Def Sci J, Vol 36, No 4, October 1986, pp 425-428

Changes in the Calorimetric Value and Ignition Temperature of Composite Solid Propellants During Ageing-A Note

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Received 14 June 1985; revised 28 August 1986

Abstract. Calorimetric value and ignition temperature of carboxy terminated polybutadiene/ammonium perchlorate propellant decrease during accelerated ageing. The behaviour has been explained on account of binder loss and condensed phase reactions in the propellant matrix.

1. Introduction

Ageing brings about significant changes in the performance parameters of composite solid propellants : the changes in mechanical properties, thermal decomposition and burning rate have been examined earlier[1-10]. But as how the ageing brings about changes in the calorimetric value and initial ignition behaviour is not known for certain. Milera[11] has observed that the calorimetric value of propellants aged for i-6 months at 65-100°C does not change.

Most of the earlier literature on ageing vis-a-vis ignition of the propellant is related to the safety aspects of the propellant[12-19]. In the present investigation, we have examined different kin of ignition behaviour which has a relevance to the initial. ignition temperature of the propellant and bears a direct consequence to our earlier finding that thermal decomposition rate changes during ageing". The objective of this paper is to examine the changes in the calorimetric value and explain the decrease in the ignition temperature, reported earlier[20], during the accelerated ageing of carboxy terminated polybutadiene (CTPB)/ammonium perchlorate (AP) propellants.

2. Experimental

CTPB/AB propellant was prepared as described elsewhere[21]. For comparative studies the neat prepolymer was also cured under similar conditions. Aluminised propellant

(CTPB/AP/Al) was prepared by adding 18 wt per cent of aluminium in the propellant mix.

Ageing was carried out in incubators (in air) in the temperature range 60-120°C and the ignition temperature and calorimetric values were determined for the aged samples. Cylindrical samples of 4 mm diameter and about 1 cm length having 25-50 mg wt. were used. The samples were removed periodically and cooled to the room temperature to determine the ignition temperature and calorimetric values.

The calorimetric values were determined for the aged samples using parr adiabatic bomb calorimeter model 1243 coupled was a microprocessor model 1680. The calorimetric values were measured in nitrogen at 25 atm for a known weight of sample and the error in the measurement varied from 0.5 to 0.9 per cent. Three measurements were done for each set of experiments.

3. Results and Discussion

3.1. *Effect of Ageing on the Calorimetric Values*

The calorimetric values of the aged samples are presented in Table 1. The observed decrease in the calorimetric values can be explained from the following facts.

Table 1. Effect of ageing on calorimetric values

Temperature (°C)	Calorimetric value (cal. g^{-1})		
	CTPB/AP Days		CTPB/AP/Al Days
	20	60	20
unaged	1010	1010	1365
60	1009	991	1360
70	995	980	1351
80	942	936	1304
100	935	936	1242

The weight loss in PS/AP propellant*' (aged at 60-100°C, IO-40 days) is about 0.3-0.6 per cent. A similar weight loss (0.5 per cent) has also been observed by Nagatomo[23] for polybutadiene and polyurethane composite propellants (at 85°C for 10 to 17 days). In present studies we have observed a maximum weight loss of about 1 per cent.

A maximum change of 6.5 - 7.0 per cent in the 'calorimetric values of CTPB/AP propellant, which may be attributed either to the loss of the oxidizer or the binder as shown in Table 1. Nagatome[22] has observed that the neat binder (polybutadiene/polyurethene) undergo weight loss to the same extent as that of the corresponding propellants when aged under identical conditions. Korobeinichev et al[24] have also observed that the binder degrades first during thermal stability of AP when compared to the binder under ageing conditions suggests that the propellant weight loss is due to the binder loss. The maximum weight loss during ageing approximately compares to the maximum change in the calorimetric value which accounts for 1.5 wt per cent of the binder.

The activation energy for the change in calorimetric values was found to be 15 kcal mole $^{-1}$ which is concordant to the corresponding values for the change in the thermal decomposition and burning rate during ageing[9].

3.2. Effect of Ageing on Ignition Temperature

The ignition temperature of the propellant[20] decreases with the ageing as shown in Table 2. The gel content of CTPB propellant increases during ageing which is

Table 2. Change in the ignition temperature of CTPB/AP propellant during ageing

Ageing temperature 120°C
Heating rate 10°C min $^{-1}$
Sample weight 25 mg

Ageing time (days)	Ignition temperature† (°C)
0	347
4	328
8	318
12	314
16	312
20	272

† error ± 2°C, ref. 20.

attributed to the formation of additional cross-links at the double bonds[5]. As a result of this cross-linking the propellant matrix becomes rigid and the escape of decomposition products of AP/binder is prevented which leads them to react exothermically inside the matrix. The above condensed phase heat release in the matrix lowers the ignition temperature as the ageing proceeds (Table 2).

4. Conclusion

It may be concluded that the calorimetric value and ignition temperature change during ageing. However, we have used small samples in our present study and therefore the results are relevant to the changes which might happen to surface layer rather to the bulk of the propellant.

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