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NONMETALLIZED SOLID PROPELLANT IN HIGH
ACCELERATION ENVIRONMENTS

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September 1973

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Nonmetallized Solid Propellant Combustion
in
High Acceleration Environments

by

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Lieutenant, United States Navy
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requirement for the degree of

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ABSTRACT

Nonmetallized double base propellant and ammonium perchlorate/binder sandwich combustion were studied in standard and high acceleration environments. Experimental techniques used were high speed motion pictures, two-color schlieren and pressure-time trace determination of burning rates. The double base propellant was studied at pressures to 1250 psia and accelerations to ± 1000 g's. Two binder systems were used in the AP/binder sandwiches. Tests were conducted with two binder thicknesses at 400 psia and with acceleration levels of zero and 100 g's. It was found for double base propellant that the temperature increased continuously from the surface to the visible flame and that acceleration induced burning rate augmentation occurred. Acceleration apparently modified the surface or subsurface combustion zones. AP/binder sandwich combustion was found to be acceleration sensitive with binder flow being the most plausible mechanism.

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I. INTRODUCTION

Investigations have shown that accelerations directed normal and into the burning surface of solid propellants usually affect the burning rate. Augmentation of the burning rate can cause solid propellants to deviate from their static characteristics and result in off-design performance. This study considered the burning rates of nonmetallized double base and composite propellants in high acceleration environments.

Few studies have been conducted with nonmetallized double base propellants. An investigation by Bulman and Netzer [Ref. 1] reported the following results for a non-aluminized double base propellant with copper and lead additives:

(1) The burning rate augmentation decreased with increasing pressure and acceleration.

(2) The augmentation decreased with the weight of the molten metal (copper and lead) layer formed on the burning surface.

(3) High accelerations caused instabilities in the burning rate by flooding and unflooding the burning surface with the molten layer.

The same study [Ref. 1] reported the following for an aluminized double base propellant with copper and lead additives:

(1) The augmentation increased with increasing pressure and acceleration.

(2) Aluminum increased the augmentation but the effect was nearly cancelled by the opposite behavior of the copper and lead additives.

In this investigation, no metal additives were present in the double base propellant. Thus, the propellant consisted of principally nitrocellulose and nitroglycerin [Table I (a)] with no ballistic modifiers. Using this propellant, acceleration sensitive mechanisms in the basic combustion process (no metallic agglomeration due to acceleration) could be investigated.

The investigation of nonmetallized composite propellants is a continuation of a study by Brown, Kennedy, and Netzer [Ref. 2]. That study included an investigation of ammonium perchlorate (AP) with a binder of polybutadiene acrylic acid (PBAA). These sandwiches were burned under high accelerations. The following is a summary of their results which are applicable to this investigation:

- (1) Binder thickness had little effect on the burning rate.
- (2) The burning rates of AP/PBAA sandwiches comprised of ultra high purity (UHP) AP were acceleration sensitive.
- (3) A small amount of binder flow onto the AP increased burning rates but excess flow quenched the reaction.
- (4) Augmentation was due in part to interaction between the binder melt and the AP/AP melt.

In order to further verify these conclusions, this investigation studied two additional binders, polyurethane (PU) and hydroxyl terminated

polybutadiene (HTPB), and two binder thicknesses. These sandwiches were tested at one pressure and two accelerations.

To determine the mechanism responsible for burning rate acceleration sensitivity of nonmetallized double base and composite propellants, the following data were obtained: (a) burning rates, (b) burning rate augmentation at high accelerations, and (c) surface and gas phase behavior by using high speed motion pictures of the burning at zero and high g's.

II. METHOD OF INVESTIGATION

High speed motion pictures (7500 PPS) in a nitrogen purged combustion bomb were taken of the double base propellant combustion. A film consisted of color schlieren with alternating real light frames. These films were used to determine the flame position and structure, and the vertical and horizontal temperature profiles as a function of pressure (500 and 800 psia).

The static burning rate (zero g) was determined from a pressure-time trace in a combustion bomb attached to a high acceleration centrifuge. The pressure-time trace not only showed the burn time but also any fluctuations in pressure caused by instabilities in burning. Strand lengths of one and two inches were investigated and compared to burn data received from the Naval Ordnance Station [Ref. 3]. Most of the strands employed had a cross section of three-sixteenths by one-half inch. A few strands with a larger cross section, one-half by one-half inch, were also used. The pressure for both strand lengths was varied from 100 to 1250 psia. A somewhat less accurate burn rate was also calculated from the high speed motion picture photography obtained in the combustion bomb and the optical centrifuge.

The burning rate augmentation was calculated from the high acceleration centrifuge data. The pressure-time traces showed the burn time and any instabilities for two-inch strands with the same cross

section as above. At pressures of 500 and 1000 psia, the acceleration was varied from zero to 1000 g's directed normal and into the burning surface. Additional runs at negative 1000 g's (normal and out of the burning surface) were run at 1000 psia. The calculated augmentation from the optical centrifuge was compared to that obtained from the high acceleration centrifuge.

The optical study was performed using a high speed motion picture camera (3000 PPS) to observe the burning surface of the propellant and the flame position and behavior. Because the combustion bomb on the optical centrifuge was small, the double base strands were one-half inch in length with a cross section of three-sixteenths by one-quarter inch.

The composite AP/binder sandwiches were visually studied under accelerations of zero and 100 g's at a pressure of 400 psia. An optical centrifuge equipped with a high speed motion picture camera was used to record the surface behavior during combustion. The sandwiches were made with ultra high purity ammonium perchlorate and two different binders, PU and FTPB. To determine the effect of the binder thickness on the burning rates, the sandwiches were constructed with two different thicknesses, 25 and 100 microns. The strands were one-half inch high with a cross section of three-sixteenths by one-tenth inch. Zero g burning rates, augmentation in acceleration environments, and AP/binder interactions were determined from the films.

III. EXPERIMENTAL APPARATUS AND PROCEDURES

A. PROPELLANT SPECIFICATIONS

The constituents of the double base propellant are listed in Table I (a). The propellant was supplied by the Naval Ordnance Station at Indian Head, Maryland.

Specifications for the AP and binders are shown in Table I (b). The AP listed was used with both types of binder. The two binder thicknesses were approximately 25 and 100 microns.

B. HIGH ACCELERATION CENTRIFUGE

The high acceleration centrifuge had a nominal diameter of 76 inches. Propellants were burned in a nitrogen atmosphere to pressures of 1250 psia and accelerations of 1000 g's. The 115 cubic inch bomb was vented to surge tanks with a total volume of 1450 cubic inches. A pressure-time trace of the burn was produced on a Honeywell Visicorder model 1508.

The strands were rigidly inhibited on all sides and the base with Selectron 5119 resin and "Garox" curing agent.

A detailed description of the high acceleration centrifuge and the associated procedures has been presented in references 4 and 5.

C. OPTICAL CENTRIFUGE

The centrifuge was equipped with a Hycam model K1001, 16mm high speed motion picture camera mounted above a 24-inch diameter

rotating table. The nitrogen purged bomb was capable of operating to 800 psia and 110 g's with the associated equipment installed. The non-metallized propellant required the use of a General Electric Marc 300/16 projection lamp as a light source. A timing mark was produced on the film edge by a Red Lake Laboratories Millimite TLG-4 timing oscillator. The camera was operated at 3000 pictures per second.

The optical centrifuge has been discussed in references 4, 6, and 7.

D. COMBUSTION BOMB AND SCHLIEREN

The schlieren was produced with a red-blue matrix and was used to obtain both vertical and horizontal density gradients. A light source chopper was placed between the bomb and the schlieren source to create alternating frames of real light photography. A film speed of 7500 pictures per second was used. The bomb had a maximum operating pressure of 1000 psia. A Hycam model K2004E-115 high speed motion picture camera and a Red Lake Laboratories timing oscillator recorded the burn.

The combustion bomb has been detailed in reference 6, while the changes to the bomb and the color schlieren are discussed in reference 8.

E. AP WAFER AND SANDWICH FABRICATION

The AP wafers were molded at a pressure of 30,000 psi for 20 minutes. The binder curing processes are given in Table I (b).

The fabrication techniques have been presented in references 6 and 8.

F. CALCULATION OF BURNING RATES FROM FILMS

The timing oscillator was set at 1000 Hz and produced a mark on the edge of the film. The burn was measured from the film after ignition transients had disappeared. Distance burned was always taken to the point where the maximum burn depth could be observed.

IV. RESULTS AND DISCUSSION

The figures 1 through 6, and 9 through 15 are reproduced in black and white from color prints. The color prints along with two edited films, one on double base propellant and the other on composite propellants, are available on loan from Associate Professor D. W. Netzer, Naval Postgraduate School, Monterey, California.

A. DOUBLE BASE PROPELLANT

The study of the horizontal density profile using the vertical knife edge schlieren, figures 1 and 3, showed distinct burning sites on the propellant surface. The size of these sites was found to be independent of pressure (at 500 and 800 psia). Site width varied from 150 to 200 microns. The sites moved very slightly in their horizontal position and remained well defined for periods of 25 to 50 milliseconds. This was similar to observations of AP combustion by Murphy and Netzer [Ref. 8].

The vertical density profile, figures 2 and 4, showed the density continuously decreasing from the surface to the visible flame. Assuming that the density variation is predominantly determined by temperature variations, the films indicate a continuously increasing temperature from the surface to the visible flame. This result is different from many previous studies which used double base

propellants containing ballistic modifiers. According to Shorr and Zachringer [Ref. 9], this "dark zone" has a region of constant temperature.

Reference 9 also presents an expression for the height of the dark zone (distance from the surface to the visible flame) as $10^7/p^3$ inches, with p in psi. The flame heights calculated from the films at 500 psia were 0.08 and 0.06 inches [Figures 1 and 2 respectively]. At 800 psia the flame heights were 0.03 and 0.02 inches [Figures 3 and 4]. These measured flame heights are in agreement with that predicted by the formula presented in reference 9.

The zero g burning rates determined from the two-inch strands had less variation than the shorter one-inch strands and therefore, the longer strands were used throughout the study. The pressures in the high acceleration centrifuge were varied from 100 to 1250 psia. There were no combustion instabilities observed in the pressure-time traces taken at zero g 's. This data was repeatable to 5 per cent. This also indicated a stable burning process. The burning rate supplied by the Naval Ordnance Station [Ref. 3] included pressures from 500 to 4000 psia. Figure 7 compares the burning rate data at pressures that were common to both. The two lines in Figure 7 have nearly equal slopes, with the Naval Ordnance Station data higher. This was due primarily to the different temperatures at which the propellant was burned. Tests with a larger cross section strand (one-half by one-half inch) showed that the burning rate was not affected by strand cross section. Therefore, the smaller cross section was used for all subsequent tests.

The zero g burning rates obtained from the combustion bomb and the optical centrifuge were within a maximum difference of 30 per cent from those determined in the high acceleration centrifuge. The average difference was below 20 per cent. These differences were probably due to the transient effects of ignition and the relatively small size samples required in the combustion bomb and the optical centrifuge. In addition, the strands used in the combustion bomb and the optical centrifuge were not inhibited. Those used in the high acceleration centrifuge were rigidly inhibited for support. The burning rate data taken from the films had a minimum burn time of 0.5 seconds with the exception of the schlieren films. These times were about 0.2 seconds.

Burning rate augmentation was observed at high accelerations for the nonmetallized double base propellant. Figures 8 (a) and 8 (b) show the augmentation as a function of acceleration at 500 and 1000 psia respectively. The zero g burning rates at 500 and 1000 psia were 0.271 and 0.452 inches per second respectively. Instabilities in combustion at high accelerations were indicated by observed oscillations in the pressure-time trace and may be the cause for the data scatter shown in Figure 8. The burning was more stable at the lower g's and the higher pressure (1000 psia). Tests at negative 1000 g's showed no augmentation and indicated the same stable combustion exhibited at zero g's.

The optical centrifuge showed the yellow visible flame at zero g's [Figure 5]. At accelerations of 100 g's the visible flame was not observed at any time [Figure 6]. The viewing area of the camera was large enough to record any visible flame present during combustion.

Calculations of the acceleration induced pressure increase at the bottom of a 100 micron liquid layer on the propellant surface showed it was only about 3 per cent at 100 g's and therefore, was not responsible for the observed augmentation. The gas phase would be affected even less. These results indicate that the primary mechanism for augmentation is most likely contained in a two-phase region at/or within the burning surface. In this region, density differences are more pronounced and could be more significantly affected by acceleration fields. Huggert, Baryley and Mills [Ref. 10] refer to this region as the subsurface zone. The subsurface zone is just below the propellant surface and is comprised of gas and liquid in which an exothermic reaction occurs. One obvious effect of the acceleration environment was the elimination of the visible flame. This may have occurred as a result of a change in the products of combustion.

One possible mechanism for the observed augmentation is that the acceleration causes a change in the interaction of the gas and liquid phases, thereby increasing the heterogeneous reaction rates. Coupled with this is the possibility that the acceleration induced changes in the combustion products increases the radiation to the surface in the

ultraviolet spectrum. The double base propellant contained no opacifying agents such as carbon black.

B. COMPOSITE PROPELLANT

Tables II and III summarize the results obtained with sandwich burners. Figures 9 through 15 are photographs which were typical of the burns obtained for the various binders, binder thicknesses and accelerations.

As shown in Tables II and III, the zero g burning rates were sensitive to binder thicknesses. PU burned with approximately the same rates for both binder thicknesses, while the 0.004 inch HTPB burned faster than the 0.001 inch HTPB.

At zero g, sandwiches made with 0.001 thick binders of PU and HTPB showed similar flame characteristics. The flame width at its base was not much larger than the binder width. This fact, along with the smaller flame size, indicated that not much binder flow occurred. The 0.004 inch binders apparently had more binder flow onto the surface of the AP, as evidenced by an increase in the base width of the flame.

At accelerations of 100 g's, the 0.001 HTPB would not sustain combustion. The strands would not ignite, or would burn approximately 0.1 inch and extinguish. Sandwiches made with the two PU binder thicknesses and the 0.004 thick HTPB binder sandwich did exhibit increased burning rates at 100 g's. The flames in all cases were more

intense than the corresponding burns at zero g's. The film of the sandwich with the 0.004 inch thick PU binder showed large pools of binder flowing onto the surface of the AP. Some of these pools would not ignite and eventually dropped off the surface. The ones that did ignite produced another burning site, separate from the AP/binder diffusion flame.

The apparent mechanism for augmentation is the binder flow onto the AP which caused a larger flame. For HTPB, the binder flow is critical. At 400 psia, AP crystals with no binder would support combustion but this pressure is close to the low pressure deflagration limit. The low pressure together with the nitrogen purge system in the optical centrifuge, appears to cause AP/HTPB sandwich combustion to be very sensitive to binder flow. The 0.001 thick HTPB did not sustain combustion at accelerations of 100 g's. This binder thickness and not have enough binder to allow both binder flow and the build-up of a binder post to support the AP deflagration. The 0.004 inch thick binder allowed both the build-up of the binder post and the binder flow. It is thought that the reaction was quenched when excess binder built up on the surface of the AP.

V. CONCLUSIONS

A. DOUBLE BASE PROPELLANT

(1) Distinct burning sites exist on the burning surface of nonmetalized double base propellant.

(2) Gas phase density was found to decrease continuously from the surface to the visible flame. Assuming that the density variation is predominantly determined by temperature variations, the temperature increases continuously from the surface to the visible flame.

(3) The flame position depends on pressure and can be approximately calculated using $10^7/p^3$ inches, with p in psi.

(4) High positive accelerations cause augmentation and instabilities in combustion. Negative accelerations do not cause augmentation.

(5) Augmentation mechanisms apparently occur in the surface or subsurface zones by causing a different interaction between the liquid and gas phases, and also possibly increasing the ultraviolet radiation into the propellant.

B. COMPOSITE PROPELLANT

(1) Increased binder thickness had no effect on burning rates of AP/PU sandwiches but increased the burning rate of AP/HTPB sandwiches.

(2) Binder flow occurs at zero g's.

(3) Burning rate augmentation occurs at high accelerations for AP(UHP/binder sandwiches.

(4) The apparent augmentation mechanism is increased binder flow onto the AP (which causes larger visible flames).

(5) AP/HTPB sandwiches are very sensitive to binder flow and self extinguish at 400 psia and 100 g's.

TABLE I
PROPELLANT SPECIFICATIONS

(a) Double Base Propellant

<u>Constituents</u>	<u>Per cent by Weight</u>
Nitrocellulose	50.5
Nitroglycerin	46.8
2-nitrodiphenylamine	2.2
Di-n-propyl Adiapate	0.4
Candelilla Wax	0.1

(b) Composite Propellant

AP

<u>Designation</u>	<u>Crystal Size*</u>	<u>Principal Impurities (wt per cent)</u>
UHP	38.1% > 297 μ 81.9% > 211 μ 99.6% > 104 μ	Sulfated Ash 0.01%

Binders

<u>Type</u>	<u>Constituents</u>	<u>Per cent by Weight</u>	<u>Cure**</u>
HTPB	HTPB	93.7	168.0 hr at 60°C
	IPDI	6.3	
PU	Adiprene	72.0	120.0 hr at 48°C
	Castor Oil	27.9	
	1, 4 Butane Diol	0.1	

* Typical values from manufacturer data sheet

** First three hours in vacuum in excess of 28 in. Hg.

TABLE II

Summary of Data from AP (UHP)/PU Sandwich Tests

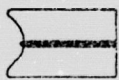
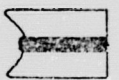
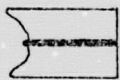

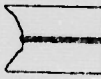

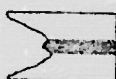
Pressure (psia)	Acceleration (g)	Average Burning Rate (in/sec)	Binder Thickness (in)	Burn Profile	Remarks
400	0	0.08	0.001		Small nonsteady flame at the AP/binder interface. Small amount of binder flow onto the AP.
400	0	0.09	0.004		Larger turbulent flame at the AP/binder interface. Small amount of binder flow onto the AP.
400	100	0.11	0.001		Small, but somewhat larger than at zero g, burning at the AP/binder interface. Small amount of binder flow onto the AP.
400	100	0.12	0.004		Larger flame than zero g burning with much binder flow onto AP. Pools of binder on the surface of the AP. Some ignited to produce secondary burning sites.

TABLE III

Summary of Data from AP(UHP)/HTPB Sandwich Tests

Pressure (psia)	Acceleration (g)	Average Burning Rate (in/sec)	Binder Thickness (in)	Burn Profile	Remarks
400	0	0.08	0.001		Small, but closely spaced separate flames at the AP/binder interface. Very little binder flow onto the AP.
400	0	0.12	0.004		Large continuous flame burning with a larger width than the binder. Some binder flow observed.
400	100	-	0.001	-	No sustained combustion in five attempts.
400	100	0.15	0.004		Large continuous flame which was wider than the binder. Binder flowed on both sides until it finally quenched itself.

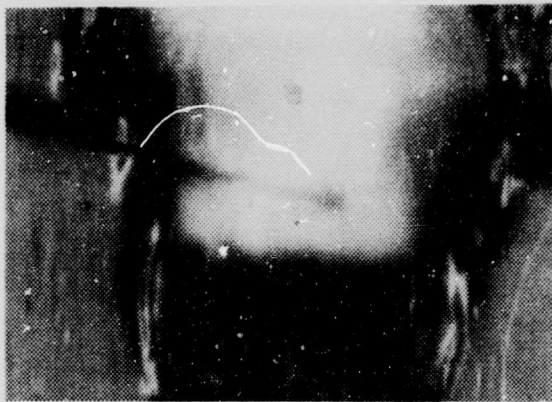


Figure 1. Horizontal Color Schlieren of Double Base Propellant at 500 psia



Figure 2. Vertical Color Schlieren of Double Base Propellant at 500 psia

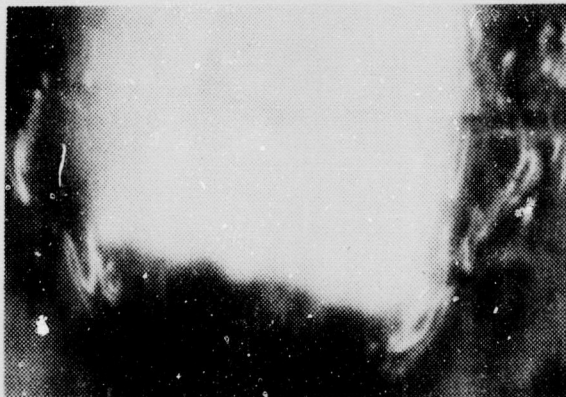



Figure 3. Horizontal Color Schlieren of Double Base Propellant at 800 psia

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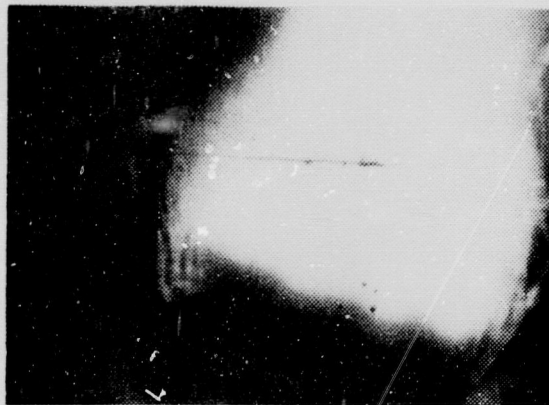


Figure 4. Vertical Color Schlieren of Double Base Propellant at 800 psia



Figure 5. Double Base Propellant Combustion at 0 g's, 400 psia



Figure 6. Double Base Propellant Combustion at 100 g's, 400 psia

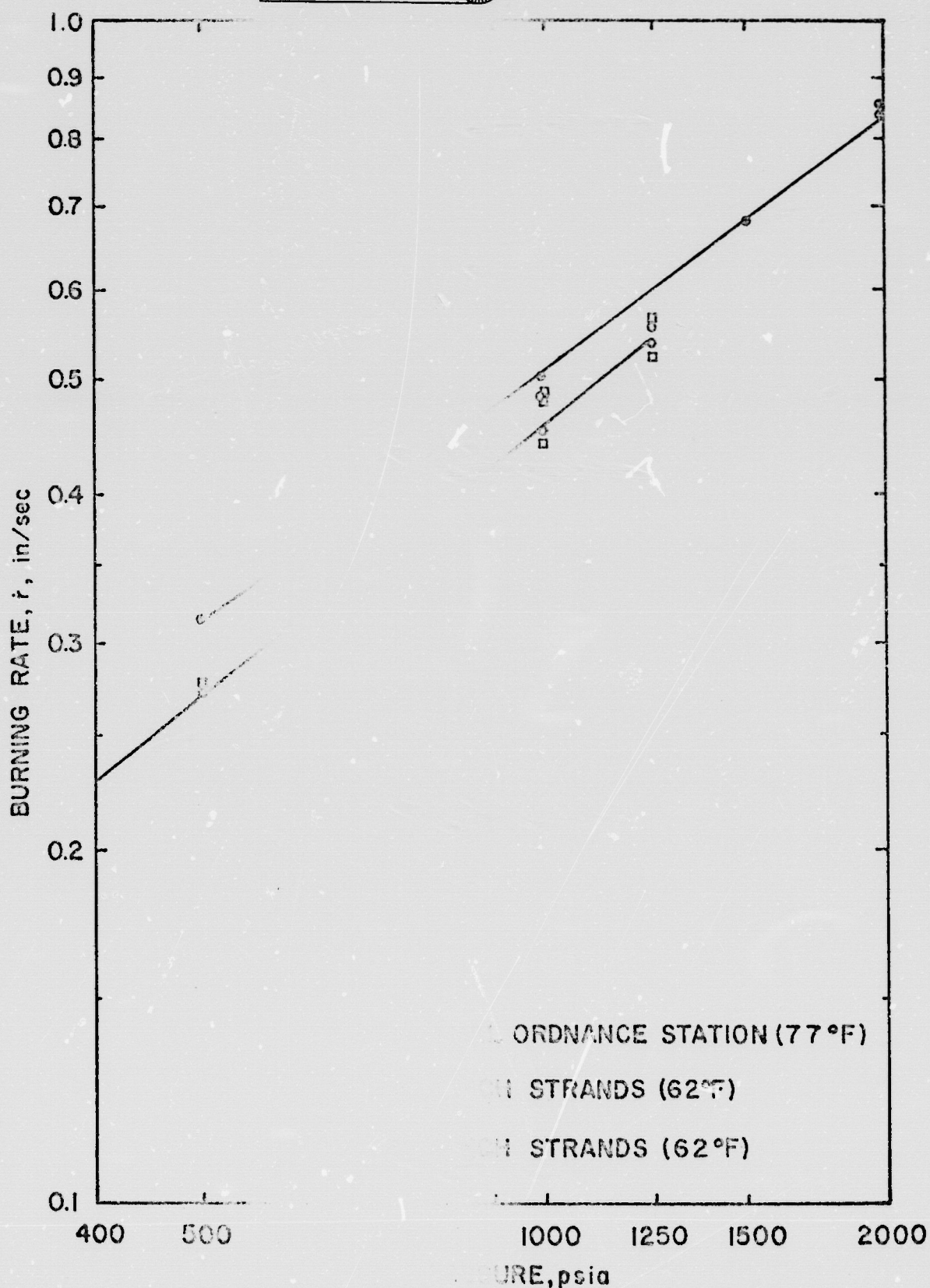
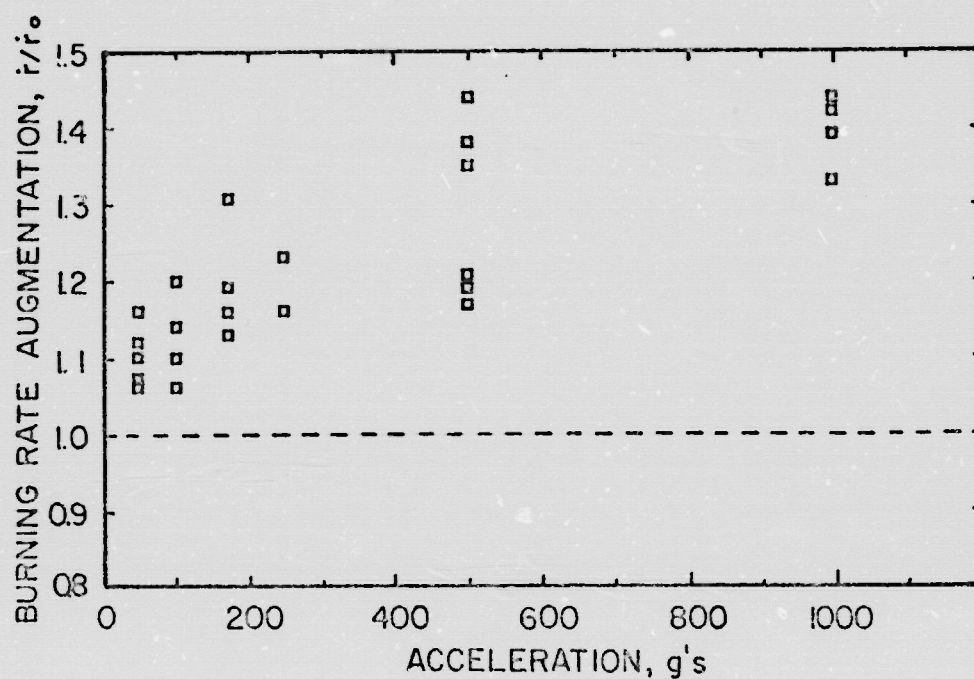
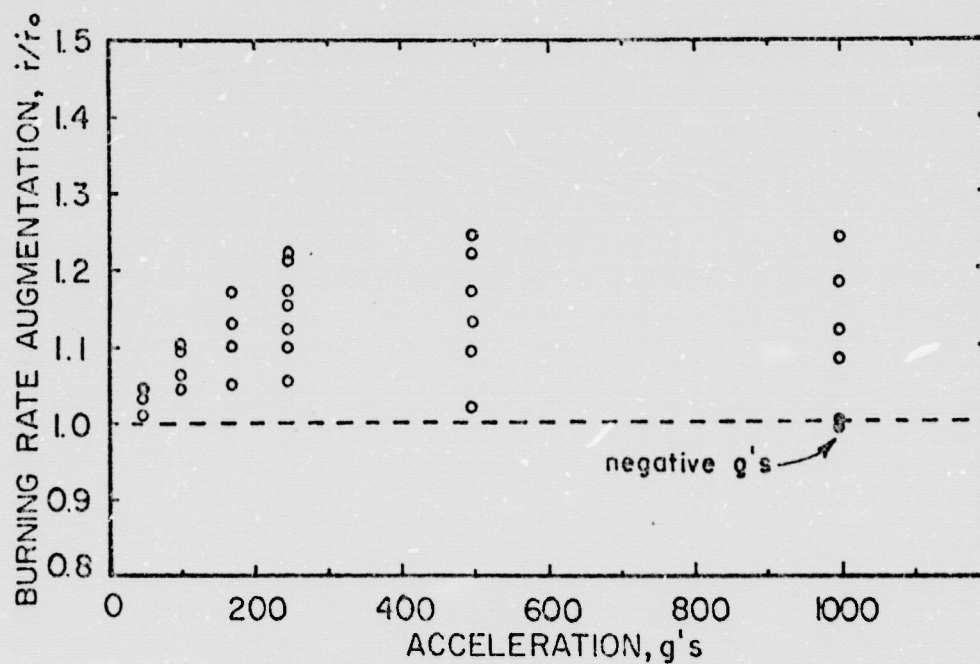


Figure 7. The Effect of Pressure on the Burning Rate of Nonmetallized Double Base Propellants



(a) 500 psia



(b) 1000 psia

Figure 8. The Effect of Acceleration on the Burning Rate of Nonmetallized Double Base Propellant.



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Figure 9. AP/PU Sandwich Combustion, 0.001 inch Binder at 0 g's,
400 psia



Figure 10. AP/PU Sandwich Combustion, 0.004 inch Binder at 0 g's,
400 psia



Figure 11. AP/PU Sandwich Combustion, 0.001 inch Binder at 100 g's,
400 psia



Figure 12. AP/PU Sandwich Combustion, 0.004 inch Binder at 100 g's,
400 psia



Figure 13. AP/HTPB Sandwich Combustion, 0.001 inch Binder at 0 g's,
400 psia



Figure 14. AP/HTPB Sandwich Combustion, 0.004 inch Binder at 0 g's,
400 psia



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Figure 15. AP/HTPB Sandwich Combustion, 0.004 inch Binder
at 100 g's, 400 psia

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