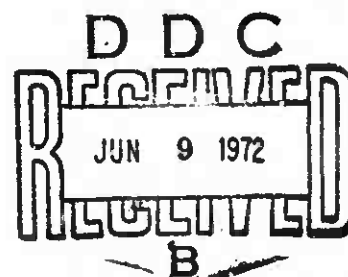


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THESIS

CINEMATOGRAPHIC STUDY OF AP/PBAA SANDWICH
BURNERS IN A POSITIVE ACCELERATION FIELD

by

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MAR 1972

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I. INTRODUCTION

Composite solid propellants subjected to an acceleration field normal and into the burning surface (i.e. positive "g") show an increase in the burning rate over that observed under standard gravity conditions [1, 2, 3]. This phenomenon is of concern to the design engineer as the design of composite solid propellant rocket motors is dependent upon the consumption rate of the propellant enclosed within its walls.

The phenomenon of change in burning rate of composite propellants subjected to acceleration field has been studied by many investigators [3 through 10].

Past investigations have been directed more towards modeling acceleration effects upon metalized propellants with less effort being expended on nonmetalized composites. As a consequence of this, a satisfactory qualitative model for the acceleration-induced burning rate augmentation of metalized composite propellants exists, while models proposed for nonmetalized propellants seem either to be incorrect or are still unconfirmed by a sufficiently large amount of experimental effort.

Application of the phalanx flame model [8] seems to be incorrect because no evidence of preferential sub-surface reactions at the binder/ammonium perchlorate (AP) interface has been found in quench tests [10, 11, 12].

Glick [9] has proposed that the burning rate augmentation mechanism for nonmetalized composite propellants results from an effect of acceleration upon the diffusion burning of small pockets of fuel vapor as they leave the propellant and travel away from its surface. The validity of this model in acceleration fields of less than 1000 g is in doubt. For the vapor pockets to be consumed close enough to the surface of the propellant to cause augmentation, acceleration loadings would have to be in excess of those where augmentation is first observed [14].

A recent proposal for the mechanism responsible for composite solid propellant burning rate augmentation has been given by Cowles and Netzer [5]. It suggests an acceleration-induced forced mixing of molten binder with AP oxidizer crystals and/or AP surface melt.

The work in this thesis represents an attempt to determine the causes for the burning rate acceleration sensitivity of AP/Polybutadiene-acrylic acid (PBAA) nonmetalized composite propellants.

The method of investigation was one of high-speed motion picture photography of AP/PBAA sandwich burners. This method of investigation was chosen because previous work (Schroeder [6] and Pinney [7]) was relatively unproductive in obtaining good photographic data on nonmetalized composite propellants. Both of the above investigators identified the difficulties involved in obtaining photographs of the burning surface of nonmetalized propellants.

They are smoke, the inability to see through the flame, etc. These difficulties encountered in attempting to extract photographic data from nonmetalized composites led to the idea of using a two-dimensional sandwich burner.

Two-dimensional sandwich burners allow good photographic analysis of the interface between AP oxidizer and PBAA fuel binder [10, 12, 13] and as such provide the basis for this investigation.

The validity of assuming that sandwich burner data describe the burning of three-dimensional composite propellants is questionable. However, sandwich burners allow photographic evaluation of the binder/AP interface during combustion. These interfacial conditions should be the same for sandwich burners and propellants.

II. METHOD OF INVESTIGATION

AP/PBAA sandwich burners formed by bonding two polycrystalline AP wafers together with PBAA, were burned in a combustion bomb at controlled pressures and acceleration environments. Runs were made at 200, 500, and 800 psig for both unaccelerated and the one hundred positive "g" condition. The AP used for the oxidizer was graded ultra high purity for one set of runs, and commercial with tricalcium phosphate (TCP) additive for the other set of runs. The burns (or runs) were recorded photographically as motion pictures, and from these motion pictures, burning rates and qualitative data were taken.

III. EXPERIMENTAL PROCEDURES

Sandwich burner preparation for this investigation started with the fabrication of the AP wafers from two lots of AP powder. Ultra high purity AP was provided by the Naval Weapons Center (NWC), China Lake (manufactured by American Potash and Chemical Corporation). This AP was 99.8 percent pure. The commercial grade AP (same manufacturer) was 99.4 percent pure with 0.2 percent TCP added as an anti-caking agent.

The ultra high purity AP had particle sizing ranging from 297 microns to 74 microns with 99.6 percent of it being larger than 104 microns. The commercial grade AP with TCP had particle sizing ranging from 500 microns to 74 microns. Micro-photographs showed that the TCP additive had a particle size of less than one micron.

The AP wafers were fabricated by weighing out 1.3 grams of AP and then placing it in a one-inch diameter die shown in Figure 1. This die was then placed in a twelve ton capacity Carver Laboratory hydraulic press and pressurized to 30,000 psi for twenty minutes. The completed polycrystalline AP wafer was then removed from the die. In all cases the wafers were whitish opaque in appearance. The completed wafers were weighed and measured and then density calculations were performed to ensure that they were of uniform construction and within two percent of the density of pure AP crystals.

AP wafers were then bonded together in pairs with PBAA binder to form the sandwich. This bonding was accomplished by thorough mixing of PBAA with EPON 828 as a catalyzer in the ratios of 84 percent by weight to 16 percent by weight respectively. The PBAA/EPON 828 mixture was uniformly smeared upon the face of one AP wafer; then the second AP wafer was placed over the first, sandwiching the PBAA. One-thousandth inch thick brass shim stock was placed between the AP wafers at three equally spaced points along their edges to ensure uniformity of binder thickness. During later portions of this investigation, small (15 gram) stainless steel weights were placed on the top AP wafer of the sandwich to further ensure binder thickness uniformity, and to reduce the tendency for the two wafers to slide over one another when the curing jar was evacuated. The sandwiches were then placed in a constant temperature oven at 72°C under a vacuum bell and were cured for a ninety-six hour period. During the first three hours of the cure period the vacuum bell was evacuated in excess of 28 inches of mercury.

Single-faced sandwiches (PBAA bonded to one AP wafer only) were constructed by placing the PBAA/EPON 828 mixture on a flat of Teflon or RTV and then placing an AP wafer over the top of the binder. These were cured in the same manner as described above, and were then lifted from the Teflon or RTV for cleaving.

Using a razor knife, the bonded AP/PBAA sandwiches were cleaved into small burners with dimensions of 0.45 inch high by 0.35 inch depth. These burners were then scraped to produce a squared face on all edges. Final dimensions of the scraped sandwich burners were 0.40 inch by 0.27 inch.

A pencil mark was made on the right-hand side AP wafer of the sandwich. This mark was made 0.15 inch up from the bottom edge of the burner. This pencil mark served to mark a focal point for the optical axis as well as to supply a reference point on the wafer from which photographic determination of burning rate could be made.

The sandwich burners were mounted with model-airplane cement on an aluminum pedestal as shown in Figure 2.

Ignition of the sandwich burners was accomplished using an 0.008-inch diameter nichrome resistance wire over the top of the burner. The wire was so oriented as to lie on the exposed binder at the top of the burner. A black gunpowder/cement/acetone mixture was then applied over the ignition wire to the top of the burner and allowed to dry. Preparation of a sandwich burner for a run was completed by this step. The completed sandwich burner mounted on the combustion bomb end cap is shown in Figure 3.

The sandwiches were burned in the horizontal position in the combustion bomb of the photographic centrifuge located in the Rocket Laboratory at the U. S. Naval Postgraduate School, Monterey, California. A description and figures of the photographic centrifuge and accompanying

Hycam motion picture camera together with information on their operation are given in Reference 6.

During runs the combustion bomb was purged with nitrogen to clear as much smoke as possible from the sandwich burner and to provide an inert atmosphere in which the burn took place.

Burning rates were taken from the films by projecting them onto a screen and measuring a length of burn over 0.4 to 0.6 of a second elapsed time. The top 0.075 inch of the sandwich was not included in the burning rate measurements in order to allow the burning rate to stabilize. The average burning rates were calculated from the burn occurring between 0.075 inch from the sandwich top to 0.24 inch from the sandwich bottom. This distance was about 0.080 inch long. The projected screen distance was scaled to real distance by forming a ratio between the thickness of the projected image of the burner and the measured burner thickness. All burning distance measurements of the projected image could then be scaled to real dimensions using this ratio. The time elapsed between two points on the film was taken by counting the number of 0.001 second timing marks placed on the film edge by a Red Lake Laboratories Millimite TLG-4 timing oscillator. From the real distance burned and the actual time elapsed, burning rate was calculated.

When burning the sandwiches, sometimes the flame zone on one side of the binder would extend deeper into the burner than on the other side. On some runs this lowest

point would shift back and forth from one side of the binder to the other. All burning rate data were taken for the maximum point of advance of the flame zone.

The calculated burning rates are average burning rates for the zone over which the burn was observed.

All runs were made at a camera framing rate of 1500 pictures per second and at an "f" stop of 1.9. The optics arrangement gave a magnification of 1.4 on the film plane.

IV. RESULTS AND DISCUSSION

The experimental results of this investigation are summarized in Tables I, II, III, and IV.

The remarks in this section represent a composite of the general and detailed information derived from the films of all runs which could be considered successful.

Figures 4 and 5 show selected frames from runs made for varying "g" loadings, combustion bomb pressures, and AP grade.

No successful run for the commercial grade AP (with TCP) sandwiches burned at 800 psig and +100 g was obtained. All attempts to obtain data at these conditions were met with either unsuccessful ignition, or with the flame being extinguished within one-tenth inch of burn.

It is thus apparent that the burners fabricated from the commercial grade AP with TCP additive burned less readily than the ultra high purity AP sandwiches at all pressures and "g" loadings, other than the 200 psig runs. This might be due to a catalytic augmentation by the TCP or another impurity compound in the commercial grade AP. It is apparent that at 200 psig, which is below the low pressure deflagration limit (P_{dl}) of AP, there is some mechanism that causes the commercial grade AP with TCP to be consumed more readily than the ultra high purity AP.

At other pressures above P_{dl} for AP, the sandwiches made with ultra high purity AP show higher burning rates in all cases than the corresponding tests with sandwiches made with commercial grade AP with TCP conditioner. Burn profiles show that the ultra high purity AP is self-deflagrating while the commercial grade with TCP doesn't appear to self-deflagrate; rather it appears to thermally decompose. The scope of this study did not permit an investigation of why the AP with TCP was not self-deflagrating at pressures in excess of 350 psi.

The burning rates for AP with TCP at 500 psig and 0 g indicate that binder thickness apparently has little observable effect upon burning rates of AP/PBAA sandwich burners. This same observation also is made where the AP was graded ultra high purity and run conditions were 500 psig and +100 g. This phenomenon has also been observed by Jones and Strahle [13].

The flames for all the 200 psig, 0 g runs were laminar in nature. In the acceleration runs at 200 psig some flame turbulence was noted as a flickering of the flame from side to side. It was also observed from the increased width at the bottom of the burn profile that there was a tendency for the molten binder to be forced by the acceleration out past the binder AP interface and onto the AP. Binder flow onto the AP at +1 g conditions has been reported by Varney [10] and Jones and Strahle [13]. It is believed that the flame flickering seen in the +100 g runs at 200 psig was caused by

small pockets of oxidizer rich gases being liberated under the molten binder by thermal decomposition of the AP.

At pressures of 500 and 800 psig all flames were turbulent in appearance regardless of the acceleration field. In the case of the ultra high purity AP runs, this may be attributable to the self-deflagration of the AP. In the case of the commercial grade AP it is believed that the increased burning rate liberates sufficient heat to thermally decompose the AP above the primary flame zone. This decomposed oxidizer then diffuses outward from the wafer face creating a turbulent diffusion flame.

From Table I it may be seen that AP/PBAA sandwich burners made with ultra high purity polycrystalline AP wafers exhibit burning rate acceleration sensitivity. Below the P_{dl} of AP, average burning rate decreased with increasing acceleration. Above P_{dl} of AP, average burning rate increased with increasing acceleration. Sandwiches made with commercial grade AP with TCP additive showed no significant augmentation in average burning rate for accelerated conditions over those of no acceleration.

These results indicate that burning rate acceleration sensitivity of nonmetalized composite propellants is due in part to the interaction of the binder melt with the self-deflagrating AP. For pressures below the P_{dl} of AP (approximately 350 psig for pure AP and apparently greater than 800 psig for commercial grade AP with TCP), acceleration induced binder flow onto the AP inhibits AP decomposition

and the average burning rate decreases or remains unchanged. For pressures above the P_{dl} of AP, acceleration induced binder flow appears to affect the burning rate by mixing of the binder melt with the "active" AP. The higher the pressure, the higher the binder "post" and the greater the binder/AP interaction (puddling, etc., see Figures 4 and 5). This could affect both heterogeneous and gas phase reaction rates. The average burning rate augmentations at 100 g of approximately ten percent at 500 and 800 psig (see Table I) are also in general agreement with propellant augmentation data [1, 5].

As indicated above, the burning rates reported in Tables I, II, and III are average burning rates. To obtain an estimate for the transient nature of the burn rate, the increment of burn over which the data was taken was split into two equal parts for 100 g and 0 g runs. This was done for ultra high purity AP/PBAA sandwich runs which were made at 500 psig and 800 psig. It was found that the burning rates at 0 g for both pressures increased between increments while those at 100 g decreased. For the 500 psig runs, the increase in the average incremental burning rate of the 0 g run did not exceed the average second increment burn rate for the 100 g run. For the 800 psig runs this was not found to be lower than the second increment average burning rate of the 0 g run. This points out the complexity involved in determining the mechanism(s) for acceleration induced burning rate augmentation of sandwich burners. The deflagration

rate of pure AP at pressures above its P_{dl} is a function of pressure. At 800 psig the AP is self-deflagrating at a higher rate than at 500 psig. As a consequence, the amount of binder not pyrolyzed and consumed by the AP oxidizer is greater in the 800 psig runs than in the 500 psig runs. Apparently a small amount of binder overflow onto the AP enhances the average burning rate [10, 13] of the sandwich. If excess binder builds up upon the surface of the AP it is possible that it acts as a heat sink and quenches the reaction.

The possible existence of preferred interfacial reactions between the binder and the AP was briefly considered. A sandwich was constructed in which only one AP wafer was cured to the binder. A matching AP wafer was placed firmly against the cured binder to form a sandwich. This sandwich burner was identical to the normal burner except one side was "dewetted", i.e., it had a significantly different AP/binder interfacial condition on one side. This configuration should bias the reaction front toward interfacial reactions. A test was conducted with this sandwich at 500 psig and 0 g. No large order preferential burning down the unbonded interface was observed in the motion picture. However, it appeared that the unbonded AP wafer decomposed at a slightly faster rate than did the bonded wafer. In addition, the average burning rate for this sandwich was significantly greater than that obtained when both AP wafers were bonded to the PBAA (Table III).

The one test conducted is not adequate for drawing any strong conclusions.

The significance of the third place to the right of the decimal point in the average burning rate values is questionable. Although the measurements for burning rate calculations were taken from a projected image with a vernier caliper out to the thousandths inch place, the uncertainty of the exact location of the nadir of the burn prevents assigning too much significance to the third decimal place.

V. CONCLUSIONS

Test results indicate that burning rate acceleration sensitivity of AP/PBAA sandwich burners is due in part to the interaction of the binder melt with the self-deflagrating AP. For pressures below the P_{dl} of AP (approximately 350 psi for pure AP and apparently greater than 800 psi for commercial grade AP with TCP), acceleration induced binder flow onto the AP inhibits AP decomposition and the average burning rate decreases or remains unchanged. For pressures above the P_{dl} of AP, acceleration induced binder flow appears to affect the burning rate by mixing of the binder melt with the "active" AP. The average burning rate augmentation, at +100 g, of approximately ten percent at 500 psig and 800 psig are also in general agreement with composite propellant augmentation data [1, 5]. At 800 psig the AP is self-deflagrating at a higher rate than at 500 psig. As a consequence, the amount of binder not pyrolyzed and consumed by the AP oxidizer is greater in the 800 psig runs than in the 500 psig runs. Apparently a small amount of binder overflow onto the AP enhances the average burning rate [10, 13] of the sandwich. If excess binder builds up upon the surface of the AP it is possible that it acts as a heat sink and quenches the reaction.

VI. RECOMMENDATIONS

It is recommended that more tests be made using the same run parameters as were used in this study. This would give an increased sampling of data, thereby increasing the level of confidence in the findings of this study. In addition, burning rates should be determined as a function of time for the entire run.

It is also suggested that studies should be pursued utilizing a wider range of binder thicknesses. This should be done to test for sensitivity of burning rate in acceleration environments to varying binder thicknesses.

Other tests should be made with different binder systems, such as polyurethane (PU), carboxyl-terminated polybutadiene (CTPB), etc. Such tests would reveal whether or not the acceleration-induced burning rate augmentation mechanism proposed in this study is applicable to other than AP/PBAA systems.

TABLE I
Summary of Data from AP(UHP)/PBAA Sandwich Tests

Pressure (psi)	Acceleration Loading (g)	Average Burn Rate (in/sec)	Binder Thickness (in)	Burn Profile	Remarks
200	0	.07(9)	.003		Small laminar flame burning only in the vicinity of the binder AP interface. Some evidence of AP pyrolysis above the flame.
200	100	.06(4)	.003		Small flame burning only in the vicinity of the binder AP interface. The flame appears more turbulent than the 200 psi, 0 g run. The AP appears to pyrolyze above the flame.
500	0	.17(7)	.006		Burning with wide turbulent flame. AP decomposes below the level of the flame zone.
500	100	.20(9)	.003		Burning with wide turbulent flame. AP decomposes below the level of the flame zone. Binder pools on the AP.
500	100	.19(5)	.003		Burning with wide turbulent flame. AP decomposes below the level of the flame zone. Binder pools on the AP.
500	100	.20(2)	.007		Burning with wide turbulent flame. Can't see binder pooling of AP, however greater width of flame at binder AP interface suggests binder overflow onto AP.

TABLE I (cont)
Summary of Data from AP(UHP)/PBAA Sandwich Tests

Pressure (psi)	Acceleration Loading (g)	Average Burn Rate (in/sec)	Binder Thickness (in)	Burn Profile	Remarks
800	0	.26(0)	.009		Burning with wide turbulent flame. AP decomposes much faster than the binder, leaving a binder post stick- ing up. A lot of gray smoke from the AP was observed.
800	100	.29(7)	.008		Burning with wide turbulent flame. Binder was observed to puddle on both AP wafers. Thick gray smoke from the AP was observed.

TABLE II
Summary of Data from AP(TCP)/PBAA Sandwich Tests

Pressure (psi)	Acceleration Loading (g)	Average Burn Rate (in/sec)	Binder Thickness (in)	Burn Profile	Remarks
200	0	.08(9)	.002		Burns with a small laminar flame only in the vicinity of the AP/binder interface. There is less evidence of AP pyrolysis than for the same run conditions with AP(UHP).
200	100	.08(4)	.003		Burns with a small flame more turbulent than the above run. Burning occurs in the vicinity of the AP/binder interface. Binder appears to puddle near the center of the sandwich and puddle remains there during remainder of burn.
500	0	.12(7)	.002		Burns with a turbulent flame. It appears that AP pyrolysis goes on some distance above the flame zone.
500	0	.12(8)	.004		Burns with a turbulent flame. AP pyrolysis goes on for some distance above the flame zone.
500	100	.12(6)	.004		Burns with a turbulent flame. Pyrolysis of the AP goes on for some distance above the flame zone. No binder puddling was observed.
800	0	.18(9)	.002		Burns with a turbulent flame. AP pyrolysis appears to occur for some distance above the flame zone.
800	100	xxx	xxx		Had no successful runs for this condition.

TABLE III
Summary of Data from AP(UHP)/PBAA Single Face Sandwich Test

Pressure (psi)	Acceleration Loading (g)	Average Burn Rate (in/sec)	Binder Thickness (in)	Burn Profile	Remarks
500	0	.19(9)	.003		

One might possibly see a preferential consuming of the unbonded side (right) AP wafer. It appears to decompose faster than the left side wafer. A great quantity of gray smoke is liberated from the surface of the AP. Burns with a wide turbulent flame.



TABLE IV

Summary of Incremental Burning Rates for AP(UHP)/PBAA Sandwich Tests

Pressure (psi)	Acceleration Loading (g)	First Increment Average Burn Rate (in/sec)	Second Increment Average Burn Rate (in/sec)	Average Burn Rate (in/sec)
500	0	.16(5)	.18(3)	.17(4)
500	100	.20(4)	.19(9)	.20(2)
800	0	.22(4)	.31(1)	.26(7)
800	100	.37(1)	.21(2)	.29(6)

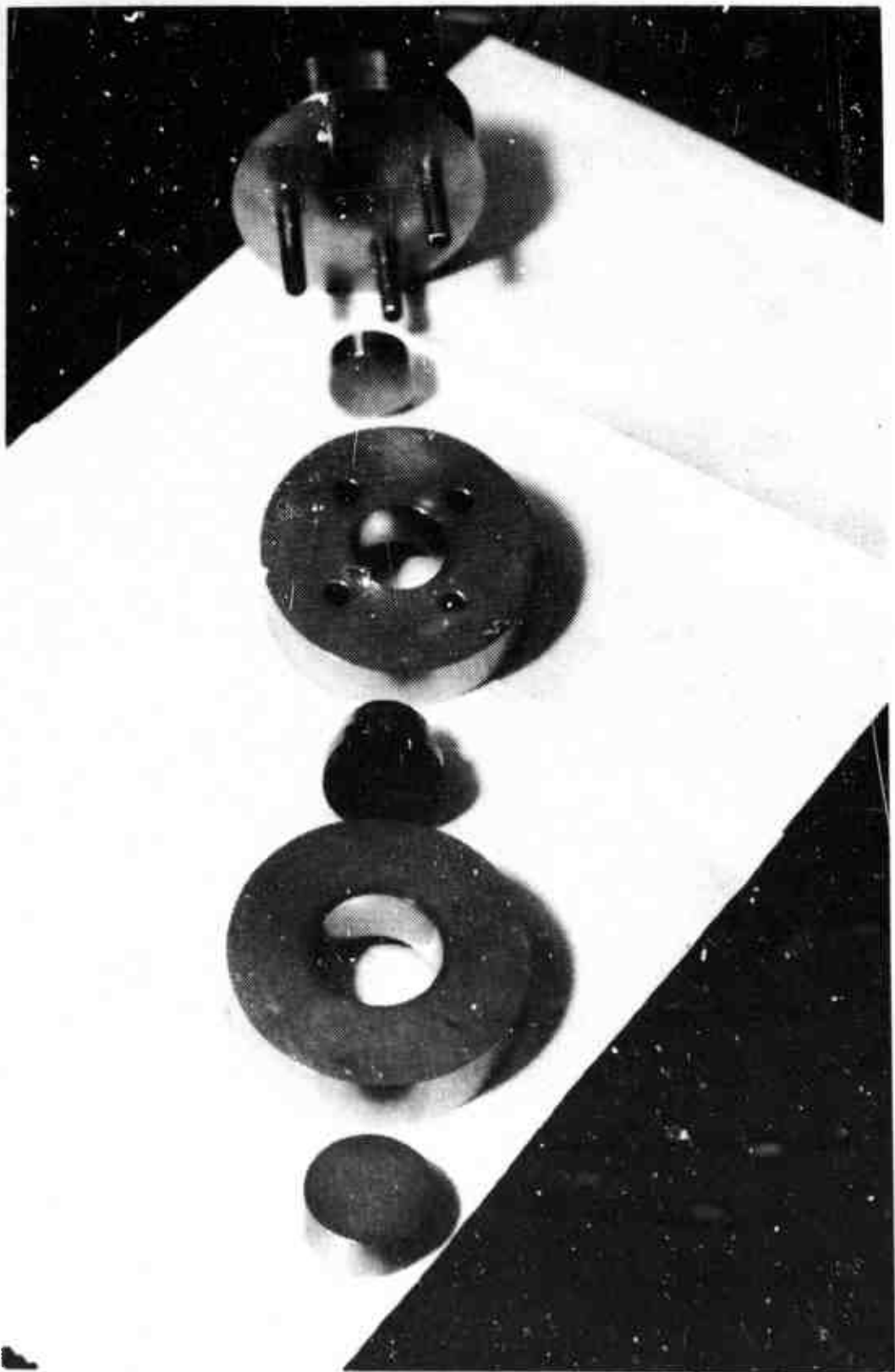


Figure 1. Ammonium Perchlorate Wafer Forming Die

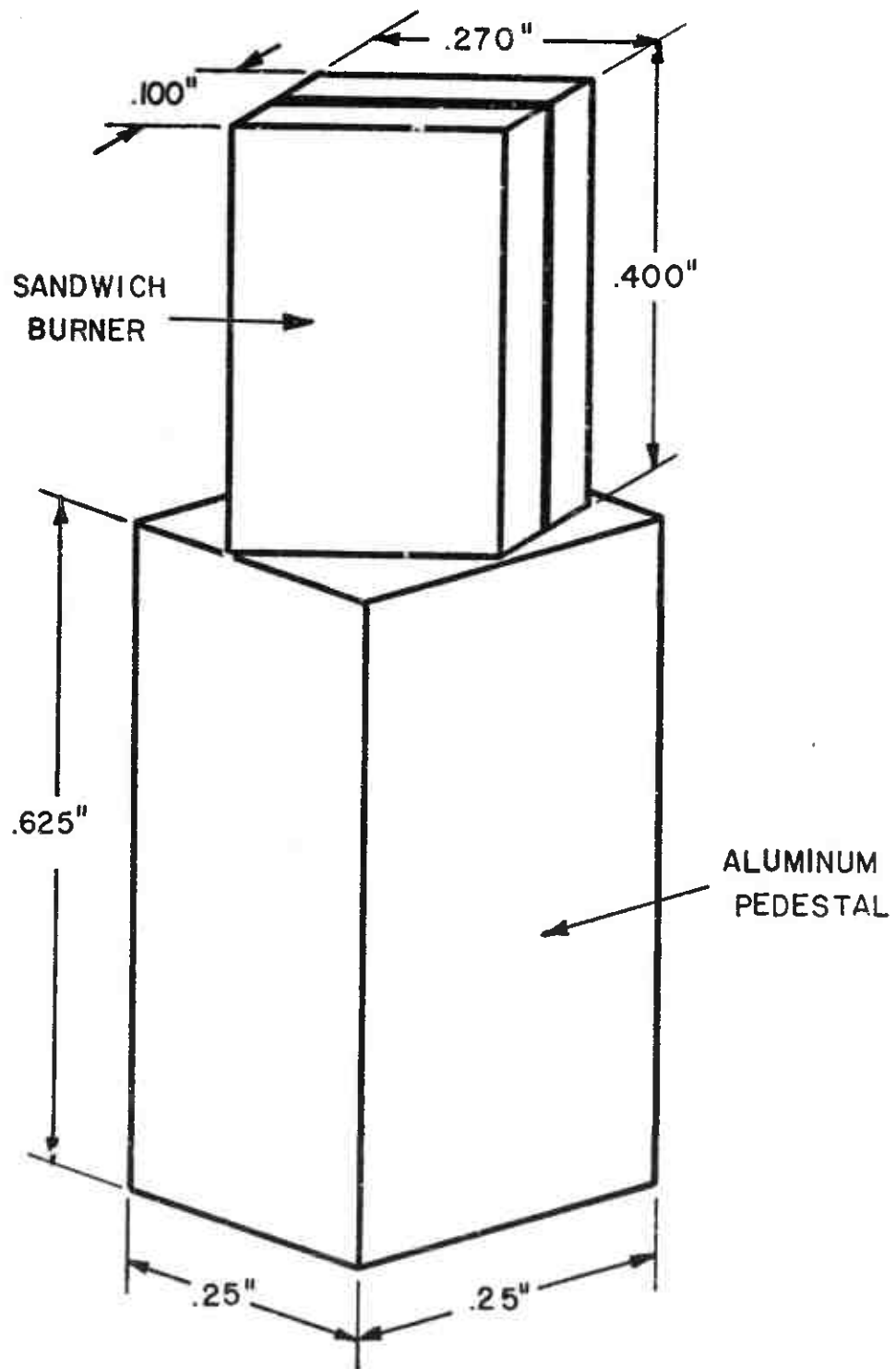


Figure 2. Dimensioned Sandwich Burner



Figure 3. Combustion Bomb End Cap With Sandwich Burner Mounted



(a) 200 psi
0 g



(b) 200 psi
100 g



(c) 500 psi
0 g



(d) 500 psi
100 g

Figure 4. Burn Profiles of AP(UHP)/PBAA Sandwich Tests



(e) 800 psi
0 g



(f) 800 psi
100 g

Figure 4 (cont). Burn Profiles of AP(UHP)/PBAA Sandwich Tests



(a) 200 psi
0 g



(b) 200 psi
100 g



(c) 500 psi
0 g



(d) 500 psi
100 g

Figure 5. Burn Profiles of AP(TCP)/PBAA Sandwich Tests



(e) 800 psi
0 g

Figure 5 (cont). Burn Profiles of AP(TCP)/PBAA Sandwich Tests

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