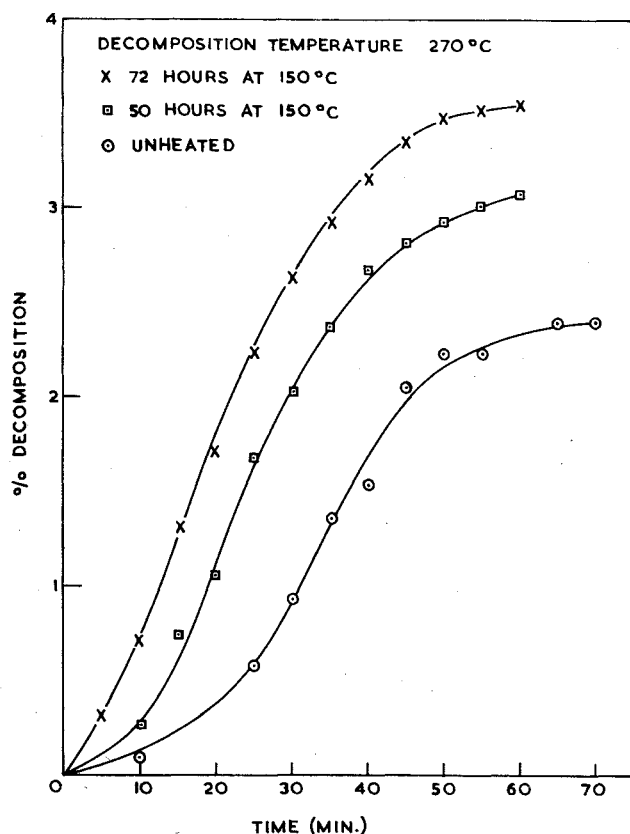


Fig. 2 Percentage decomposition vs time at 270°C of the preheated propellant at 150°C for different preheating time.

propellant shows a change in weight as a function of time and temperature of preheating. The data are presented in Table 1. It may be noted that the volume of the sample remains the same as in the preceding preheating experiments. This implies that the percentage weight loss is also the percentage change in density and that the gaseous products during preheating escape from the propellant and make the propellant porous. Therefore, one may argue that the observed change in the burning rate may be due to change in porosity of the propellant. Table 1 shows a comparison of the percentage change of the weight loss which in fact is proportional to the change in porosity and the percentage change in burning rate. It may be seen clearly that the percentage change in the weight loss, and hence the porosity, is almost negligible when compared to the extent of change of burning rate, thereby showing

that the porosity has very little effect on the burning rate changes due to the preheating. However, even if the increase in the burning rate is due to the increase in porosity, the porosity itself is caused by decomposition and thus the change in the burning rate is related to the decomposition of the propellant. Further, we find that the propellant becomes yellow in color during preheating; this suggests that the increase in the burning rate is due to the accumulation of the yellow substance. Attempts are being made to analyze this yellow substance so that it could be used as a natural catalyst.

The present work, has shown that preheating of the propellant brings about a sensitization in the thermal decomposition and the burning rate of the propellant. It has shown further that a correlation exists between thermal decomposition and burning of the propellant. The present work together with earlier work² is a part of a program designed to clarify the role of condensed-phase reactions in combustion.

It may be of interest to note that Glaskova's data show pronounced desensitization in burning rate by additives known to inhibit the decomposition of AP.⁵ This effect becomes insignificant beyond 200 atm, but in the pressure range of interest in rocket motors the data show a two- to threefold change. Similarly, Boggs et al. write that "The inclusion of dichromate into the crystal was responsible for increasing the deflagration rate (of AP) as a function of dopant concentration and pressure."⁶

To have a deeper insight into the role of decomposition during combustion, we have observed that the propellant in the actual combustion decomposes in a few layers below the surface. This residue has been subjected to analysis and our preliminary observations have shown that this residue is somewhat similar to the residue obtained in the partial decomposition of the propellant. Thus, the foregoing arguments indicate that the thermal decomposition of the propellant, and the AP could be related to the burning rate.

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On the Buckling of Shallow Spherical Caps Subjected to Uniform External Pressure

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- a = base radius of spherical shell
 h = shell thickness
 n = circumferential wave number

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