Technical Notes

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Mechanistic Studies on Composite-Solid Propellants

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Introduction

A lot of work has been done on various aspects of composite solid propellants but very few attempts have been made to understand the actual mechanism of the combustion process.[1-4] The mechanistic studies are useful and potentially rewarding for the proper modification of the propellant characteristics based on educated information. The broad objective of the present work, therefore, is to throw some light on the mechanism of combustion.

Earlier work has demonstrated a correlation between thermal decomposition and burning of the propellant.[2] This observation along with the enthalpy measurements[5] of the propellant and its ingredients, together with the temperature profile measurements[6] have demonstrated the role of condensed-phase reactions in the combustion of the propellant.

In spite of this, no direct evidence seems to be available in favor of condensed-phase reactions. The precise objective of the present investigation is: 1) to analyze the decomposition residue and the combustion residue for stable intermediates in the polystyrene/ammonium perchlorate propellant; 2) to check for the presence of intermediate species common to both the decompostions and combustion residues; and 3) to seek changes in the burning rate by incorporating the isolated reaction intermediate of the decompositon residue, in the propellant.

Experimental

Polystyrene (PS)- ammonium perchlorate (AP) propellants (oxidizer/fuel = 3) was prepared according to the procedure described earlier.[7] Recrystallized AP of particle size 48-124 μ was used. To collect the propellant decomposition residue, about 50 mg of the propellant sample was kept in a reaction tube which was constantly evacuated by means of a vacuum pump. The reaction tube was introduced into a furnace, maintained at a temperature of $285 \pm 2°C$, and heated for half an hour. The tube was cooled, and the residue left behind was collected. Sublimate was also collected on the cooler part of the reaction tube outside the furnace but it was not subjected to analysis in the present work.

Organic part of the decomposition residue (DR) was separated by shaking the decomposition residue several times with small quantities of dry benzene, centrifuging, and evaporating the solvent. Thin layer chromatographic technique (TLC) was used to analyze DR. TLC plates were prepared by coating them with activated silica-gel adsorbent to about 0.5 mm thickness, dried in the oven at 100°C for about 30 min, and followed by cooling to room temperature. A horizontal line was drawn on the plate about 2 cm away from the lower edge. Spots of about one ml of benzene solution containing abut 5 mg of DR were applied on that line. Charged plates were placed in the developing tank containing a mixture of methanol + benzene (3:1 by volume). Before the solvent level reached the other end, plates were taken out and dried at room temperature for about 10 min for the solvent to evaporate. Two broad bands were observed corresponding to the R_F values, one (DR_I) and zero (DR_{II}). The color of DR_I was yellowish and that of DR_{II} was brown.

Combustion residue was collected by burning the propellant strands, quenching with water and followed by drying the surface and scraping it with the help of a sharp knife. The process was repeated several times to collect a sufficient amount of the material. Organic part of the combustion residue (CR) was separated from it as described in the case of decomposition residue. CR was subjected to analysis in an identical manner used for the analysis of the decomposition residue. In this case also, two bands corresponding to R_F values, one (CR_I) and zero (CR_{II}), were obtained. However, the amount separated was so small that further separate analysis of these bands could not be carried out.

Styrene-peroxide[8] was prepared from freshly distilled inhibitor free styrene monomer. The reaction between styrene monomer and oxygen was accorded in a three necked flask containing a reflux condenser at one neck, and a sintered glass bubbler in each of the other two necks. 0.328% of azobis isobutyronitrile (with respect to styrene monomer, weight by volume) was used as the initiator. Medical oxygen was passed at atmospheric pressure through the bubblers for about 24 hr. The reaction was carried out at 50°C by keeping the whole assembly in a thermostat. The liquid was observed to turn yellow in color gradually during the course of reaction. After the reaction the liquid was taken out and precipitated with methanol. The viscous liquid was separated. It was again dissolved in benzene and reprecipitated with methanol. This process was repeated for few times in order to remove the styrene from styrene peroxide. Styrene peroxide thus obtained was dried in vacuum. This peroxide was a viscous liquid having yellow color. IR spectra were recorded on a Carl Zeiss UR 10 Spectrophotometer.

Results and Discussion

Preliminary work on TLC analysis of the DR of the PS/AP (75%) propellant has been done in this laboratory[5] earlier. In that particular work a benzene + methanol (3:1 by volume) mixture was used for the separation of propellant decomposition residue obtained by heating the propellant at about 300°C for 3-4 hr. About 5 bands were observed for the DR of PS/AP propellant. Amongst all these bands the yellow band ($R_F \simeq 1$) was found in abundance. In the present work, the same propellant was decomposed for about 30 min at 285°C. TLC separation was done by using solvent methanol + benzene (3:1 by volume). Although the number of bands was more than two, for the purpose of separation and analysis, only two broad bands were considered, one having the $R_F \simeq 1$

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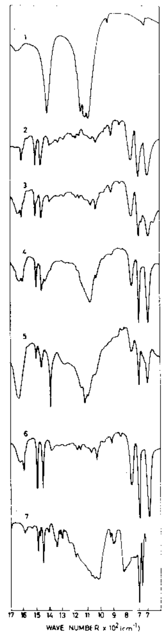

Fig. 1 IR spectra in the region 700 to 1800 $cm^{-1}-1$; 1) Ammonium perchlorate, 2) Polystyrene, 3) CR, 4) DR, 5) Dr_I, 6) DR_{II}, 7) Styrene-peroxide.

(DR_I) and the other $R_F \simeq 0$ (DR_{II}). The broad and corresponding to $R_F \simeq 0$ was found to consist of more than one band. Since the clearcut separation of each band was not possible for these bands due to their closeness with each other, the entire broad band was removed. The broad band corresponding to $R_F \simeq 0$ was also separated in a similar fashion.

On further TLC analysis, it was observed that DR_I, DR_{II}, CR_I, and CR_{II} were mixtures of more than one compound. This indicates the complexity of the mechanism of decomposition and combustion of the propellant system. Complete separation and purification of the components obtained from DR and CR is a difficult task and requires more rigorous analysis. However, the IR spectra of these residues were taken to see if any similarity exists between CR and DR.

Figure 1 exhibits the IR spectra of AP, PS, CR, DR, DR_I, and DR_{II}, for the purpose of comparison. A careful look at these spectra seems to reveal that an intense broad band of the peroxy-linkage in the region 1000 cm^{-1} – 1200 cm^{-1} seems to exist in CR and DR, showing that the binder part, during decomposition and combustion undergoes reaction leading to the formation of peroxy-linkage. The interesting thing to note is the fact that peroxide band is present only in DR_I and not in DR_{II}. The correspondence of the presence of peroxy-linkage in DR_I only, which has yellow color, suggests that the color of the intermediate bearing peroxy linkage may be yellow. It was observed that on partial decomposition of the propellant, yellow color is initially generated and this on further heating turns brown. It may be noted that the color of DR_{II} is brown. This suggests therefore that the intermediate bearing the peroxy-linkage is generated first during the decomposition and on further heating changes to some other intermediate. Since DR_I is obtained in large quantity as compared to other fractions, it indicates that the intermediate species bearing the peroxy-linkage is one of the important species formed during the decomposition of the propellant. On the basis of the above observation, we suspected that perhaps styrene peroxide is formed during the decomposition of the propellant. The IR spectrum of styrene peroxide is also exhibited in Fig. 1. The similarity between the IR spectrum of styrene peroxide to that of DR and CR in the region 100 cm^{-1} – 1200 cm^{-1} shows that: 1) peroxy-linkage is generated during the decomposition and combustion of the propellant; and 2) perhaps the styrene peroxide is one which is being formed during the decomposition and combustion of the propellant. It may be noted that styrene peroxide is also yellow in color.

A close look at the spectra of DR and CR shows that the two spectra are almost similar in the fingerprint region i.e., from 700 cm^{-1} – 1500 cm^{-1}. This strongly suggests that thermal decomposition in the condensed-phase takes place during the combustion of the propellant. This is one of the most important observations made so far to show a positive role of the condensed-phase reaction occurring during the combustion process.

The previous results together with our recently published results[3,4] show very clearly that condensed phase reactions take place during steady-state combustion process, and that the propellant burning has a correlation with the thermal decomposition characteristics of the propellant itself and that of its oxidizer. It may be noted that Sammons,[9] Waeschy[10] et al. in the past have also shown the importance of condensed-phase reaction in the solid propellant combustion. Recently Glasskova[11] and Boggs[12] et al. have shown the role of thermal decomposition of AP during the steady-state deflagration of AP.

The formation of peroxy-linkage during combustion and decomposition suggests that the intermediate bearing this particular linkage is one of the most important species formed during combustion and decomposition. The formation of this intermediate suggests that this could be used as a natural catalyst for modifying the combustion process. We therefore made PS/AP (75%) propellant containing 50% of the styrene peroxide, in the binder. The burning rate data show that there is a very significant increase in burning rate (~40 to 50%) compared to the propellant made out of polystyrene alone.

Conclusions

1) Thermal decomposition of the propellant takes place in the condensed-phase during the steady-state burning process. The TLC analysis has given a positive proof to this effect. 2) The intermediate species formed during the decomposition and combustion contains reactive peroxy-linkage. This has been confirmed from IR studies and also from the color of the intermediates. 3) The peroxide intermediate can be used as a natural catalyst for the modification of the burning rate.

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Current Distribution on Electrodes in MHD Generator Channels

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Introduction

THE current distribution curves on the electrodes in MHD generator channels are skewed, pointing upstream at the anode and downstream at the cathode because of Hall effects. Consequently, erosion on the electrodes is localized and the durability of MHD generator channel worsens. It is therefore desirable to eliminate the Hall component of the current on the electrodes and make the current distribution on the electrodes uniform.

In order to solve this problem, such methods as resistive electrodes[1] or connecting the proper resistances[2] with the segmented electrodes have been suggested and tested.

A new method, which is described in this Note, is to control the current distributions on the electrodes, not by means of using the resistive materials directly or outer resistance as aforementioned, but instead by varying the surface temperature distribution of the electrodes and as a result, the interelectrode resistances. This method was studied experimentally on an ETL Mark V MHD generator,[3] and it was found to be effective in improving the current distribution at the anode.

Experimental Results and Discussion

To obtain the current distribuiton on the electrodes, one electrode was divided into four elements in the direction of combustion gas flow, which were insulated from one another by 0.2-mm-thick wafers of mica as shown in Fig. 1.

Figure 1 shows the dimensions and constitution of one electrode and its elements. The power lines and cooling-water pipes were individually led out of each element, and then the power lines were short-circuited at the terminals of the shunts connected to each element to measure its share of the current. Each element was constructed with a base electrode and a brazed material. All of the base electrodes were made of copper and were water-cooled, but the brazed materials were made of AISI 304 for the anode and AISI 304 and Cu-W alloy for the cathode; their thicknesses were varied as the surface temperature of each element reached the expected level.

Fifty pairs of electrodes were mounted in the Mark V MHD channel, of which four were used as measuring electrodes for current distribution to check the usefulness of this method. The other experimental conditions were as follows;

1) the mass flux in the vicinity of the measuring electrodes was about 15 g/sec cm^2 at the rated mass flow of 3 kg/sec.

2) the magnetic field strength was 42 kG, and

3) the channel was of the cold-wall type with Faraday-type segmented electrodes.

Number 18 and No. 22 electrodes consisted of brazed elements of the same materials and of the same thickness to compare their current distributions with that of No. 19 and No. 21 electrodes, where the brazed materials and their thicknesses were varied to control the surface temperatures.

Figure 2 shows the surface temperature distribution on the anode without current flow. The horizontal axis shows the number of elements that were arranged in order from the upstream end of the electrode. The surface temperatures of elements for No. 18 and No. 22 electrodes varied only a little, but for No. 19 and No. 21 electrodes, they varied nearly linearly between No. 1 and No. 4 elements as predicted. Of course, in the latter case, they were determined in order to show the opposite tendency to the concentrating pattern of current, that is, at the edge of the electrode where the current was most concentrated, the surface temperature was selected to be the lowest because the low surface temperature results in thick boundary layers and also a thick deposited seed layer, which in turn generate locally high interresistances in the boundary layer. The interelectrode resistances between electrodes in the Faraday direction, consequently, varied partially on one electrode for No. 19 and No. 21 electrodes.

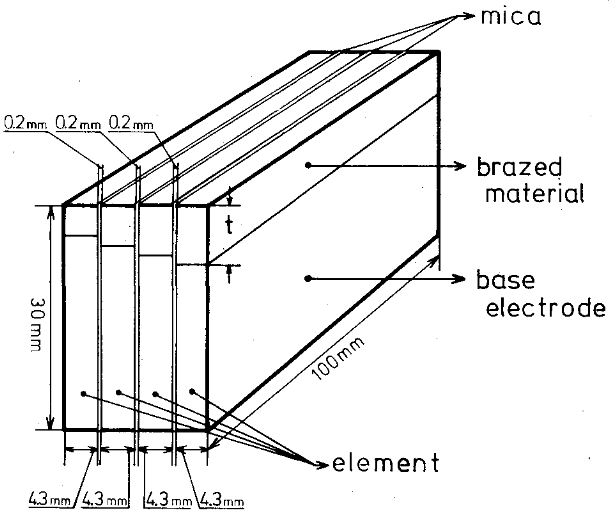

Fig. 1 The dimensions and constitution of one electrode and its elements.

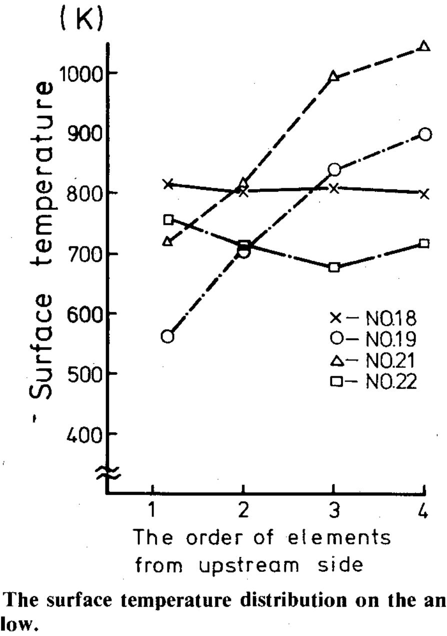

Fig. 2 The surface temperature distribution on the anode without current flow.

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