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DEPARTMENT OF THE NAVY
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Contract Nonr 1858(32) - NR 098-201
(ARPA Order No. 23-59; 23-60 Amend. 5)

BURNING RATE CONTROL FACTORS
IN SOLID PROPELLANTS

Tenth Quarterly Technical Summary Report
For the Period 1 April 1961 to 30 June 1961

Aeronautical Engineering Report No. 446-j

Superseded
AD-262770

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I. INTRODUCTION

During the past quarter, four experimental programs have been underway. The following statements describe briefly the nature and present status of each of these programs:

(1) Effects of oxidizer particle size have been studied in polysulfide propellants containing 75 percent ammonium perchlorate in a bimodal particle size distribution. Results of this study are presented in Section II. The relative effects of the fine and coarse particle sizes are clearly shown in these results.

(2) A series of polybutadiene-acrylic acid propellants have been prepared containing 72.5 percent ammonium perchlorate in unimodal particle size distributions and varying mean diameters. Strand burning rates of these propellants are presented in Section III. This program was intended as an extension of earlier work carried out with other fuels. It has been concluded that variations in oxidizer particle size produce similar effects in all two-component (fuel and oxidizer) propellants. The variations in fuel type which have been conducted thus far have produced only minor effects. However, a more comprehensive program designed to study the relation between fuel type and burning characteristics is contemplated. No further studies of oxidizer particle size effects are planned, except at high pressures.

(3) As mentioned in earlier reports, a joint program is underway between Picatinny Arsenal and Princeton University to study propellant burning rates at high pressures (1000 to 20,000 psi). Through the courtesy of Dr. Picard, Head, Propellant Research Section, high pressure burning rates are being measured at Picatinny on propellant strands prepared at Princeton. Preliminary trials have demonstrated that the Picatinny equipment performs well on Princeton propellant provided the strand diameter is reduced to 1/8 inch. Burning rates obtained during the trial runs suggest that pressure exponents in excess of unity may be characteristic of ammonium perchlorate propellants at pressures above 5000 psi.

(4) A series of polybutadiene-acrylic acid-ammonium perchlorate propellants containing ten percent aluminum have been prepared in order to determine the relative effects of aluminum and oxidizer particle size. Burning rates of these propellants are discussed in Section IV. As an initial effort in studies of aluminized propellants, these results indicate a number of interesting effects. A more carefully controlled program of burning rate studies with these propellants is contemplated in order to establish the role of aluminum particles in the combustion process. It is possible that such studies might also elucidate the mechanism by which aluminum affects unstable burning.

A polysulfide binder was used at first for studies of aluminized propellants, but was found to be unsuitable. Water produced in the curing reactions in conjunction with the aluminum produces hydrogen gas resulting in a porous propellant. No problem of this nature has been observed with the polybutadiene-acrylic acid binder.

II. PARTICLE SIZE EFFECTS IN BIMODAL DISTRIBUTIONS

Earlier work with propellants containing oxidizer in bimodal particle size distributions (Report No. 446-f) indicated that the combustion process of such propellants is more complex than in those containing a narrow particle size distribution. However, the results did not indicate clearly the relative importance of the fine and coarse particles in determining the propellant burning rate. Therefore, further studies were planned in hopes that a clearer picture might be obtained of the burning of these propellants.

Another series of propellants were prepared with varying coarse and fine particle sizes. The overall composition was fixed at 25 percent polysulfide binder (Thiokol LP-3) and 75 percent ammonium perchlorate, of which 70 percent was coarse and 30 percent fine. The increased oxidizer represents a substantial change from the 65 percent used in the previous unimodal particle size study. However, the resulting propellants are more typical of practical propellants containing bimodal oxidizer, in terms of mixing consistency and physical and ballistic properties.

The burning rates of these compositions are shown in Figure 1. The most striking characteristic of the data is the complete lack of variation of burning rate with varying fine particle size. Burning rate is seen to vary moderately with coarse particle size, the variation being greatest at low and intermediate pressures. These results are in agreement with results reported by the Thiokol Chemical Company, Elkton Division*, from work with another propellant composition. It would appear, therefore, that one is justified in concluding that the size of the fine oxidizer particles in a bimodal distribution does not significantly influence the burning rate. This conclusion is important from the standpoint of propellant quality control.

III. PARTICLE SIZE EFFECTS IN POLYBUTADIENE ACRYLIC ACID PROPELLANTS

Earlier work in this program dealt with the effects of oxidizer particle size on burning rates of propellants containing polysulfide and polyester-styrene binders. A number of interesting behavior patterns were observed in this work and these were reported in detail (Reports 446-f and 536). In order to further verify the results, similar studies have been made with a polybutadiene acrylic acid binder. A series of propellants were prepared containing 27.5 percent binder and 72.5 percent ammonium perchlorate in narrow unimodal particle size distributions. Six propellants were prepared with median particle diameters varying from 9 to 210 microns. Particle size distributions were measured by liquid sedimentation (Report 446-d). Burning rates of these propellants are shown as a function of pressure in Figure 2, and as a function of particle size in Figure 3.

*Brenner, C. S., "Oxidizer Particle Size Effects on Propellant Ballistic Properties," Paper presented at ARS Solid Propellant Rocket Conference, Salt Lake City, February, 1961, ARS Preprint No. 1598-61.

These figures indicate that the overall behavior pattern of the PBAA propellants is similar to those of the polysulfide and polyester-styrene propellants. Burning rates are found to vary inversely with particle size, but more strongly at low than high pressures. Propellants containing fine particles (9 and 16 microns) are found to extinguish at pressures above 400 psi, and propellants with somewhat larger particles (27 and 44 microns) show a tendency toward plateau burning between 400 and 1000 psi. These characteristics have been found to be common to all propellant formulations tested.

A characteristic peculiar to the PBAA propellants is the tendency toward increased particle size sensitivity at pressures above 1000 psi. This appears to be a result of low burning rates and pressure indices in this region with coarse particle propellants.

The general conclusion to be drawn is that propellants containing ammonium perchlorate as oxidizer burn with comparable rates and their burning rates vary similarly with pressure and particle size. There are, however, minor variations in behavior which are brought about by changes in the nature of the binder.

With the presentation of the data of this and the previous section the study of the influence of ammonium perchlorate particle size upon burning rates at pressures below 2000 psi is essentially complete. The most perplexing feature of the data so far obtained --- the question of what happens above 1000 psi --- will, hopefully be clarified as data emerge from the high pressure burning rate studies now in progress at Picatinny. At present it is anticipated that most future low pressure burning rate studies will be concerned with metal-(or possibly catalyst-)containing propellants, and propellants containing other oxidizers. A limited study of the influence of the molecular structure of the binder on burning rate of ammonium perchlorate compositions is also planned, however.

IV. PARTICLE SIZE EFFECTS IN ALUMINIZED PROPELLANTS

Because of the widespread use of aluminum powder in propellant formulations for control of instability and for increased specific impulse, it was decided to devote a portion of this program to a study of the effects of aluminum addition on propellant burning rate. Previous work on burning rate studies at Princeton has been devoted exclusively to simple fuel-oxidizer systems wherein the independent variables were limited to oxidizer concentration, oxidizer particle size distribution, and fuel type. In a three-component system (that is fuel, oxidizer, and aluminum) the independent variables are increased to five if the oxidizer type is limited to ammonium perchlorate. The added variables are aluminum concentration and particle size distribution. As a result, any study of a three-component system must be rather extensive, or must be limited in the variables studied.

As an initial investigation of this subject, a series of propellants were prepared with variations in aluminum and ammonium perchlorate particle size. The composition of these propellants

was fixed at 25 percent PBAA binder, 10 percent aluminum and 65 percent ammonium perchlorate. This is the composition resulting when aluminum is added to the composition described in Section III, - 27.5 percent PBAA, 72.5 percent A.P. - keeping the PBAA/A.P. ratio fixed. This composition was selected initially so as to determine qualitatively the effect of aluminum on the combustion process. If the aluminum were to have no effect on the burning propellant, burning rates would be expected comparable to those reported in Section III. If the aluminum did not react chemically, but acted as a heat sink, reduced burning rates might be expected.* If the aluminum were to react in the flame zone, or were to add significantly to the heat feedback by radiation, a higher burning rate would be expected.

The burning rates of these propellants are shown in Figure 4. Burning rates of propellants with similar oxidizer particle size and equal binder-oxidizer ratio are shown in dashed lines. A number of interesting effects can be seen in this figure. It is apparent that the addition of aluminum does not change the propellant burning rate to a significant extent, except perhaps at low pressures. In this region, fine aluminum increases the burning rate by as much as 50 percent, indicating a participation in the combustion process. Coarse aluminum, on the other hand, does not appear to alter the burning rate.

At higher pressures (above 100 psia) there is little effect on burning rate by either fine or coarse aluminum. If any effect were to be noted, it would be a slight depression of burning rate.

Other secondary effects are of interest in these data. It is apparent that aluminum has no effect on the extinguishment of propellants containing fine oxidizer. Limits of combustion have been observed in several propellants at approximately 500 psi when finely ground oxidizer is used.**

Finally, it is interesting to note the reduced burning rates at higher pressure for the propellant containing coarse aluminum and coarse oxidizer. The authors are not prepared to comment in this behavior without further study.

The investigation of aluminized propellants will continue.

*In either of these cases the aluminum might (and, to some extent at least, probably would) eventually become oxidized, but at so great a distance from the propellant surface that its heat feedback contribution would be negligible compared to that from the oxidizer-organic binder combustion flame.

**In some propellants a low pressure index or even a plateau occurs in this range of pressure (See Reports 446-f and 536).

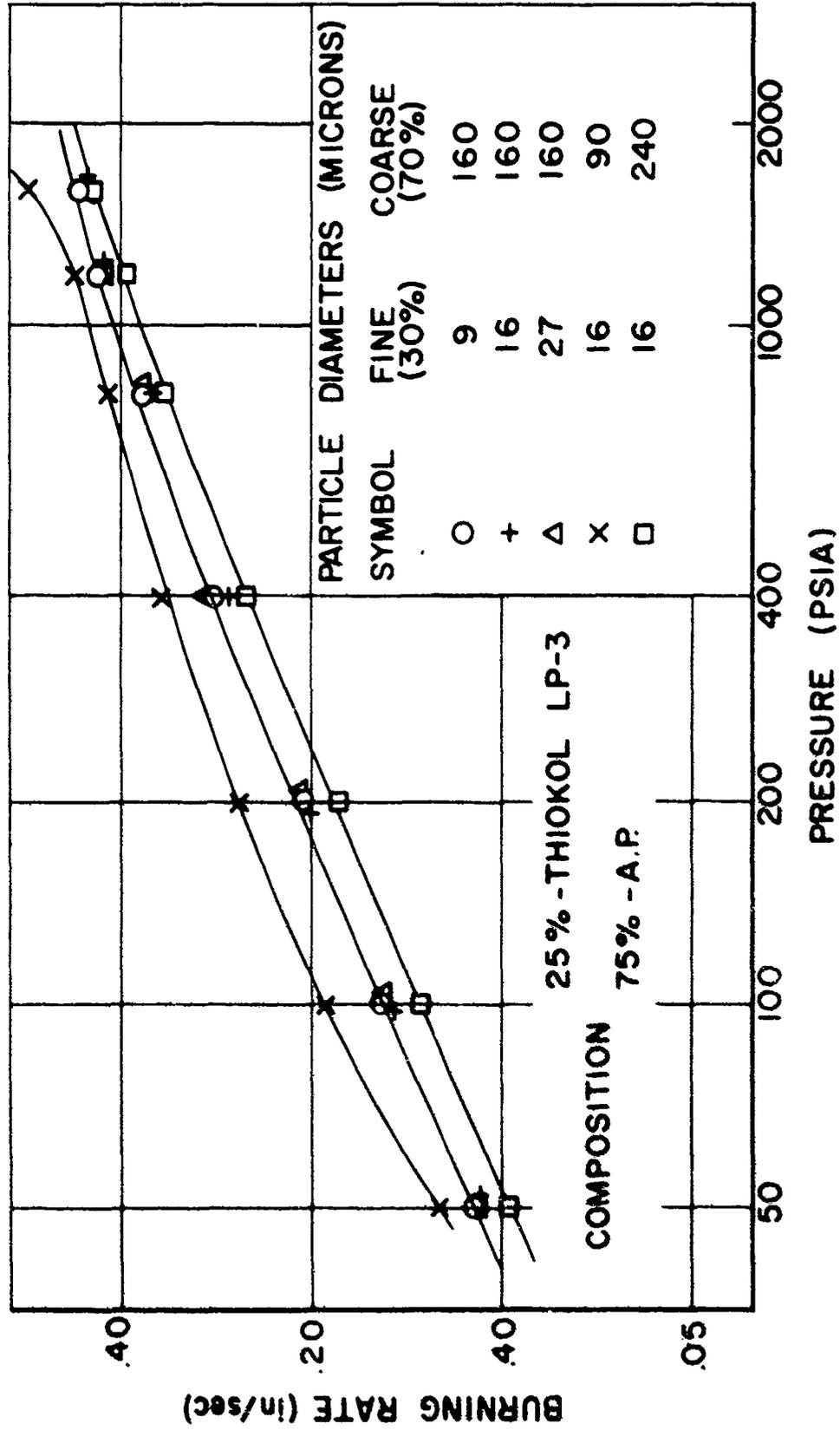


FIGURE 1

BURNING RATE VS PRESSURE, POLYSULFIDE-AMMONIUM PERCHLORATE PROPELLANTS WITH BIMODAL PARTICLE SIZE DISTRIBUTIONS

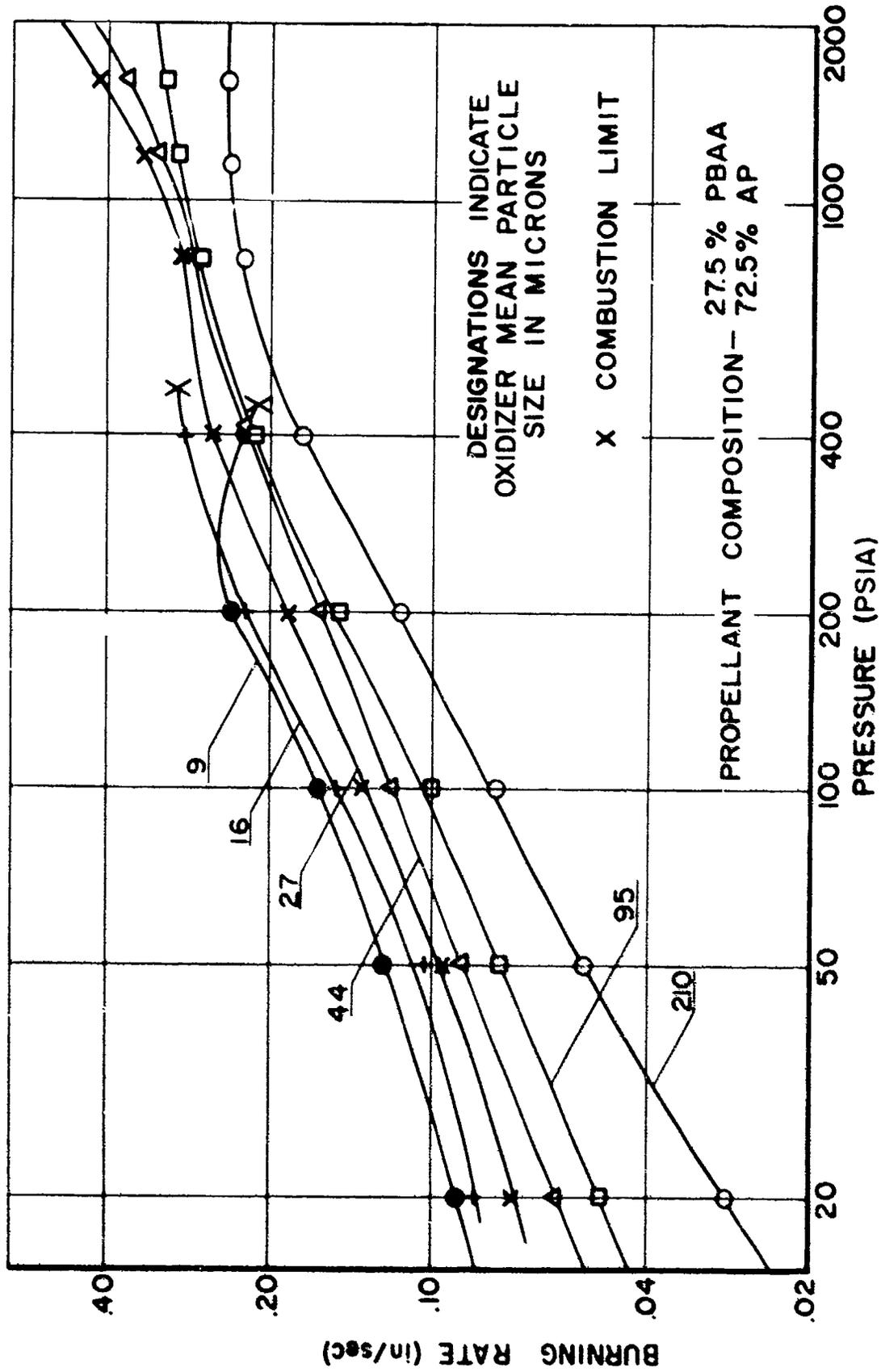


FIGURE 2

BURNING RATE VS PRESSURE, POLYBUTADIENE ACRYLIC ACID-AMMONIUM PERCHLORATE PROPELLANT WITH VARYING PARTICLE SIZE

PROPELLANT COMPOSITION - 27.5% PBAA 72.5% AP

X COMBUSTION LIMIT

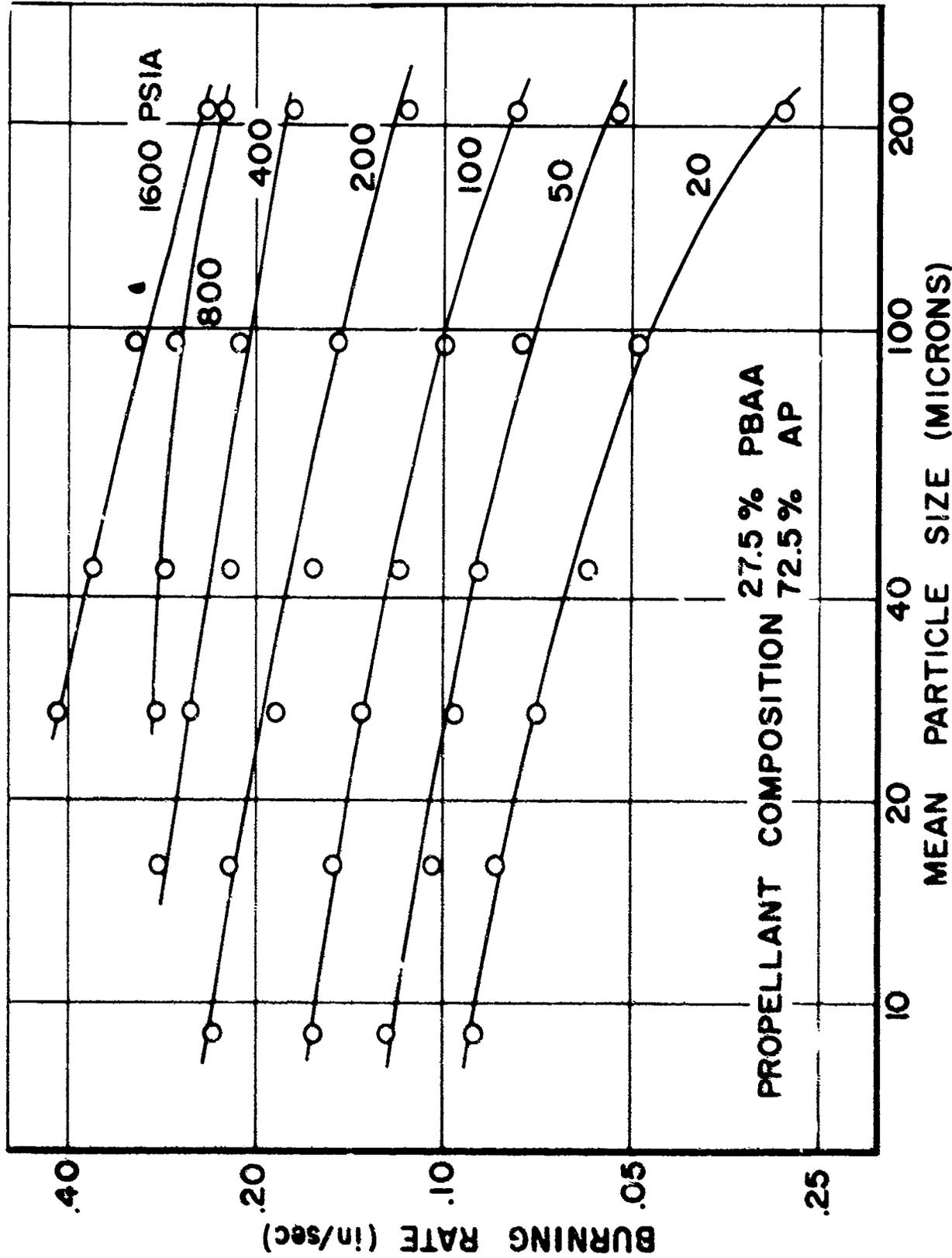


FIGURE 3

BURNING RATE VS PARTICLE SIZE, POLYBUTADIENE ACRYLIC
ACID—AMMONIUM PERCHLORATE PROPELLANT

PROPELLANT COMPOSITIONS
 CONTROL ALUMINUM ADDED 72.5 % AP; 27.5 % PBAA
 65.0 % AP; 25.0 % PBAA, 10.0 % ALUM.

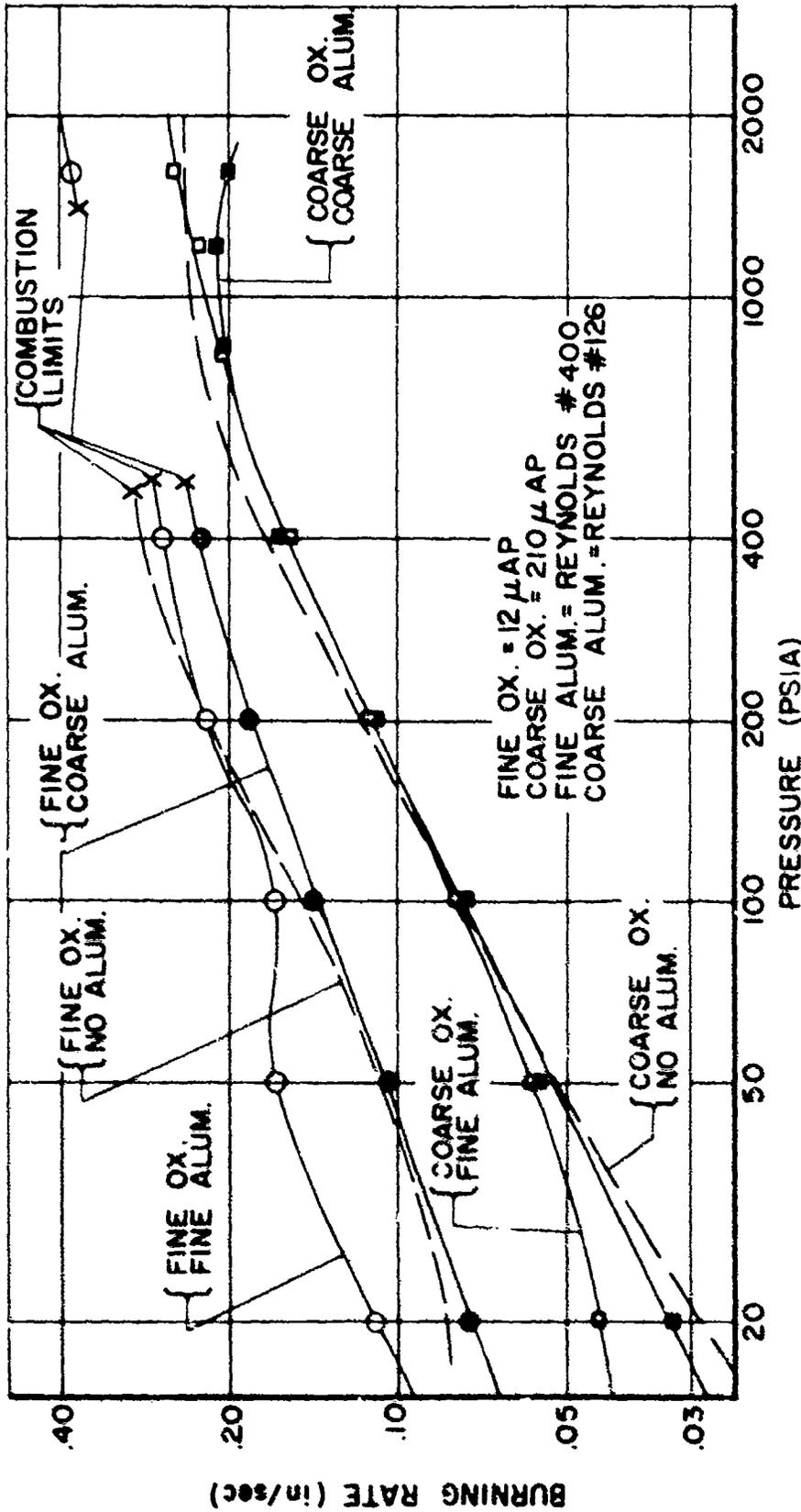


FIGURE 4

BURNING RATE VS PRESSURE, POLYBUTADIENE ACRYLIC ACID - ALUMINUM-AMMONIUM
 PERCHLORATE PROPELLANT, PARTICLE SIZES OF BOTH OXIDIZER AND
 POWDERED METAL VARYING.

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