



Studies on Aluminized, High Burning Rate, Butacene® Based, Composite Propellants

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Abstract: This paper reports on a Butacene® based composite propellant with high burning rate. The effect of replacing HTPB with Butacene® on the physical, mechanical and ballistic properties, and sensitivity towards impact and friction, has been studied. The ballistic properties were evaluated as burning rates at various pressures (7-11 MPa), pressure exponents, ignition temperatures etc. As expected, a remarkable enhancement in burning rate at low pressures was observed with increasing percentage of Butacene®. Comparatively lower n-values were observed for compositions containing Butacene® than for HTPB based propellants. The sensitivity of Butacene® based compositions, in terms of impact and friction, was found to be increased with an increasing percentage of Butacene®.

Keywords: Butacene®, ferrocene, pressure exponent

1 Introduction

Propellant scientists have attempted various methods to enhance the burn rates of composite solid propellants in order to meet mission objectives. The burning rates of ammonium perchlorate (AP) composite solid propellants are routinely adjusted by the addition of small amounts of ballistic modifiers to the formulation. Common burning rate catalysts are transition metal compounds, particularly ferric oxide and copper chromite, nano metal particles, metal chelates, ferrocene and its derivatives etc. Among these, ferrocene and its derivatives containing alkyl, acyl or ester functions have been widely used, owing to their extraordinary effects

in enhancing the burning rates of composite propellants. They are chemically compatible with other ingredients of the propellant composition, particularly the HTPB binder system. Also, they do not adversely affect the pot life and mechanical properties, and show only a minor influence on sensitivity to impact, friction and the ageing characteristics, even at high concentrations [1]. A large number of derivatives such as n-butyl ferrocene [2], 2'-bis (ethylferrocenyl) propane (catocene), 2,4-dinitrophenylhydrazine derivative of acetyl ferrocene, 1-pyrrolidinyl methyl ferrocene, di-t-butyl ferrocene, ferrocene dicarboxylic acid diesters etc. have been reported [2-5]. Based on their various properties [1], 3-diferrocenyl-1-butene (DFB) is considered superior for improving burn rates, compared to Fe_2O_3 , and being a liquid, further facilitates increases in solids loading, thereby improving the performance of the composite propellants.

However, because of their tendency to migrate and their susceptibility to oxidation, ferrocene derivatives have not found widespread use in solid propellants. The migration and oxidation associated with ferrocene derivatives however, can be eliminated by their chemical impregnation in to either HTPB or the curing agent. Societe Nationale des Poudres et Explosifs (SNPE), France, has developed a binder by grafting ferrocenyl groups on to the pendant C=C double bonds in the vinyl component of hydroxyl terminated polybutadiene (HTPB). This prepolymer is named Butacene® (Figure 1).

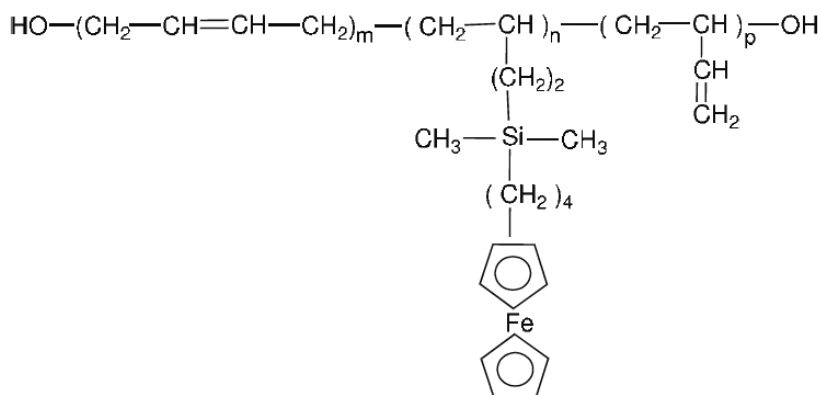


Figure 1. Structure of Butacene.

Literature reports by Doriath *et al.* [6], Gotzmer *et al.* [7], Nguyen *et al.* [8] and Gore *et al.* [9] elucidated the use of Butacene® in composite propellants for achieving high burning rates, but systematic data on the effect of Butacene® at different percentages on a composite propellant is lacking. Hence, the present

work was undertaken to study the effects on the ballistic as well as the mechanical and physical properties of incremental replacement of HTPB by Butacene® in aluminized composite propellants.

2 Experimental

2.1 Formulation and raw materials

Propellant compositions containing 84% solids and 16% binder were prepared by the slurry cast technique [10]. For propellant mixing, a vertical planetary mixer of 1 L capacity was used. The binder comprised HTPB (from M/s Anabond Pvt. Ltd, India) and Butacene® prepolymer (SNPE, France) in 90:10, 70:30, 50:50, and 30:70 ratios by wt.% and the amount of IPDI has been adjusted to keep the NCO/OH ratio constant. These binder systems were mixed with plasticizer DOA (from M/s Indo-nippon, India) in a 60:40 proportion. The additives pyrogallol, trimethylol propane (TME) and n-butane-1,4-diol (nBD) were used as bonding agents to achieve the required mechanical properties. Ammonium perchlorate (AP), bimodal 200 μ and 37 μ , (from M/s Tamilnadu Chlorates, India) was used in the formulations. Aluminium metal powder (from M/s Metal Powder Company Ltd, India) with an average particle size of 15 μ was used. The propellant formulations were mixed in 700 g batches under vacuum and cured with iso-phorone di-isocyanate (IPDI, Mercks) with ferric acetylacetonate (FeAA) as a cure catalyst. The propellants were cured at 60 °C for 5 days in a water-jacketed oven, followed by a maturation period of 15 days at room temperature (~30 °C). Butacene® (molecular weight, Mn ~13,500, hydroxyl value 35 mg KOH/g, iron 8 \pm 0.5 wt.%, viscosity ~1000 Poise at 25 °C) and HTPB (molecular weight, Mn~ 2300, hydroxyl value 42 mg KOH/g, viscosity ~70 Poise at 30 °C) were used in the present work.

2.2 Characterization methods

The physical properties of the propellants such as density and end of mix viscosity were determined by the specific gravity method and viscometry, respectively. The viscosity measurements were performed using a dial type HBT model of Brookfield Viscometer with TC spindle.

The strand burning rates of the propellants were determined in the pressure range of 7.0-11.0 MPa at room temperature, by employing an acoustic emission technique [10-11]. The method involved the combustion of strands (ignited by means of a Nichrome wire) of dimensions 140 \times 6 \times 6 mm in a nitrogen pressurized steel bomb. The acoustic signal generated, and perturbations caused

by the propellant deflagration, were unidirectionally transmitted through the water medium to a piezoelectric transducer (200 kHz) in conjugation with an oscilloscope. The burn rates were computed from the time recorded for the trial conducted at each pressure, for each sample. The standard deviation was of the order of 0.2%.

The sensitivity of the propellant compositions to impact stimuli was determined by the BAM hammer method with a 2 kg drop weight [12], and the results are reported in terms of the statistically obtained 50% probability of explosion (h_{50}). Friction insensitivity was measured on a BAM friction (Julius Peter) apparatus [13] by incrementally increasing the load from 0.2 to 36 kg, until there was no ignition or explosion in five consecutive test samples.

The ignition temperature of the propellant samples was determined in a Wood's metal bath. A sample of 40 mg was used for each experiment and the bath was heated at 5 °C/min. The temperature at which the sample ignited was taken as the ignition temperature.

The mechanical properties were obtained using an Instron (Model TIC-1185, UK). The instrumental operating parameters were always maintained constant, gauge length: 45 mm, cross-head speed: 50 mm/min. The stress and strain properties were determined using a dumbbell shaped specimen according to ASTM D638 standards at room temperature. An average of five readings were taken.

The Differential Scanning Calorimetry (DSC) studies were carried out on a Perkin Elmer DSC-7 instrument operating at a heating rate of 10 °C/min in a nitrogen atmosphere with 1-2 mg of sample. Thermal gravimetric analysis was undertaken on a Mettler Toledo TG/SDTA-8551.

3 Results and Discussion

3.1 Processing

Propellant compositions based on AP/HTPB/Al and Butacene® have been formulated. The propellant composition series comprised of 17% Al with varying percentages of Butacene®. The detailed compositions are given in Table 1. The base composition without Butacene® was processed simultaneously. The propellants were subjected to various performance tests.

Table 1. Compositions of Butacene® based propellants

| Ingredients | Approximate wt.% | | | | |
|----------------------------------|------------------|---------------|---------------|---------------|---------------|
| | Base | 1 | 3 | 5 | 7 |
| HTPB+Butacene (HTPB:Butacene) | 10 (100:0) | 10 (90:10) | 10 (70:30) | 10 (50:50) | 10 (30:70) |
| DOA | 4 | 4 | 4 | 4 | 4 |
| IPDI | 1 | 1 | 1 | 1 | 1 |
| Bonding agent | 1 | 1 | 1 | 1 | 1 |
| AP | 67 | 67 | 67 | 67 | 67 |
| Al | 17 | 17 | 17 | 17 | 17 |

3.2 Physical properties

Butacene® based propellants were observed to have a slightly higher density (1771 kg/m³ for 50% Butacene® in the binder) than HTPB based compositions (1763 kg/m³) because the density of Butacene® at 1015 kg/m³ is higher than that of HTPB (950 kg/m³). From a processing point of view, incorporation of up to 50% Butacene® did not enhance the viscosity significantly (from 240 Pa·s to 420 Pa·s, both at 40 °C) but in the case of composition 7, with 70% Butacene® in the binder, the viscosity had increased dramatically from 420 Pa·s to 700 Pa·s at 40 °C. The results are shown in Table 2.

Table 2. Physical and ballistic properties for Butacene® based propellants

| Composition | Burn rate at RT | | | Pressure exponent (n) (7-11 MPa) | Density [kg/m ³] | Viscosity at 40 °C [Pa·s] |
|-------------|-----------------|----------------|-----------------|-------------------------------------|------------------------------|---------------------------|
| | 7.0 MPa [mm/s] | 9.0 MPa [mm/s] | 11.0 MPa [mm/s] | | | |
| Base | 7.51 | 8.73 | 9.86 | 0.602 | 1763 | 240 |
| 1 | 11.44 | 12.15 | 12.79 | 0.246 | 1765 | 280 |
| 3 | 13.54 | 14.65 | 15.58 | 0.310 | 1767 | 360 |
| 5 | 17.41 | 19.03 | 21.07 | 0.419 | 1771 | 420 |
| 7 | 19.69 | 21.20 | 24.03 | 0.434 | 1773 | 700 |

3.3 Strand burn rate

The burning rates were determined in the pressure range 7-11 MPa. The base composition exhibited burning rates in the order of 7.5-9.8 mm/s (Table 2). Replacement of 10% HTPB with Butacene® lead to almost 50% increase in the burning rate at 7 MPa pressure, while replacement of 30% HTPB enhances the burning rate further by 20%, and continues upwards with the replacement of 70% HTPB with Butacene®, but after 50% replacement the increase in the burning rate is not pronounced.

3.4 Pressure exponent

It is an interesting fact of these results that the pressure exponent increases as the percentage of Butacene® in the composition increases, but even at 70% replacement it is lower than in the base composition. The data shown in Table 2 reflect this. This means that replacement of HTPB with Butacene® decreases the pressure exponent.

3.5 Sensitivity to impact, friction and ignition

All of the propellant compositions containing different amounts of Butacene® were subjected to impact and friction. The data presented in Table 3 show that the replacement of HTPB with Butacene® increases the impact and friction sensitivities. This may be due to a catalytic effect by Butacene® and the interaction of the ferrocene groups with the ammonium perchlorate, as is seen with other classes of catalysts too [14, 15].

The compositions containing higher percentages of Butacene® have lower ignition temperatures (Table 3). This supports the fact that lowering the ignition temperature may cause early initiation of the sample, thus becoming more sensitive.

Table 3. Sensitivity data towards impact, friction and ignition

| Composition | Impact insensitivity up to [N·m] | Friction insensitivity up to [N] | F of I | Ignition temperature ¹ [°C] |
|-------------|----------------------------------|----------------------------------|--------|--|
| Base | 5.6 | 110 | 44 | 280 |
| 1 | 5.2 | 108 | 41 | 267 |
| 3 | 4.2 | 64 | 33 | 260 |
| 5 | 3.4 | 56 | 27 | 231 |
| 7 | 2.8 | 48 | 22 | 229 |

¹ Heating rate 5 °C/min.

3.6 Mechanical properties

The mechanical properties of the compositions with different amounts of Butacene® have been investigated in terms of tensile strength, % elongation and E-modulus. It was observed that the mechanical properties of HTPB and Butacene® based composition are very similar as both of the prepolymers have same backbone structure. Detailed data are presented in Table 4. Additionally, the curing process becomes slightly slower if the percentage of Butacene® in the composition has been increased. This observation can be related to the fact that the reaction of the hydroxyl groups of HTPB with the isocyanate groups

of IPDI will be slower due to the presence of the bulkier butyl ferrocene silane side chains in the Butacene® molecule.

Table 4. Mechanical properties of Butacene® based propellants at RT¹

| Composition | Tensile strength [MPa] | Elongation at max [%] | Elongation at break [%] | E-Modulus [MPa] |
|-------------|------------------------|-----------------------|-------------------------|-----------------|
| Base | 0.54 | 61.49 | 65.96 | 2.81 |
| 1 | 0.49 | 50.13 | 53.67 | 3.21 |
| 3 | 0.48 | 42.37 | 45.37 | 1.90 |
| 5 | 0.44 | 32.46 | 33.16 | 1.31 |
| 7 | 0.90 | 18.5 | 19.73 | 4.92 |

¹ Uniaxial tensile test, drawing speed 50 mm/min.

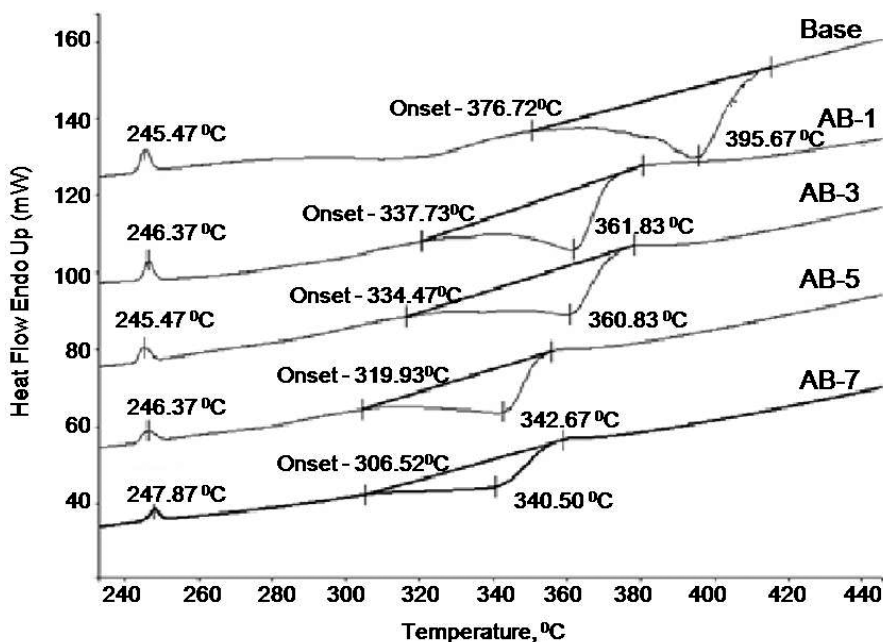
This effect is more pronounced for the 70% Butacene® containing composition 7 which does not become completely cured even with increased curing time. Hence, to overcome this problem, the NCO/OH ratio was increased from 0.8 to 0.85, to ensure complete curing, enabling the samples to be used for measurement of the ballistic properties. The mechanical properties of this composition have been presented, but are not used for comparison with the other compositions.

3.7 Thermal studies

DSC thermograms undertaken during this work, showed two prominent peaks, an endotherm at around 246 °C and an exotherm at around 395 °C to 340 °C in different compositions, which corresponds to the high temperature decomposition (HTD) of AP. The peak corresponding to the low temperature decomposition (LTD) of AP can also be seen in the thermograms, but is not very prominent. The data indicate (Table 5 and Figure 2) that the increase of Butacene® percentage in the compositions decreases the onset and decomposition temperatures of the propellants. As the percentage of Butacene® increases from 10 to 70, the decomposition temperature decreases from 361 °C to 340 °C. The lowering in the decomposition temperature is more prominent at increases of Butacene® percentage from 0% to 30%, and from 30% to 50% of the binder. This fact is also supported by the burning rate data as there is a maximum increase in the burning rates only at these two steps. The DSC data reveal that Butacene® based propellants ignite and decompose at lower temperatures. The activation energies of Butacene® based propellants determined by Gore *et al.* [9] also support this fact.

Table 5. Differential Scanning Calorimetric data for Butacene® based propellants¹

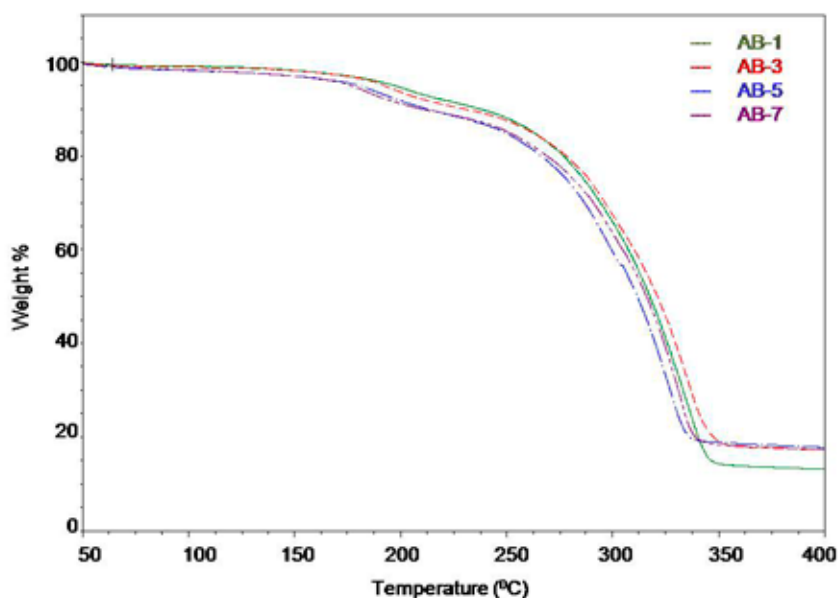
| Composition | Phase transition 1 st endo [°C] | Onset (exo) temperature [°C] | T _{max2} 2 nd exo [°C] |
|-------------|--|------------------------------|--|
| Base | 245.47 | 376.72 | 395.67 |
| 1 | 246.37 | 337.73 | 361.83 |
| 3 | 245.47 | 334.47 | 360.83 |
| 5 | 246.37 | 319.93 | 342.67 |
| 7 | 247.87 | 306.52 | 340.50 |

¹ Heating rate 10 °C/min.**Figure 2.** DSC thermogram of compositions with varying % of Butacene®.

The TGA data of Butacene® based propellant compositions also revealed that propellant decomposition occurs in two stages, which can be correlated with the low temperature and high temperature decompositions of AP respectively, in the range of 100-232 °C and 210-380 °C. The data presented in (Table 6 and Figure 3) show that an increase in the percentage of Butacene® in AP based propellants, lowers the onset of decomposition.

Table 6. Thermal Gravimetric Analysis data for Butacene® based propellants

| Sample | TGA % decomposition | T _{min} , T _{max} [°C] |
|--------|----------------------------------|---|
| AB 1 | Step 1 – 6.067 Step 2 – 79.29 | 124.57, 215.85 215.85, 381.30 |
| AB 3 | Step 1 – 7.309 Step 2 – 73.78 | 117.15, 211.85 211.85, 375.59 |
| AB 5 | Step 1 – 10.50 Step 2 – 68.87 | 102.32, 232.39 232.39, 354.48 |
| AB 7 | Step 1 – 9.32 Step 2 – 70.99 | 99.46, 222.98 222.98, 367.61 |

**Figure 3.** TGA thermograms of compositions with varying % of Butacene®.

The phenomenon of the decrease in decomposition temperature of Butacene® based propellants as derived from thermal analysis data, might be explained on the basis of a lower oxidation/reduction potential and enhanced kinetics of the ferrocene/AP reaction as compared to any other applicable iron compounds. It is also discussed in the literature that the increased rate of reaction is due to the catalytic effect of nascent Fe_2O_3 , which is formed as very fine particles during combustion of the ferrocene moiety; hence these effects, cumulatively, increase the burn rate much more than other catalysts [16].

4 Conclusions

Butacene®/HTPB binder based AP-composite propellants offer higher burning rates, with lower pressure exponent values, compared to other burning rate catalysts in HTPB based systems. The burning rate enhancement was more pronounced up to 50% replacement of HTPB by Butacene®. Thermal analysis data show a decrease in ignition as well as decomposition temperatures; hence the thermal sensitivity of Butacene® based propellants is higher than that of HTPB based propellants. The mechanical properties are more or less unchanged and can be tailored further according to operational requirements. Our results indicate that Butacene® based propellants have an edge over HTPB based propellants, especially where high burning rates are required.

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