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BURNING RATE CONTROL FACTORS
IN SOLID PROPELLANTS

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I. INTRODUCTION AND SUMMARY

This technical summary report covers the research performed during the last two quarters of the year 1961. During the period from July 1, 1961, to September 30, the research was confined largely to the topic of high pressure burning rates. During the last quarter of the year research continued on high pressure burning rates and was initiated on two new topics, namely high resolution photomicrographs of the propellant surface during burning, and thermocouple traverses of the flame zone. The status of each of these three research topics is briefly outlined below.

Through the cooperative efforts of Princeton and Picatinny Arsenal, burning rate measurements for six propellants have been completed over a pressure range from 30 to 20,000 psia. All six of the propellants studied displayed relatively low pressure indices of about one-third to one-half over the pressure range up to 2,000 psia but displayed extremely high pressure dependency with exponents of the order of unity or greater for all pressures above 5,000 psia. For two propellants containing ammonium perchlorate oxidizer, but differing from one another in the chemical nature of the binder, the burning rates were substantially different in the low pressure regime but merged and became identical for pressures from 10,000 to 20,000 psia. For propellants which were identical as to binder but differed from one another in particle size of the oxidizer four cases were studied, using unimodal oxidizer in each case. The usual difference in burning rate between fine oxidizer propellant and coarse oxidizer propellant was apparent in the low pressure regime, but virtually disappeared in the high pressure regime. At pressures above 5,000 psia propellant containing fine oxidizer burned only very slightly faster than propellant containing coarse oxidizer. The possibility that the rate of regression of propellant strands in this high pressure regime is paced by the rate of regression of the ammonium perchlorate itself will be examined by fabricating pure ammonium perchlorate sticks and investigating the burning rate of the pure perchlorate over the same wide pressure range.

The first new research area consists of photographic studies of the burning surface of the propellant during actual burning with high optical resolution. It was found possible to photograph the burning surface using electronic flash as illumination source at 1/1000th second exposure and at a magnification on the film of 5X, with a satisfactory depth of focus. While preliminary tests were performed at atmospheric pressure, the technique will now be applied to photography of propellant burning over a wide pressure range. It appears that it will not be difficult to obtain resolution at the burning surface of particles of the order of size of 10 to 20 microns. Photographs of
this high resolution have not to our knowledge been obtained by other investigators. We feel that from such photography a substantially improved understanding of the burning process will result.

The second new experiment, and the third of the research topics currently under way, is the examination of the flame zone by use of ultrafine thermocouples, imbedded in the propellant strand in a fashion such that the temperature-time history of a station in the burning strand may be resolved as the flame approaches and consumes the propellant at that station. On the basis of previous research results at Princeton and elsewhere, we have concluded that, providing the imbedded thermocouple has a bead diameter sufficiently small (probably on the order of 0.3 to 0.5 of a mil) it should be possible to detect inflections in the temperature-time trace attributable to such phenomena as emergence of the thermocouple from the solid propellant into the gas space immediately adjacent to the flame zone. If such inflection points can be identified, it will be possible to convert a temperature-time trace to a temperature-position diagram. A temperature-position diagram so obtained could yield vitally important information relative to the nature of the burning mechanism. It is hoped, for example, that we can evaluate the surface temperature of the propellant from this experiment.

Efforts to date on this topic have been devoted, first to the development of the necessary fine thermocouples, and, second, to the development of techniques for thermocouple imbedment in the propellant strand in a fashion which will not perturb the normal approach of the flame. In the very near future we expect to start obtaining temperature-time traces.

II. HIGH PRESSURE BURNING RATE STUDIES

The cooperative study of burning rates at elevated pressures being conducted jointly by Princeton and Picatinny Arsenal* has yielded some very intriguing preliminary data.

* Since the propellant burning rate equipment at present available at Princeton is not capable of operating at pressures in excess of 2,000 psia, all burning rates reported for pressures above 2,000 psia to 20,000 psia were measured at Picatinny Arsenal, through the kind courtesy of Dr. Jean P. Picard, Head, Propellant Research Section. In order to evaluate the quality of match between the low-pressure Princeton data and the high pressure Picatinny data, Princeton reported burning rates up to 1500 psia and Picatinny reported burning rates down to 1,000 psia. The satisfactory quality of match obtained is exemplified by the data reported in Figure 1.
The results obtained to date are summarized in Figures 1, 2 and 3. Two striking features are apparent in all three figures. First, the value of the burning rate exponent, \( n \), at pressures below 2000 psia is generally of the order of 1/3 to 1/2 (somewhat greater at pressures below 200 psi). But for all the curves shown in the three figures the value of \( n \) exceeds unity for pressures greater than 5000 psia.

The second feature which the three figures in common is a tendency for all burning rate curves to approach one another and lie within a rather narrow band from about 5,000 psia on up to 20,000 psia. For Figure 1, in which the particle size of the oxidizer is the same for both propellants, the curves become superimposed at pressures above 10,000 psia even though the two propellants are based on entirely different binders. In Figures 2 and 3 the dependence of the burning rate upon oxidizer particle size is slight at pressures above 4,000 to 5,000 psia, in contrast to the strong influence of particle size upon burning rate in the low pressure regime.

The data for Figure 1 are based on recent burning rate measurements on freshly prepared propellant, performed in the low and high pressure regimes by Princeton and Picatinny Arsenal respectively. The data forming the basis for Figures 2 and 3 are more preliminary. Curves depicting burning rate against pressures over the range, 15 to 1,000 psia, are taken from Bastress' thesis (Reference 1). The data in the high pressure regime for these two figures is based on burning rates performed at Picatinny Arsenal using propellant that remained on hand at Princeton after Bastress had completed his research program. Thus, the low pressure rates for Figures 2 and 3 are based on burning rate measurements performed two to three months prior to the burning rate measurements performed for the high pressure regime. It is our intention to repeat these burning rate measurements using freshly prepared propellant to confirm the data of Figures 2 and 3.

Data are available in the literature which suggest that the striking increase in pressure dependence of the burning rate observed for these ammonium perchlorate propellants at pressures above 5,000 psia is also characteristic of strands of pure pressed ammonium perchlorate. It is possible that the burning rate of ammonium perchlorate is the basic rate determining process in the high pressure regime. In view of this possibility we feel it desirable to re-examine the burning rates of pure ammonium perchlorate pressed sticks at high pressure. To this end we intend to acquire the necessary equipment for fabrication of pressed strands and to perform a cooperative burning rate program; Princeton at low pressure, Picatinny at high pressure, on the pure oxidizer. We believe it is important to clarify
the role of ammonium perchlorate in pacing the burning rate in the high pressure regime (if any) since the rate pacing process which predominates at high pressure may still be ballistically significant in the pressure regime of practical interest in modern rocket motors, namely from 500 to 1000 psia.

III. HIGH RESOLUTION PHOTOMICROGRAPHS OF PROPELLANT SURFACE DURING BURNING

Photographic studies of the burning of solid propellants have, of course, been performed by many other investigators. Notable among such studies are high-speed movies taken in color by Dr. Wood of the Rohm & Haas Company, Redstone Research Division, and similar high-speed color movies taken by Dr. Ellis Lansbaum at the Jet Propulsion Laboratory. Such photographic studies have been most instructive, especially in a qualitative way, but we consider it important to examine the burning process photographically with a substantially higher degree of resolution. It would be revealing, for example, to examine the propellant surface during burning with magnifications comparable to those used by Bastress in his photographs of extinguished burning surfaces (References 1, 2). In the Bastress photographs propellant burning at low pressure was seen to offer an extinguished surface in which the oxidizer crystals extended above the surrounding fuel matrix. The surface of propellant which has been extinguished while burning at high pressure, on the other hand, is characterized by an absence of oxidizer crystals. Instead, a pock-marked appearance is evident, the pock marks corresponding to the location of oxidizer crystals in the matrix prior to the arrival of the burning surface. Photographs of this burning process taken at both high and low pressure, if sufficiently high in resolution, should reveal the difference in the nature of the burning surface suggested by Bastress' photographs, and would probably aid our understanding of the burning process substantially.

Some preliminary efforts aimed at securing photographs of the required high resolution have been expended with encouraging results. Preliminary considerations indicated that if the burning surface were photographed on film capable of discriminating 200 lines per mm, and if the magnification on film were 10X, it should be possible to discriminate details of the order of five microns in size. According to Eastman Kodak data sheets, Kodak Panatomic X film is capable of discriminating 150 lines per mm providing exposure and fine grain development are optimum. The
remaining question then was whether it was possible to magnify the image 10X on the film and still have adequate depth of focus to observe the details in the burning surface. From optical considerations it was apparent that the two incompatible factors were depth of focus and adequate exposure of the film, but that these factors could be made compatible providing illumination is externally supplied.

To evaluate the feasibility of such a technique an experiment was set up in which strands were photographed while burning at atmospheric pressure in a stream of nitrogen gas. The experimental arrangement is depicted in Figure 4. By placing the electronic flashgun sufficiently close to the burning strand ample lighting intensity is available, even though the nominal aperture setting on the lens was f22*. (When the nominal f number setting on the lens was less than f16, depth of focus became marginal.) The use of electronic flash as the source of illumination has the added advantage of limiting the exposure time to about 1/1000th second, thus providing time resolution of the moving burning surface similar in order of magnitude to the spatial resolution we are seeking.

For this preliminary experiment existing equipment was used, which limited the magnification on the film to 5X. The camera used was an Alpa Model 6-b equipped with a Kern apochromat f1.8 lens, and extension tubes. Figure 5 is a photograph taken with the set up of Figure 4 of a typical composite propellant containing a relatively coarse ammonium perchlorate oxidizer. While this constitutes only a preliminary test, it is apparent that the depth of focus and spatial resolution are quite good.

On the strength of photographs such as that of Figure 5, we are proceeding to modify existing burning rate bomb equipment containing slit windows, so that photographs of this sort can be taken over the pressure range from 15 to 1500 psia.

IV. THERMOCOUPLE TRAVERSES OF THE FLAME ZONE

In the field of double base propellant burning, investigators have studied the nature of the flame zone

* True f number = (nominal f number) x (1+ magnification).
by mounting a small thermocouple in the strand and allowing this thermocouple to emerge to the burning surface as the strand is burned. The time dependency of the thermocouple temperature is then recorded. It is possible to derive a temperature-position diagram (position being relative to the propellant burning surface) from such a temperature-time record, provided some point of reference can be identified—for example, an inflection point corresponding to emergence of the thermocouple bead from the propellant into the gas space above the propellant. Such techniques have been instructive to students of the nitrocellulose propellant burning process, but relatively little emphasis has been placed upon application of the technique to pure composite-type propellants.

Preliminary studies by Sutherland at Princeton (Reference 3) suggested that data significant to the study of the composite propellant combustion zone could be obtained by this technique, providing sufficiently fine thermocouples were used. Sutherland's thermocouples, which were fabricated from $\frac{1}{2}$ mil wire, were not quite capable of resolving the moment of passage of the burning surface because of their large size; but his results were sufficiently interesting to suggest that with refinement, through the use of smaller diameter wire, the technique could produce data of considerable significance in the study of the burning zone.

With this objective in view, techniques have been developed for fabrication of microthermocouples based on wire diameters of the order of 0.3 mil or finer. Thermocouples made from 0.3 mil wire and having beads not greater than 0.5 mil in diameter are now being manufactured routinely, and techniques have been developed for imbedding these thermocouple beads in the propellant strand in such a fashion that the thermocouple will scan or traverse the flame as the strand burns in a cigarette fashion. Attempts to imbed the couples by splitting strands and then gluing the split halves back together with the thermocouples in the glue line did not prove too successful because the glue line was not homogeneous in nature with the balance of the propellant, and it was feared that the glue line would perturb the flame in the region where the thermocouple traverse was to take place. Consequently, a different technique was resorted to in which the procedure suggested by Figure 6 is followed.

In View 1, Figure 6, the mold assembly without propellant is shown. View 2 is a sectional view of the
lower half of the mold still containing no propellant. Propellant is vacuum-mixed in the usual way and the void-free but uncured material is carefully placed in the lower half of the mold as shown in View 3. The thermocouple is then carefully laid on top of the lower half of the mold and on the smoothed off surface of the uncured propellant as shown in View 3. The upper portion of the mold is then put in place and an additional increment of propellant is inserted in the space provided, such that the thermocouple, which now is held between the upper and lower portions of the mold, is covered by the additional propellant (View 4). The entire assembly is then placed in an oven and cured for the appropriate period of time, after which the cured strand with the thermocouple imbedded in position is carefully removed from the mold. Using this technique it is possible to imbed the thermocouple in a homogeneous strand of propellant such that when the strand is burned there will be no perturbation to the flame front as it arrives at the thermocouple station.

Several strands with thermocouples imbedded have been successfully prepared. We are confident that this technique is applicable to even finer thermocouples based on finer wires as our methods of manipulation become improved. Temperature-time records obtained with this type of strand should be forthcoming in the very near future.
REFERENCES


EFFECT OF BINDER ON BURNING RATE
OVER BROAD PRESSURE RANGE—
75 WT. % AP BIMODAL (20 μ, 200 μ)

△ PRINCETON DATA  △ PICATINNY DATA  △ POLYSULFIDE
○ PRINCETON DATA  ○ PICATINNY DATA  ○ PBA
EFFECT OF OXIDIZER PARTICLE SIZE ON BURNING RATE OVER BROAD PRESSURE RANGE—65 WT. % AP UNIMODAL IN POLYSULFIDE BINDER

FIGURE 2

NOTE: no data taken for 9% AP over the indicated pressure range.
FIGURE 3

EFFECT OF OXIDIZER PARTICLE SIZE ON BURNING RATE OVER BROAD PRESSURE RANGE - 70 W.T. % AP UNIMODAL IN POLYSULFIDE BINDER

- 20 µ AP
- 200 µ AP

BURNT RATE, in/sec

PRESSURE, psi
ATMOSPHERIC BURNER FOR PHOTOGRAPHY OF BURNING SOLID PROPELLANT STRAND

FIGURE 4
SURFACE OF POLYESTER-STYRENE PROPELLANT PHOTOGRAPHED WHILE BURNING (1 atm. press. in N₂)
20 × MAGNIFICATION AS SHOWN
TECHNIQUE FOR IMBEDDING THERMOCOUPLE IN STRAND

FIGURE 6