Behavior of Several Catalysts in the Combustion of Solid Propellant Sandwiches

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Theme

THE two-dimensional solid propellant sandwich has evolved as a convenient test vehicle for theories dealing with both physical and chemical behavior of composite solid propellant ingredients. It allows detailed observation of the binder-oxidizer interface over a range of test conditions. Sandwiches have been used by several investigators.[1-6] Hightower and Price[1] used laminated, two-dimensional sandwiches of single crystals of ammonium perchlorate and hydrocarbon binder. They considered this configuration to be "a compromise between the complexity of the three-dimensional 'combustion zone' and the naivety of a one-dimensional approximation." Jones[2] investigated the catalytic behavior of Harshaw Catalyst, Cu 0202 and ferric oxide, Fe_2O_3 in solid propellant sandwiches of polycrystalline ammonium perchlorate (AP) and carboxyl terminated polybutadiene (CTPB). Hydroxyl terminated polybutadiene (HTPB) was substituted for CTPB and the behavior of the same catalysts over the pressure range 600–3200 psia was investigated.[3] The sandwich vertical burn rate, the normal regression rate of the oxidizer and qualitative details of the deflagration process were obtained by cinephotomacrography. The current study has extended the investigation to include two additional catalysts, iron blue, a complex ammonium iron hexacyanoferrate, and ferrocene, an organometallic compound, biscyclopentadienyl iron. Quenched combustion scanning electron microscopy is used to obtain details of the structure of the binder-oxidizer interface and oxidizer surface for the four catalysts.

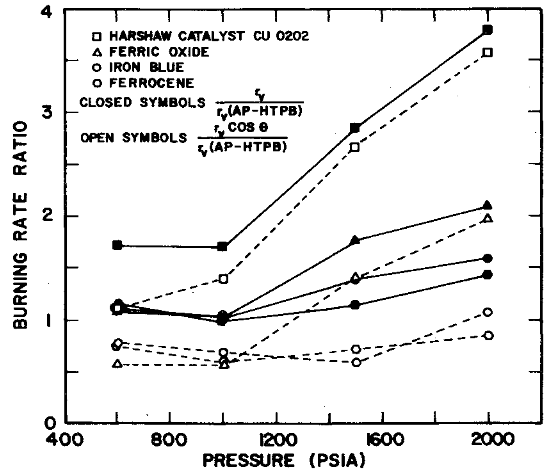

Fig. 1 **Burn rate ratio for catalyst in ammonium perchlorate (2w%).**

The pressure range covered by the current study is from 600–2000 psia. This was selected to avoid irregular results near the low pressure deflagration limit of AP and currently unexplained AP deflagration phenomena above 2000 psia. The feasibility of using an electron microprobe X-ray microanalysis of the surface of the burned oxidizer with catalysts present was investigated.

The two-dimensional samples for this investigation were prepared by the method outlined in Ref. 3. The binder thickness was controlled by Teflon spacers to a nominal 150 μm. The catalysts used were loaded onto either the oxidizer or the binder. For dispersal in the oxidizer, 2% by weight of catalyst was added to the AP prior to grinding and pressing. For loading in the binder, the same volumetric loading as occurred in the AP was mixed into the binder prior to curing. For HTPB this was 4.37% by weight.

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Full details of this work are contained in Ref. 7. The samples for the cinephotomacrography were cut into 4 mm by 8 mm sizes from 2.54 cm diam sandwiches after proper curing of the binder. The prepared samples were mounted in the pressurized combustion apparatus of Jones.[2] Motion pictures of the burning sample were obtained at a rate of either 1600 or 3200 frames/sec, at a latent image magnification of 2 to 1. These motion pictures were used to obtain an accurate value of the sample burning rate by observing the central 2.50 mm section of the sample. The sandwich vertical burn rate and the burn rate normal to the oxidizer surface, as defined in Ref. 3, were obtained for the two types of catalyst addition at four pressures, 600, 1000, 1500, and 2000 psia. Burning rate data were taken only after a steady profile had been achieved and the surface was clearly visible over a substantial portion of the run. For the steady profile the sandwich vertical burn rate is the same regardless of the perpendicular distance from the binder-oxidizer interface. The burn rate normal to the oxidizer surface must be taken at a distance sufficiently far away from the interface for the oxidizer to have a definable, constant slope.

The burn rates for the case of catalyst added to the oxidizer are shown in Fig. 1. The solid curves are the ratio of the sandwich vertical burn rates to the vertical burn rate of a pure AP-HTPB sandwich. The dashed curves are the ratio for the burn rates normal to the oxidizer surface. The dashed curves represent the effect of the catalyst addition to pure ammonium perchlorate burn rates. The data for Harshaw Catalyst Cu0202 and ferric oxide were obtained earlier.[3] Data on the deflagration of AP and catalysts was also obtained by Friedman.[8] For 3 w% of Harshaw Catalyst Cu0202 the burning rate ratios were above the current data for pressures greater than 800 psia. For 3 w% of ferric oxide Friedman's results were always lower than these results with a crossover point of 1500 psia for changing from an inhibitor to a catalyst.

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Index categories: Combustion in Heterogeneous Media; Solid and Hybrid Rocket Engines; Heat Conduction.

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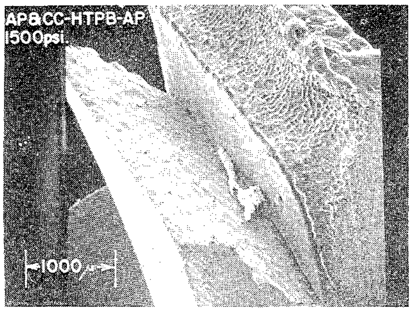

Fig. 2 AP and Harshaw Catalyst Cu0202-HTPB-AP sandwich quenched at 1500 psia.

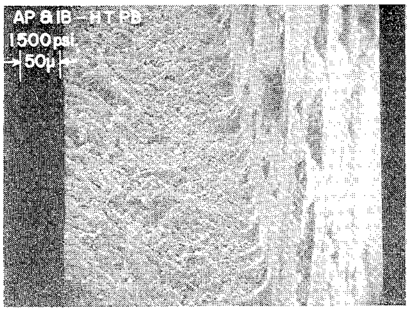

Fig. 4 AP and iron blue-HTPB sandwich quenched at 1500 psia (×177).

The separation between the dashed and solid curves is representative of the amount of catalytic activity taking place in the binder-oxidizer reactions. The compounds in Cu0202 have a greater catalytic effect upon the AP deflagration rate than do the iron compounds, which often inhibit the AP rate, but the iron compounds appear to have a stronger catalytic effect upon the binder-oxidizer reactions.

Very little catalytic effect was observed when the four catalysts were placed in the binder. At low pressures (<800 psia) iron blue and ferrocene did augment the burning rate. This effect was not seen at higher pressures or with other catalysts.

The samples for the scanning electron microscopy investigation were prepared in the same manner as those for the cinephotomacrography experiments. Partially burned samples were obtained by terminating combustion by rapid depressurization using the burst diaphragm method.[4] An electronic timer circuit was used to obtain accurate, reproducible time delays between the ignition of the sample and interruption of burning of the sample. The sample observation was carried out in the Physical Science Division of the Engineering Experiment Station of the Georgia Institute of Technology. A Cambridge Stereoscan Scanning Electron Microscope, Mark IIa, was used for all observations. It has been found experimentally that the appearance of the surface oxidizer changes very little with pressure, over the range 600–2000 psia. Three representative micrographs are presented. In Fig. 2 the oxidizer on the left-hand side has 2 w% of Harshaw Catalyst Cu0202 added. The oxidizer on the right-hand side is pure AP. The pure oxidizer surface is similar in appearance to the results of Boggs and Zurn[5] where experiments are common to both works. There is a binder melt flow out over the pure AP of at least 200 μm. This melt flow is approximately one μm thick. The cant angle of the left side is responsible for the separation of the dashed and solid curves of Fig. 1. There is a noticeable smoothing of the oxidizer surface. The binder melt flow is substantially reduced to less than 40 μm.

When ferric oxide is added to the oxidizer, a frothy structure was observed on a smooth sub-surface. This is visible on the left-hand side of Fig. 3. There is an indication of a binder melt flow of less than 50 μm with a definite cusp at the binder-oxidizer interface. Moving from left to right the interface is approached by a binder melt sloping upward. Then there is a dip before the main part of the binder is reached. It is believed that the dip occurs because less viscous binder is expelled by the quench process. Analysis indicates that the region of maximum solid phase temperature will occur in the binder.

Fig. 3 AP and ferric oxide-HTPB-AP sandwich quenched at 1500 psia (×177).

The oxidizer surface containing iron blue or ferrocene resembles the pure AP, with additional particles visible on the surface. A close-up of the binder oxidizer interface is shown in Fig. 4 for AP and iron blue. An attempt was made to identify these surface particles but the electron microprobe studies with iron blue in AP were inconclusive.

When the catalysts were added to the binder the quenched samples showed no large-scale effects. The oxidizer surface remained unchanged while the binder seemed to exhibit more viscosity with reduced binder heights and melt flows and more sagging and wrinkling upon solidification.

A significant physical or chemical effect of catalyst addition is the apparent removal or inhibition of the binder melt flow. While the mechanism of removal is not certain, the melt removal alone may be an important "catalytic" mechanism in the augmentation of deflagration rate. The point of maximum regression is always in the oxidizer and tends to be positioned by the extent of the binder melt flow.

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