

Studies on the Pyrolysis of Composite Solid Propellants leading to Ignition

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ABSTRACT

Studies on the pyrolysis leading to ignition of polystyrene (PS)/ammonium perchlorate (AP), polyvinyl chloride (PVC)/AP and polyphenol formaldehyde (PPF)/AP propellants revealed that the activation energy for the ignition strongly depends upon the binder. Double base propellants exhibit an empirical relationship between the ignition delay (τ) and the oxidiser concentration; when the same equation is applied to composite solid propellants, the plot of $\ln \tau$ vs $\ln C$ (C =Concentration, %) yields a straight line with a knee corresponding to 65-70 per cent AP above which the dependence on τ becomes less sensitive.

1. INTRODUCTION

In composite solid propellants the oxidiser and binder play a significant role in controlling the ignition and combustion. It is not known precisely whether the binder degradation behaviour or oxidiser decomposition behaviour would control the ignition of the propellant. Sufficient information is not available on the ignition of the composite propellant as a function of oxidiser concentration.

2. METHOD

The AP/PS propellants (oxidiser concentration of 60, 65, 70 and 75 weight per cent; particle size of 58-155 μ m) were prepared as described earlier.¹

Polyphenolformaldehyde (PPF) resin was prepared by refluxing phenol (56.49) sodium hydroxide (5.4 ml of 40 per cent solution) and formaldehyde (115.6 ml of 40 w/v per cent) for 8 hr at 70°C. Afterwards, 2N hydrochloric acid (5.4 ml of 10N) was

added to neutralise the alkali and the refluxing was continued with stirring till the prepolymer of desired viscosity was obtained. Water from the polymer was removed by vacuum distillation. The preparation of the propellant ($O/F = 3$) from this prepolymer was achieved in the same manner as used for AP/PS propellant except that the curing was done only for 5 days at 50°C .

AP-Polyvinyl Chloride (PVC) propellant ($O/F = 3$) was made as follows. 20 g of PVC powder was taken in a beaker and to it 20 g of dry dibutyl phthalate (DBP) was added in little amounts with continuous stirring so that a thick paste is obtained. AP was mixed with this paste and cast in small diameter glass moulds which were subsequently cured at 100°C for 8 hr followed by heating at 130°C for 5 hr.

25 mg cube shaped propellant samples were prepared by rubbing the propellant samples against fine emery paper followed by cleaning with a fine brush. Care was taken to keep the sample geometry same in all the runs. The line diagram of the assembly for the measurement of τ is given in Fig. 1. The variac was adjusted so that the furnace is maintained at the required temperature, which is always above the

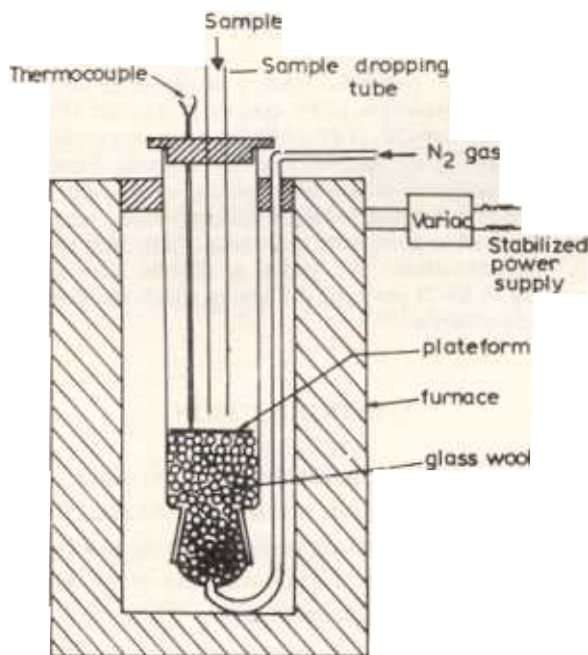


Figure 1 Ignition delay measuring assembly.

ignition temperature of the propellant sample. The temperature of the stainless steel **platform** was monitored with a chromel-alumel thermocouple. The guide tube which is kept about one centimeter above the **platform** ensures the sample to fall at the centre of the **platform** everytime; the sample was dropped into the furnace through the guide tube and simultaneously the timer was started. It was stopped when the visible flame appears; the time between the introduction of the sample and the appearance of the flame (τ) was noted. Since the ignition of the sample raises the

platform temperature, sufficient time was allowed for the platform to attain the original temperature for subsequent measurement. The average of several experiments, at the same temperature, was taken as the ignition delay. The τ was measured by using a manually operated electronic timer whose sensitivity was 0.01 Sec. The experiments were carried out in flowing N_2 atmosphere (10 cc/min). The fluctuation of the furnace temperature was within $\pm 1^\circ\text{C}$.

3. RESULTS AND DISCUSSION

3.1 Effect of the Binder

The dependence of τ on temperature is shown in Fig. 2 for different binders and at a fixed oxidiser loadings ($O/F = 3$). τ could be related to the activation energy (E) of the ignition process by the Arrhenius equation;

$$1/\tau = 1/(\tau_1 + \tau_2) = A \exp(-E/RT) \quad (1)$$

where τ is the total ignition delay time, τ_1 is the physical delay which is the time taken for heating the sample to a temperature where chemical reactions commence and τ_2 is the chemical delay time. In the present investigation all the three propellants have the same AP/binder ratio. Since in these propellant formulations AP is in large excess, it is appropriate to consider that thermal diffusivity in the three propellants are similar and hence τ_1 has the same value for all the propellants. Thus, any change in the overall E of the process may be due to the change in the rate controlling step associated with the chemical reactions during the ignition process. If rate controlling step is in the oxidiser decomposition, one would get the same E for all the three propellant

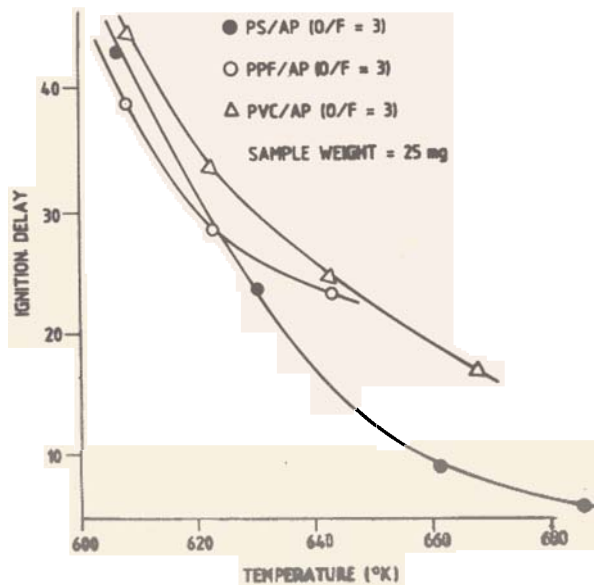


Figure 2. Effect of the binder type on ignition delay.

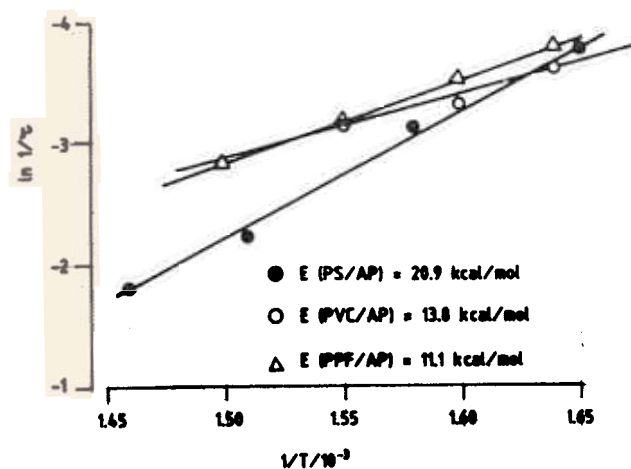


Figure 3. Arrhenius plot for the ignition delay of AP based propellants containing different binders.

systems. Fig. 3 shows that E varies with the change in the binder suggesting thereby that the rate controlling step may be associated with the binder degradation process rather than the oxidiser decomposition.

At this juncture it is to be mentioned that though the work of Baer *et al*² has shown that E for the ignition and AP decomposition was similar (~ 30 K.cal mole⁻¹) but according to Shannon³ the ignition may depend on both the oxidiser and binder degradation.³

3.2 Dependence on Oxidiser Loading

At two different temperatures, the dependence of τ on oxidiser loading is shown in Fig. 4. At a particular temperature, the dependence of τ on C (oxidiser concentration) was found to fit the following equation :

$$\tau = \lambda / C^m \quad (2)$$

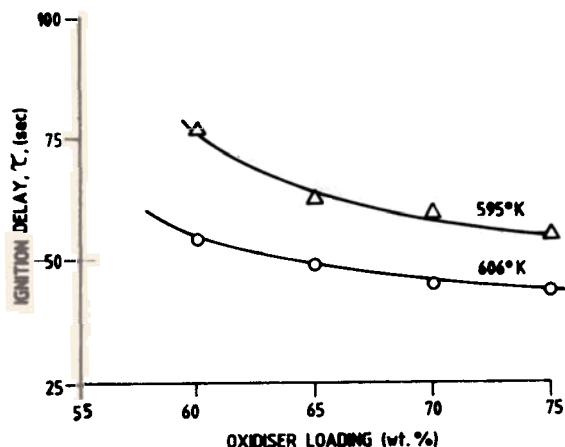


Figure 4. Effect of oxidiser loading on the ignition delay of AP/PS propellants.

where λ and m are constants for a particular system. Eqn. (2) is similar to the one given for double base propellants.⁴ From the plot of $\ln \tau$ vs $\ln C$, as shown in Fig. 5,

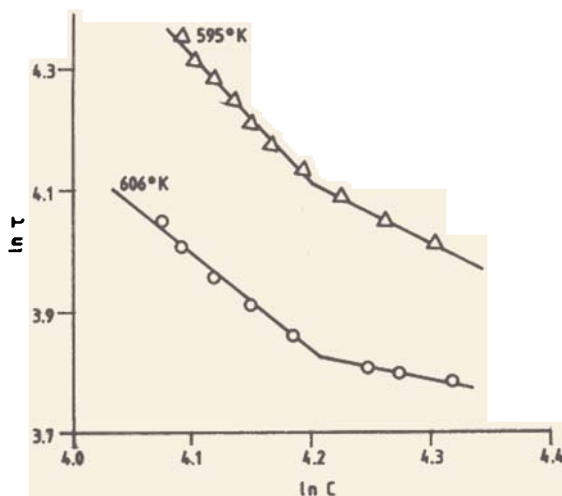


Figure 5. Dependence of ignition delay on the oxidiser concentration of AP/PS propellants.

it can be seen from the plots that there are two linear portions having a knee at a composition of 65-70 per cent oxidiser. For the PS/AP system, we can write the following equations.

Below 65 per cent of the oxidiser at 595°K,

$$\tau = 25 \times 10.6065/C^{2.32} \tag{3}$$

Above 65 per cent of the oxidiser at 595°K

$$\tau = 25 \times 5.6786/C^{1.14} \tag{4}$$

Similarly, below 65 per cent of the oxidiser at 606°K

$$\tau = 25 \times 7.9015/C^{1.74} \tag{5}$$

and, above 65 per cent of the oxidiser at 606°K

$$\tau = 25 \times 1.9411/C^{0.32} \tag{6}$$

The influence of oxygen and other reactive oxidiser gases on ignition characteristics has been investigated in detail by several workers.^{5,6} It has been found that τ increases by increasing the oxygen partial pressure at a level where oxygen concentration is more than 0.6 to 0.7 mole fraction.⁶ Further, it has been observed⁶ that AP decomposition contributes towards ignition when the surrounding atmosphere contains less than 0.5 to 0.6 moles of oxygen. Shannon³ has also observed that the τ decreases as the oxidiser loading increases. Our results show that below 65-70 per cent oxidiser, the influence of oxidiser concentration on τ is more pronounced and above this region it is less pronounced.

REFERENCES

1. Kishore, K., Pai Verneker, V.R. & Prasad, G., *Combust. Sci. Technol.*, **19** (1979), 107.
2. Baer, A.D., Cheng, J.T., Bench, L.S., Keller, J.D. & Pyan, N.W., Ignition and combustion of solid propellants, University of Utah Technical Reports AFOSR, Oct. 1964, p. 40-65.
3. Shannon, L.J., *AIAA Journal*, **8** (1970), 346.
4. Brown, R.S., Anderson, R. & Shannon, L.J., *Advances in Chemical Engineering*, (Academic Press. Inc., New York), Vol. 7, 1968, p. 1.
5. Summerfield, M., Shinner, R., Hermance, C.E. & Wenograd, J., A chemical review of recent research on the mechanism of ignition of solid rocket propellants, Princeton University, Department of Aeronautical Engineering Report No. 661, Aug. 1963.
6. Kashiwagi, T., Mac Donald, B.W., Osad, H. & Summerfield, M., Ignition of a solid polymeric fuel in a hot oxidising gas stream, XIIIth Symposium (International) on Combustion, 1971, p. 1073-1084.