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Aerospace and Mechanical Sciences Report No. 446p

by

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ABSTRACT

In order to explore the limits of validity of the granular diffusion flame theory of solid propellant combustion in the limiting low pressure regime, a systematic study of burning rates and particle size effects has been conducted at subatmospheric pressures. In addition, flame extinction phenomena were explored and flame photographs and chemical analysis of reaction residues were carried out. It was found that particle size effects on propellant burning rates persisted at the lowest pressures at which combustion experiments could be conducted.

In connection with the extinction study a new regime of combustion was discovered for certain polysulfide composite propellants containing fine oxidizer particles. When the flames of these propellants are visibly extinguished by reducing the environmental pressure, a combustion wave continues to propagate through the propellant with the formation of an ash. Thermocouple measurements have shown the maximum temperatures in such combustion waves to be less than 300°C. Other properties of these flameless combustion waves including crude burning rates have been elucidated by further experiments.

There are at least two possibilities for interpreting this flameless regression. The first interpretation is that it is evidence of an oxidation reaction taking place at the solid surface or inside the thermal wave. If this is true, such a heat release term cannot be ignored in the theory of solid propellant combustion. The second interpretation is that the combustion wave in an AP propellant propagates simply as the result of exothermic pyrolysis of the AP without additional heat from subsurface or surface oxidation. If subsurface or surface oxidation can be ruled out in such waves, oxidation in the condensed phase can probably be omitted in the normal theory of burning. More refined measurements of the characteristics of these flameless combustion waves might help settle this question of whether condensed phase reactions are of any significance. The mere existence of such a wave cannot be taken as proof that such oxidation takes place. The observed oxidizer particle size effects are a significant clue that must be followed up.

I. INTRODUCTION

A. Background

The most widely considered composite solid propellant burning rate theory today is the granular diffusion flame theory (1). This model, first proposed by Summerfield as early as 1955 leads to a burning rate-pressure relationship in simple two parameter form:

$$\frac{1}{r} = \frac{a}{p} + \frac{b}{p^{1/3}} \tag{1}$$

where a is a function of the chemical reaction rate and b a function of the diffusion rate of oxidizer and fuel vapors. Although it would be difficult to compute theoretical values of these coefficients, a full development of this equation delineates the sensitivity of a to the flame temperature as controlled by the mixture ratio and catalytic additives and b sensitive to oxidizer particle size. Such correlation has been found by Sutherland (1) and to a slightly less extent by Webb (2). However, Bastress (3) points out that the theory suffers certain restrictions as to the range of pressures and oxidizer particle size over which it is applicable. The Summerfield theory is felt to apply only in the pressure-particle size regime where the particles are small compared to the flame thickness. The explanation for this behavior is that only under these conditions does the surface behavior conform to the postulated model. As research along those lines has progressed, it has become increasingly apparent that no single physical model can be postulated which will cover the entire range of variables. However, this does not lessen the significance of the Summerfield theory in that it does account for the influence of many important variables and provides very valuable insight regarding the physical process within its range of applicability.

In order to examine the theory"s predict on for subatmospheric pressures, equation (1) can be rewritten in the form:

$$\frac{1}{r} = \frac{a}{p} + \frac{b'' dm}{p^{1/3}} \tag{2}$$

where dm = diameter of the oxidizer particle (not to be confused with d , the diameter oxidizer vapor pocket).

$b' = b/dm$

b' is seen to be independent of both pressure and particle diameter. By using a and b' ,as determined experimentally by Bastress (3), equation (2) can be easily plotted (Figure 1). It is seen that b tends toward zero for decreasing oxidizer particle size. These particle size effects are seen to diminish with decreasing pressure and the slope approaches that of the theoretical $d_m = 0$ curve. This would represent the uncoupled equation $r = p/a$.

B. Previous Subatmospheric Work

Several researches have been carried out in the pressure regime of particular interest to this paper - pressures from atmospheric down to the minimum sustained combustion pressure. Webb (2) was able to obtain burning rates down to 6.5 psia and Silla (4) obtained rates down to 2.45 psia. The only difference in the propellant employed in these two cases is the difference in oxidizer particle size and the lack of inhibitor in the latter work. Neither of these sets of burning rate data agree with the Summerfield equation but do claim agreement with his physical model. Webb reports that the pressure exponent increases with decreasing pressure and that at low (subatmospheric) pressure it is largest for coarse oxidizer particle size. Silla's work appears to follow this trend.

As Silla notes, if the Summerfield equation is rewritten in the form $\frac{p}{r} = a + bp^{2/3}$ and a plot of p/r vs $p^{2/3}$ is constructed, straight horizontal lines are obtained. Recalling that a is related to the diffusion time we can conclude that the chemical reaction is indeed the rate controlling mechanism in this pressure regime and that it has been completely uncoupled from the postulated high pressure mechanism. This is precisely the physical criterion used by Summerfield: the molecular diffusion is very much faster than the oxidation reaction and thus a pre-mixed second order gas flame is approximated. Hence, it becomes apparent that in this pressure regime the Summerfield equation can be simplified to the form $r \propto p$, again consistent with the analysis presented.

Several other points concerning the physical behavior of the burning propellants were made in these two researches and should be noted. Webb describes the deposits remaining on the inside surfaces of his bomb as changing in color from black to gray to almost white as the pressure decreased. At high pressures soot deposits would be expected for such a fuel rich propellant. Bircumshaw and Newman (5) have shown that ammonium perchlorate sublimes directly to the pure perchlorate as well as decomposing at subatmospheric pressures. Only approximately 30% decomposition occurs and the residue is still chemically the same as before heating was started. This would, of course, explain the shift in the color of the deposits and also raise questions as to the mixture ratio which actually enters into the reaction as the amount of gray-white product is reported to increase with decreasing pressure. This could conceivably lead to a model for this pressure regime with the mixture ratio as a function of the pressure.

Webb also notes the condition of the surface of extinguished strands. At subatmospheric pressures the surfaces appear extremely irregular, exhibiting burning down the sides of the strand. At high pressure (500 psia) the surface is very regular, remaining normal to the strand but is slightly concave. Note that these conditions were produced with strands 3/16" square by 7" long.

Streaks in the flame at atmospheric pressure have been noted by Sutherland and have been attributed to soot particles originating from the burning surface. Silla, however, notes that these streaks disappear as the pressure is reduced. The reduction in pressure should have little effect on the number of soot particles emanating from the surface. Thus, it is suggested that these streaks may be attributed to abnormally large zones of gaseous fuel or oxidizer and their disappearance at lower pressures being due to more rapid diffusion. This would then be additional proof of the pre-mixed gaseous diffusion flame as being the controlling mechanism in this regime.

C. Purpose of This Work

The severest test which can be applied to any theory is its application to a limiting case or region. Thus, subatmospheric pressures provide an interesting and extremely arduous test for the granular diffusion flame theory - both in regard to the mathematical analysis and to the physical model proposed. This study was undertaken with such a purpose in mind. It was also hoped that some further light could be shed on the nature of the controlling mechanism for low pressure combustion by isolating it as the limits of combustion are approached. It was proposed that this mechanism be studied by careful observation of the pressure-burning rate relationship, by comparison of flame photographs taken over the pressure regime in question, by observation of the surface behavior and by quantitative and qualitative chemical analysis of the variation in combustion residue composition with pressure. Further, it was decided to extend the work of Webb (2) and Bastress (3) by a systematic variation of oxidizer particle size, observing the effect of this parameter on burning rate. This would be of particular interest since the granular diffusion flame theory predicts a disappearance of such effects at low pressures. The convergence of burning rate curves for small oxidizer particle size-low pressures is predicted due to the extremely rapid diffusion of the smaller gas pockets (their size being proportional to the originating crystal diameter). As stated in the analysis, this then can be approximated by a pre-mixed gas flame treatment. However, if particle size effects persist, as the low pressure limits of combustion for small particle size oxidizers are approached, the validity of the approximation can be questioned.

II. EXPERIMENTAL PROGRAM AND RESULTS

A. Introduction

Polysulfide (LP-3) binder with a 65% concentration of unimodal oxidizer was used to study oxidizer particle size effects. The particle size was varied from 5μ to 325μ with an average width ratio of 2.84. Burning rates were obtained and the variation in flame structure observed photographically for this series of propellants. A small number of thermocouple traces were also taken for the 15μ oxidizer particle size propellant.

The PBAA binder was studied for two AP concentrations (75 and 80) and for two bimodal particle size distributions (a fine mixture of 30% 5μ and 70% 45μ and a coarse mixture of 30% 45μ and 70% 180μ). Again, burning rates and flame photographs were obtained over this range of variables in the subatmospheric regime.

The amount and physical characteristics of the composition products deposited on the walls of burning chambers as a function of pressure for both binders was noted. It was felt that this would indicate the nature of the reactions taking place and note any marked change in this reaction with pressure.

An interesting pattern of behavior came to light when attempts were made to find the minimum sustained combustion pressure for the LP-3 with oxidizer particle sizes less than or equal to 45μ. At a pressure of approximately 1.5 psia, the normal flame blossom extinguished, but a reaction wave continued to propagate through the propellant with the formation of an ash. A great deal of effort was spent in obtaining thermocouple traces and burning rates for this form of combustion. A chemical analysis was performed on the ash as well as on the vapors coated on the walls of the combustion chamber. Movies of this behavior, both colored and black and white, were also obtained.

The discovery of this flameless combustion stimulated an interest in the behavior of the flame and the reaction of other binders as the limiting pressure was approached. This was studied through color movies of LP-3, PBAA, polyurethane and plastisol propellants over a wide range of compositions and oxidizer particle size distributions. No other samples of flameless combustion were noted except for polysulfide propellants.

B. Burning Rates

The polysulfide burning rate data are tabulated in Table 2 and displayed in Figure 2. The limits of combustion for the 325 to 80 micron propellant are indicated.

The burning rate curve for the 5 micron propellant is the only one which does not display a regular pattern in the normal combustion regime. This can be attributed to the difficulty involved in processing propellant with such fine oxidizer particles. Several batches of propellant were prepared, but each exhibited a large number of holes. In order to complete the series, the best batch was selected. However, the scatter noted in the tabulation remains much higher than that exhibited by the other propellants.

The other curves are regular within the normal combustion regime and display a remarkable parallelism. The slope of these curves indicate an exponent of approximately 0.77. It is noted that an apparent particle size effect of some magnitude does persist throughout the pressure regime and there is no sign of convergence as predicted by the theory.

The burning rate curves for the PBAA bimodal propellants are displayed in Figure 3. All points given for these propellants were taken with the primary burning rate technique. The relative placement of these curves is quite contrary to what was anticipated. The propellant containing 80% oxidizer of fine bimodal distribution (30% - 5µ, 70% - 45µ mean diameters) would be expected to give the gastest burning rates, followed by the propellants containing 75% oxidizer of the same fine bimodal distribution, then the 80% of coarse bimodal distribution (30% - 15µ, 70% - 225µ) and finally the 75% oxidizer of the same coarse bimodal distribution. It is quickly seen that this is not the case. Several separate batches of propellant were tested in an attempt to resolve this difficulty with no success.

C. Extinction Behavior and Flameless Combustion

During the study of the unimodal LP-3 propellants, attempts were made to determine the minimum sustained combustion pressure and in turn obtain burning rates as close as possible to this pressure. It was noted that this minimum pressure seemed to increase with decreasing oxidizer particle size. This trend continued from 325μ propellant to 80μ propellant. Over this particle size range the minimum pressure increased from approximately 3.8 psia to approximately 7.6 psia. Note that ignition could not be achieved at these pressure levels. This is consistent with previous work indicating the minimum ignition pressure is well above the minimum sustained combustion level. This appears to be true in general throughout this work, but is was also found that the ignition pressure approaches the minimum combustion pressure with decreasing particle size.

The behavior of the flame with decreasing pressure was very interesting. As the pressure decreased, the flame became increasingly unstable, flickering and fluttering as if in a breeze. Gradually, a blue layer became apparent at the base of the normally yellow flame. This became more and more dominant as the pressure decreased further. This layer appeared to stabilize the flame during this period. As the pressure was reduced further, the flame again became increasingly unstable until the reaction waves began to wash about the surface. Arden, Powling and Smith (6) report behavior similar for ammonium perchlorate with small amounts of fuel added. These authors believe this to be fundamental to all solid propellants without a completely homogeneous burning surface.

As the pressure continued to decrease, this behavior intensified with the period of oscillation of these longitudinal waves increasing until the flame sputtered out completely.

When attempts to find the extinction pressure for the LP-3 45μ oxidizer particle size were made, a previously unobserved mode of regression was established. The previously observed trend of increasing minimum combustion pressure with decreasing particle size was reversed, with the flame continuing well below the minimum combustion pressure of the LP-3 80μ propellant. This continued until the pressure was reduced to approximately 1.7 psia. During this period the upper region of the flame became increasingly unstable and the blue layer became more and more dominant as previously described for the larger oxidizer particle size propellants. At this pressure the flame would extinguish and then re-establish itself. However, at a pressure of approximately 1.5 psia the flame* extinguished completely and a new mode of regression became apparent. An interface could be observed continuing downward through the propellant. As this interface progressed an ash was produced and left standing on top of the reacting propellant. This proceeded at an extremely slow rate (approximately 0.007 in/sec) and its physical appearance was very similar to that of a pyrotechnic smoke (Figure 4). This analogy was not found to carry beyond the physical appearance. During this behavior, very dense clouds

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*The word flame is used here to indicate the visibility radiating gaseous blossom and is not to be taken in the general sense of a propagating combustion wave.

of smoke were given off. This made observation of the phenomena very difficult until an oil purge (described elsewhere) was added to clear the window. The burning continued with decreasing pressure until the propellant was consumed, provided that the ash remained in place. The vacuum system was capable of reaching a pressure of about 0.25 psia before this occurred.

The ash appeared to act as an insulation throughout this regime. If this ash was disturbed the process failed to re-establish itself.

Following this work with the 45μ oxidizer particle size propellant, similar results were obtained with the smaller oxidizer sizes - 15μ and 5μ. Although basically the same behavior was noted, there were several variations. For these smaller particle sizes the process appeared to be more stable. If the ash was disturbed during these runs, the combustion wave would re-establish itself. This would seem to indicate less dependence on the insulating or stabilizing effect of the ash.

Several samples of the ash were collected and analyzed. The results of this analysis and the accompanying analysis of the unburned propellant and the AP are found in Table 1. Due to problems with the analyses, interpretation of results is difficult as the samples are not equivalent.

It was also found that a flame could be re-established on the propellant by admitting a short burst of air or nitrogen to the combustion chamber. This was done by simply opening the respective valve for an instant. Once this had been observed, care was taken to provide bursts that would not raise the pressure above that at which a stable regression of the flameless form occurs. It was found that these bursts could be limited to give a pressure rise of approximately 0.2 inches of Hg. By applying such a burst, a flame would be re-established which would last for a few seconds. Following the eventual extinguishing of this flame, the flameless combustion would begin again. Noting that this behavior can be obtained with either nitrogen or air, it would appear that the effect is not related to the addition of oxygen. The magnitude of the pressure rise would indicate that it is not caused by raising the pressure to a level above which this behavior occurs. These two considerations would indicate that the dominant factor is the flow condition (the gas field) under which the process takes place. The question of the gaseous environment was studied further by a subsequent test. It was noted that for the burning rates at higher pressure, a coaxial flow of N_2 was provided to inhibit surface slanting. When this flow was adjusted to the smallest possible level, a stable regression of this flameless form could not be established. Instead the intermittent behavior previously described as occurring at the onset of the flameless regression persisted until a pressure of approximately 0.5 psia at which time the strand was completely consumed.

Burning rates were determined for this flameless combustion as described in Section (III-C). Regretably the error involved in this crude method is rather large. However, the data displayed in Figure (2) indicates a definite particle size dependence. This is in keeping with the observation of the apparent chemical vigor and stability of the reaction for the smaller particle sizes.

The present equipment does not lend itself to a study of the possible pressure dependence of this process. Much finer controls will be necessary. However, it is conceivable that this behavior is a function of the local pressure developed within the grain of the propellant rather than of the ambient pressure directly. This pressure would be a function of the mechanical strength of the fuel-oxidizer matrix with the ambient pressure being transmitted in a ratio somewhat less than one to one.

A small number of thermocouple traces were obtained in the subatmospheric pressure regime and three were obtained for the flameless regression (Figure 5). As long as there was a visible flame, the traces were very similar to those obtained by Sabadell (7) and others at higher pressures. However, with the onset of the flameless regression, marked changes occur. As seen in Figure (5), heat penetrates into the propellant to a much greater depth and a relatively long slow temperature rise is noted. The leveling off of this trace is believed to indicate the passage of the combustion interface. The temperature above this point is maintained by the insulating qualities of ash. The trace is eventually terminated by the mechanical movement of the ash breaking the thermocouple.

D. Extinction of Other Propellants

A limited number of attempts were made to achieve this flameless behavior with other compositions and other propellants. A bimodal LP-3 65% oxidizer (30%, 5μ and 70% 45μ oxidizer particle size) was tried with a limited degree of success. One strand was ignited at 4.9 psia and the pressure reduced to 0.92 psia. Due to difficulties with the vacuum system on this run, the pressure could not be further reduced. It was noted that the flame extinguished intermittently. During these periods of extinction the interface could be seen propagating down through the strand. This was accompanied by a good deal of sparking in the ash. Combustion proceeded in this fashion until the strand was consumed. It is felt that the intermittent flame and the sparking can be attributed to the fact that the pressure was not low enough to establish a good steady state.

This same composition was tried again and it was found that a steady state flameless regression established itself at 0.67 psia. This continued at an extremely slo rate until approximately 1/2 inch of ash had been produced. At this point the ash fell off and the behavior failed to re-establish.

Next, a composition of LP-3 75BM (30% 5μ, 70% 180μ oxidizer particle size) was tried. The strand was ignited at 9.6 psia and the pressure slowly reduced from there. The strand did not maintain a flat surface as it burned. Instead, it became markedly connical. At about the pressure the flameless regression was expected to establish itself (less than 1 psia) approximately 3/8 in. of the cone lifted off the propellant surface. This portion appeared to be similar to the ash previously described. It is felt that there is a distinct possibility that both the flame and subsurface reaction are at work here - that they are not completely uncoupled as previously observed. In any case the reaction obviously penetrated to a considerable depth.

A second strand of this same composition was tried. Before it disappeared, the visible flame became very transparent, such that very little was discernible above the blue layer. It finally extinguished at approximately 0.75 psia. At this point the flameless regression established and sustained itself down to a pressure of 0.52 psia. This proceeded at a rate so slow that it was almost overlooked.

The ash layer remained in tact for this run and was recovered. It measured 1/4 inch deep. Although it was basically of the same nature as previously observed, it exhibited several dissimilarities. In comparison to previous ash, it was very dense, having considerably greater structural strength. It did not appear to be breaking off in layers as noted before. However, the ammonium perchlorate crystals were again present.

A large number of AUP and PBAA compositions were tried. These covered the composition and particle size range used with the LP-3 - 60% to 75% oxidizer and oxidizer particle sizes from 5μ to 180μ. These included both bimodal and unimodal mixtures. Also, several additives were used: ferrious oxide and copper chromate in small percentages to raise the burning rate and dyes to simulate the black color of the LP-3. Throughout this range no flameless regression was observed. However, there appeared to be a considerable difference in the mode of extinction. The AUP extinguished very abruptly without exhibiting the gradually increasing instability observed with the LP-3. The flame remained quite strong and stable and the blue layer did not become as apparent. The reaction waves washing across the surface with the LP-3 were not observed here. However, this could be due to very short periods of oscillation. The extinguished surface appeared quite smooth and was a chocolate brown in color. This layer was only approximately 1/32 to 1/64 inch in depth and flaked off very easily leaving a complete undisturbed propellant beneath it.

The PBAA behaved quite similar to the LP-3 with decreasing pressure. The flame became increasingly unstable until the blue layer became apparent. This seemed to stabilize the flame to some degree. As the pressure was further reduced, the flame again became increasingly unstable until the reaction wave began to wash about the surface. This behavior intensified with the period of oscillation becoming longer and longer, until at last the flame sputtered out completely. During this last period the behavior was remarkably similar to the LP-3 just before the flameless combustion established. The extinguished surface was similar to the larger particle size LP-3 being intimately attached to the remaining propellant. It did not flake off as with the AUP. Due to this, there was no clear indication of the depth of penetration of the reaction. However, it did not appear to be excessively thick.

E. Flame Photography

Flame photographs of the various LP-3 and PBAA compositions were obtained over the pressure regime studies at a magnification of 4.5X. With the LP-3 the streaks and their disappearance with reduced pressure was observed much the same as reported by Silla. However, with the PBAA propellant an opposite trend was observed. Although this study is incomplete and no counter explanation can be offered, preliminary analysis would disallow the simple argument employed by Silla of the streaks disappearing due to more rapid diffusion with reduced pressure.

III. EXPERIMENTAL TECHNIQUES

A. Equipment

A schematic of the experimental equipment is shown in Figure (6) and a series of typical burning rate photographs are shown in Figure (7). Details of this equipment and operating procedure can be found in report number 446-o by Richard B. Cole (8).

One significant improvement was made on this apparatus. As the limits of combustion are approached and during the flameless combustion, heavy vapors coated the inside of the window making visual and photographic observation impossible. To remedy this, a purge was installed to provide a net nitrogen flow over the window. This had the effect of amplifying the problem by entraining and impinging the vapors on the window. An interesting solution to this problem was finally arrived at by providing a flow of polyglycol B-2500 (Dow Chemical Company) over the window. Any high boiling oil suitably outgassed should do as well. The supply injector was made from fine stainless steel tubing with small pin holes where it touched the window. By mounting the oil reservoir at the top of the control panel, the combination of gravity feed and air pressure was found to be sufficient to provide a low velocity flow across the window. This rate can be adjusted to carry off the vapor as it coats onto the oil screen. Although some optical distortion was caused by the intermittent variations in the thickness of the oil screen, the system was highly successful. It is felt that, should further work require a more sophisticated injection system, it could easily be devised to eliminate this minor difficulty.

B. Thermocouples

The thermocouples were prepared with techniques developed in this laboratory by Sabadell (7). They consisted of 0.0003 inch platinum vs. platinum - 10% rhodium wire. The weld beads at the wire joint were held to about 1.5 wire diameters to insure a response time in the low millisecond range.

These thermocouples were cast into strands. The strands were then burned in cigarette fashion with the thermal combustion wave passing over the thermocouple. This produces a voltage-time trace which was converted to a temperature-distance trace by knowing the amplification factor and the burning rate of the propellant in question. This portion of the work was accomplished with the cooperation of Mr. Phillip Graham.

C. Data Reduction

The normal burning rates were obtained from photographs similar to those displayed in Figure (7). The negatives were read by placing them in a microfilm reader. For a given run, eight to ten individual frames were read and in turn eight to ten combinations were used for the calculations.

For the flameless rates a 16 mm Bolex movie camera with motor drive was used. Prior to each run a scale was placed in the same plane as the front of the strand and photographed. The developed film was measured in three foot lengths (120 frames). This was then placed in a microfilm reader. The entire run was examined for irregularities and, if none were found, a scale was constructed from the first frames to match the precise magnification of the camera and film reader for the run in question. The first few feet of each run were disregarded to allow the camera to reach a steady state framing rate. Using the prepared scale and the top of the frame as a reference, the film was read at each frame corresponding to the three foot marks. This gave between eight and ten readings per row which were reduced in the manner described above.

IV. CONCLUSIONS

Any remarks concerning this work must be tempered by the fact that the research is far from complete. However, a number of interesting observations can be made.

Considering the polysulfide burning rates in the normal combustion regime, it is noted that noticeable particle size effects persist to a remarkably low pressure. However, the spread of these burning rate curves is smaller than that seen in Figure (1). What appears to be missing is the convergence of these curves predicted by the granular diffusion flame theory. It is possible, however, that this behavior can be attributed to the effect of oxidizer particle size on the reaction rate rather than simple diffusional effects. The theory acknowledges the possibility of such an effect, but no allowance for it is coupled into the Summerfield equation because it would be quite negligible at higher pressures. When interpreted in this manner, it is quickly seen that the uncoupled or low pressure equation remains valid with some small adjustments in the reaction rate coefficient a .

No quick interpretation of the PBAA burning rate curves can be made until further testing is carried out. However, the effects of oxidizer particle size are seen to diminish greatly at these pressures in the polysulfide work and the effect of a 5% difference in oxidizer concentration in this pressure regime is known to be small. These two facts together with the direct sublimation of ammonium perchlorate reported by Bircumshaw and Newman and noted in this research may hold the key to this behavior.

if the particle size and concentration of the oxidizer control the amount of direct sublimation in some undetermined manner, the shift in effective mixture ratio would explain the results.

There appears to be a significant difference in the modes of extinction observed for the three fuel binders tested. An explanation of this would require a detailed study of the heat losses involved and in the activation energies of these fuels. This is beyond both the scope of this research and the current experimental equipment. Plans are being formulated to pursue this at a later time.

The observation of the flameless combustion is both interesting and puzzling. The data reported should be interpreted as preliminary and regrettably crude. This effect was not anticipated and consequently the equipment was not designed to attack the problem with a sufficient level of sophistication. However, several points of interest can be noted. The effects of oxidizer particle size and pressure appear to persist even in this regime. When this behavior was first noted, it was not thought that this would be the case. Much more extensive work must be carried out in order to detail these effects.

The thermocouple traces show a very deep heat penetration with a relatively slow rise, as expected for these very low regression rates. Most importantly, they show that maximum temperature reached in the combustion wave is less than 300°C. These traces also give an indication of the function of the ash. It apparently serves as an insulation, preventing radiative heat losses.

The behavior of the combustion wave with the flow field around the propellant is also puzzling. When a burst of gas is emitted to the chamber the convective heat losses are increased. This would cause extinction in a weak reaction. Instead, the flame is seen to re-establish. This would indicate a complex interplay between the several heat loss mechanisms and the heat generation by the combustion wave.

The unsuccessful attempts to obtain this type of behavior with other propellants and compositions points out the importance of the fuel binder in the combustion mechanism.

REFERENCES

1. "The Mechanism of Combustion of an Ammonium Perchlorate - Polyester Resin Composite Solid Propellant" by G. S. Sutherland, Doctoral Thesis, Princeton University, 1956.

2. "The Dependence of Linear Burning Rate Upon Pressure for Ammonium Perchlorate - Polyester Resin Composite Propellant" by M. Webb, MSE Thesis, Princeton University, 1958.

3. "Modification of the Burning Rates of Ammonium Perchlorate - Solid Propellants by Particle Size Control" by E. K. Bastress, Ph.D. Thesis, Princeton University, 1961.

4. "Burning Rates of Composite Solid Propellants at Subatmospheric Pressure", by H. Silla, American Rocket Society Journal, Volume 31, No. 9, September, 1961, pg. 1277.

5. "The Thermal Decomposition of Ammonium Perchlorate" by Bircumshaw and Newman, Proceedings of the Royal Soceity, London, A227, 115, 1954.

6. "Observations on the Burning of Ammonium Perchlorate" by Arden, Powling and Smith, Combustion and Flame, Vol. 6, 1962.

7. "The Measurement of the Temperature Profiles of Burning Solid Propellants by Microthermocouples, A. Sabadell, MSE Thesis, Princeton University, 1963.

8. "Experimental Studies of Composite Solid Propellant Combustion Mechanism-Burning Surface Photomacroscopy and Low Pressure Burning Rates", R. B. Cole, MSE Thesis, Princeton University, June 1965. (Also, Aerospace and Mechanical Sciences Report No. 446-o)

TABLE 1

A CHEMICAL MICROANALYSIS OF AN ASH

(Done by Chemco Laboratories, Inc. Washington, D. C.)

Sample	Analysis	Found (Average % by Weight)
LP-3 - 65% 15μ		
	Carbon	13.46
	Hydrogen	4.52
	Nitrogen	7.80
	Sulfur	14.07
Ammonium Perchlorate		
	Chlorine	30.25
	(Theoretical)	30.21
Ash		
	Carbon	7.20
	Hydrogen	2.94
	Nitrogen	13.46
	Sulfur	1.01
	Chlorine	24.48

TABLE 2

TABULATION OF THE POLYSULFIDE BURNING RATE DATA

5μ		15μ		45μ		80μ	
r ips	P psia	r ips	P psia	r ips	P psia	r ips	P psia
0.0504	14.69	0.0562	14.46	0.0528	15.05	0.0498	14.85
0.0464	12.22	0.0521	14.17	0.0453	12.61	0.0469	14.18
0.0415	11.05	0.0489	12.20	0.0421	11.11	0.0515	13.85
0.0377	9.80	0.0468	12.00	0.0385	10.11	0.0457	12.31
0.0358	7.34	0.0413	9.74	0.0327	7.61	0.0428	12.20
0.0272	4.88	0.0413	9.57	0.0303	7.81	0.0355	10.95
0.0252	3.91	0.0359	7.61	0.0123	2.39	0.0360	9.81
0.0217	3.22	0.0345	7.29	*0.0137	1.81	0.0346	9.74
+*0.0075	0.77	0.0328	6.64	*0.0109	1.32	0.0308	8.86
		0.0305	5.90	*0.0089	1.32	0.0302	7.33
		0.0267	4.84	+*0.0050	0.70	0.0266	7.29
		0.0262	4.66			0.0258	6.58
		*0.0238	2.45				
		*0.0181	2.06				
		*0.0112	1.50				
		+*0.0070	0.80				
		+*0.00613	0.66				
		+*0.00578	0.61				

137μ		195μ		325μ	
r ips	P psia	r ips	P psia	r ips	P psia
0.0425	14.59	0.0340	12.59	0.0304	12.67
0.0401	12.13	0.0286	9.99	0.0303	12.52
0.0327	9.70	0.0224	7.40	0.0782	11.72
0.0268	7.25	0.0184	4.99	0.0250	9.19
0.0232	6.26			0.0248	9.66
0.0211	5.19			0.0238	9.65
				0.0226	7.54
				0.0216	7.35
				0.0167	5.05
				0.0143	3.79

*Regression rates taken with movie camera

+Flameless regression rates

PLOT OF THE SUMMERFIELD EQUATION IN THE FORM

$$\frac{1}{r} = \frac{a}{p} + \frac{b'' d_m}{p^{1/3}}$$ WITH $a = 150$, $b = 0.417$

DETERMINED EXPERIMENTALLY BY BASTRESS

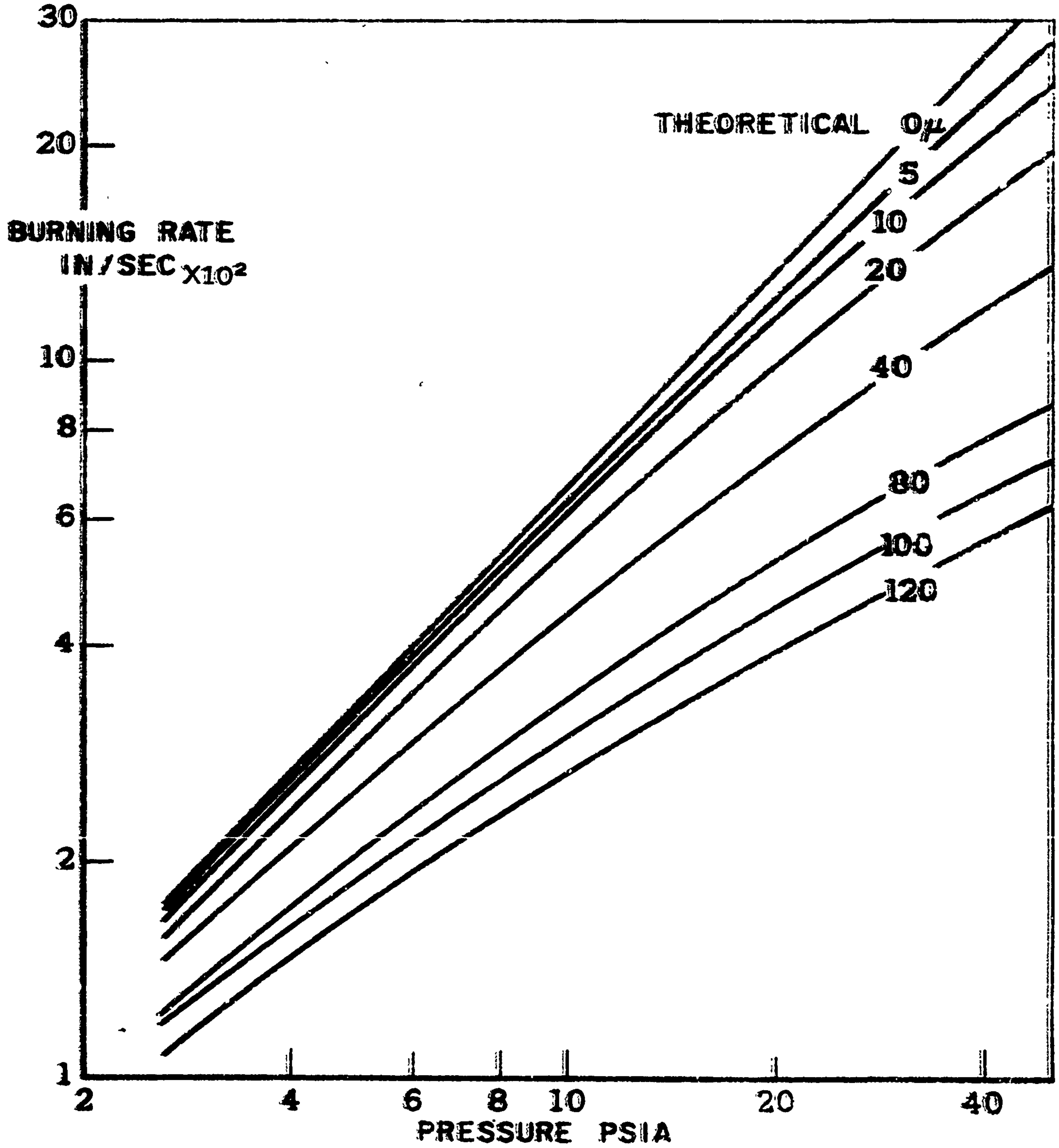


FIGURE 1

JP 19 - JPC 4018 - 65

BURNING RATES OF POLYSULFIDE (LP-3) PROPELLANTS WITH
65% UNIMODAL AMMONIUM PERCHLORATE PARTICLE SIZE AS INDICATED

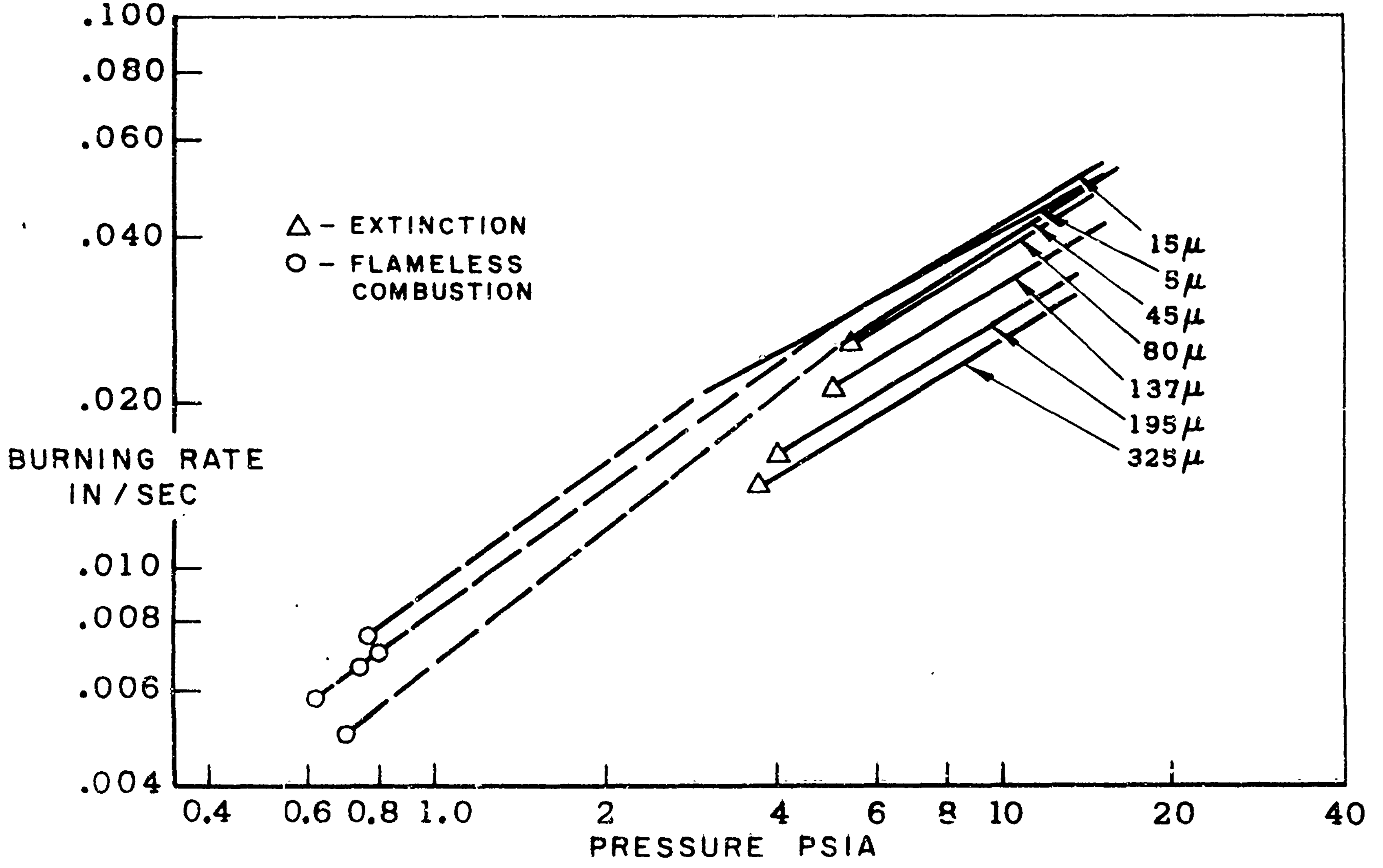


FIGURE 2

JP19-JPR4017-65.

BURNING RATES OF PBAA PROPELLANTS WITH BIMODAL AMMONIUM PERCHLORATE PARTICLE SIZES

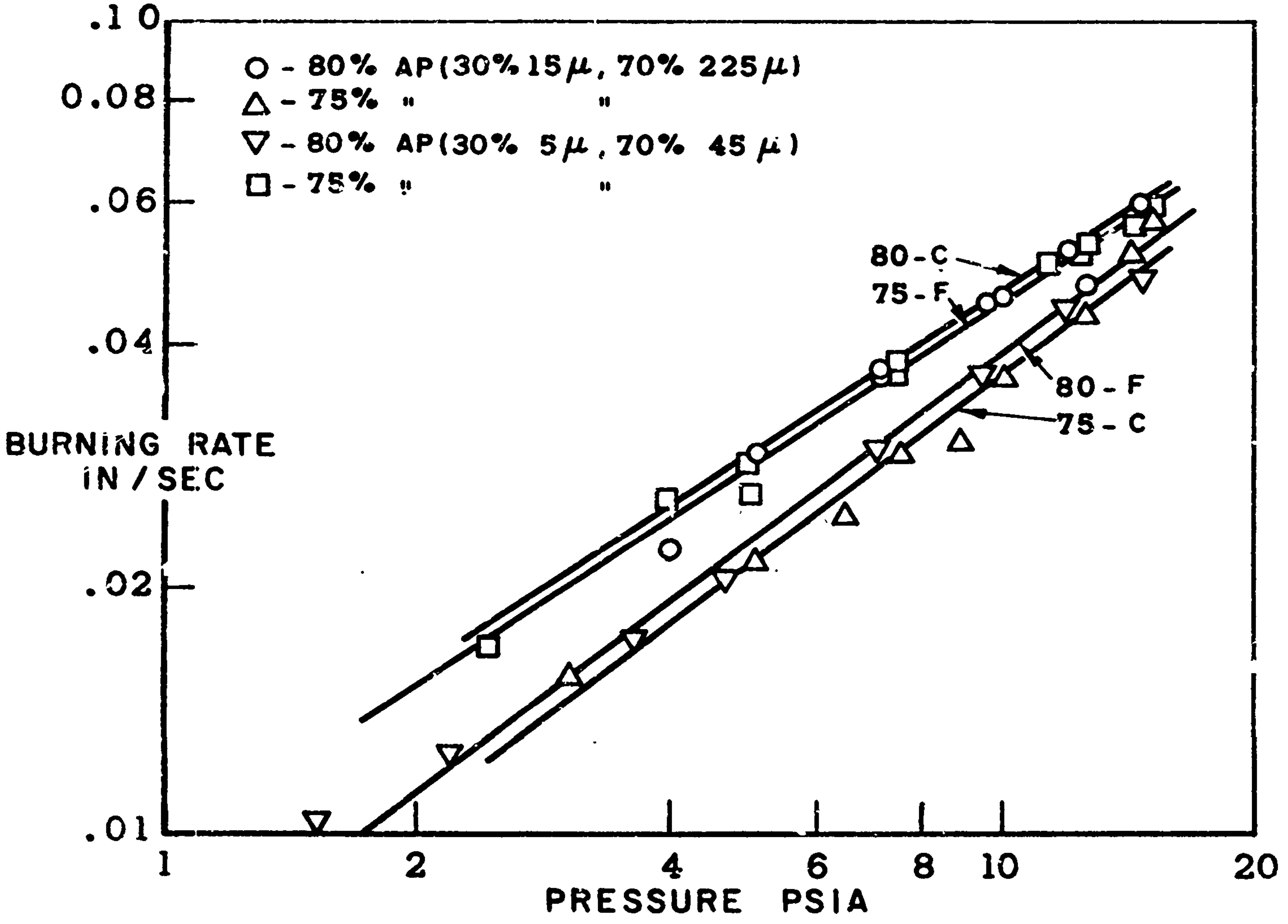


FIGURE 3

ASH FROM FLAMELESS REGRESSION

FIGURE 4

JP19-P3-65

AP19- JPR 4019-65

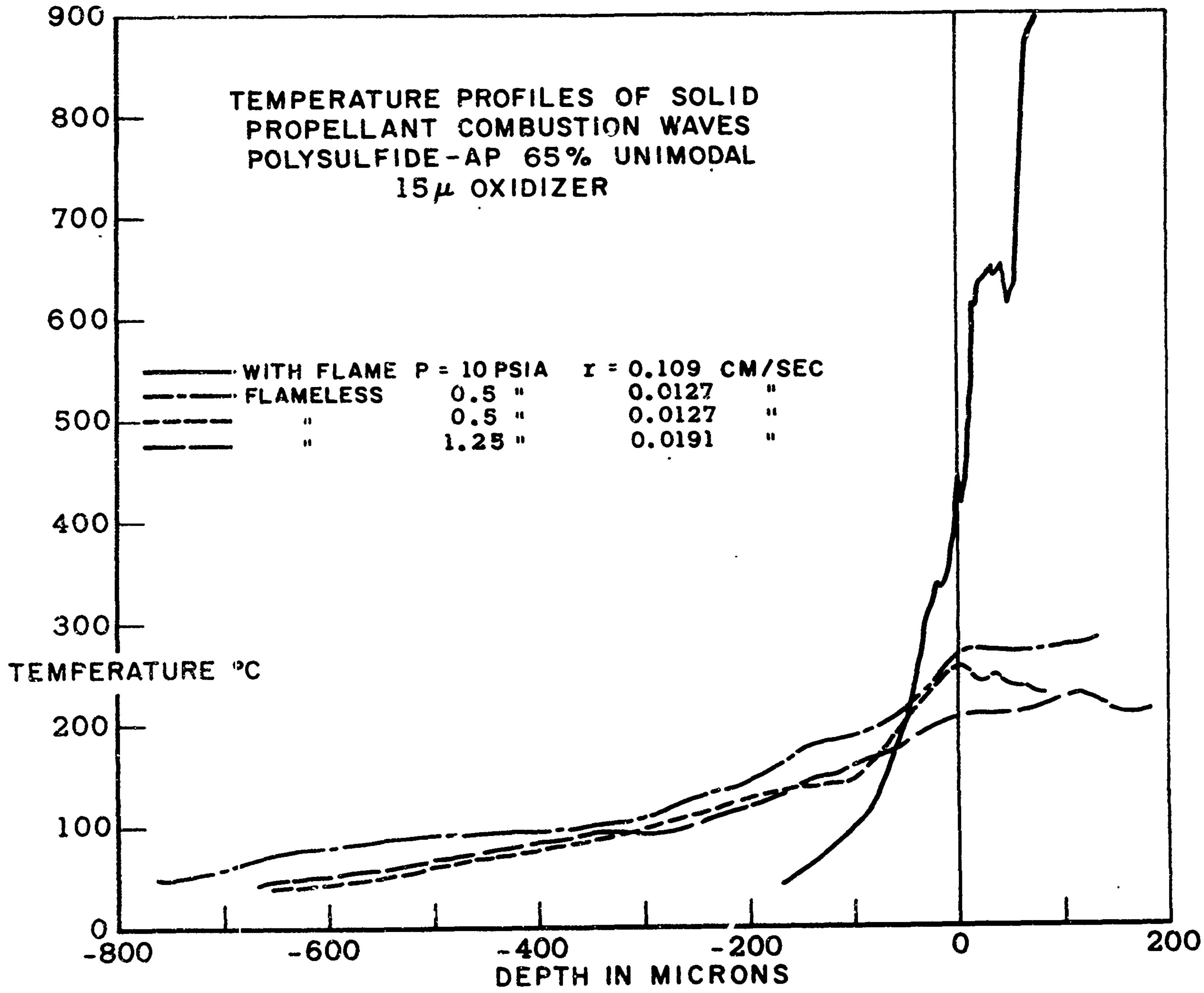
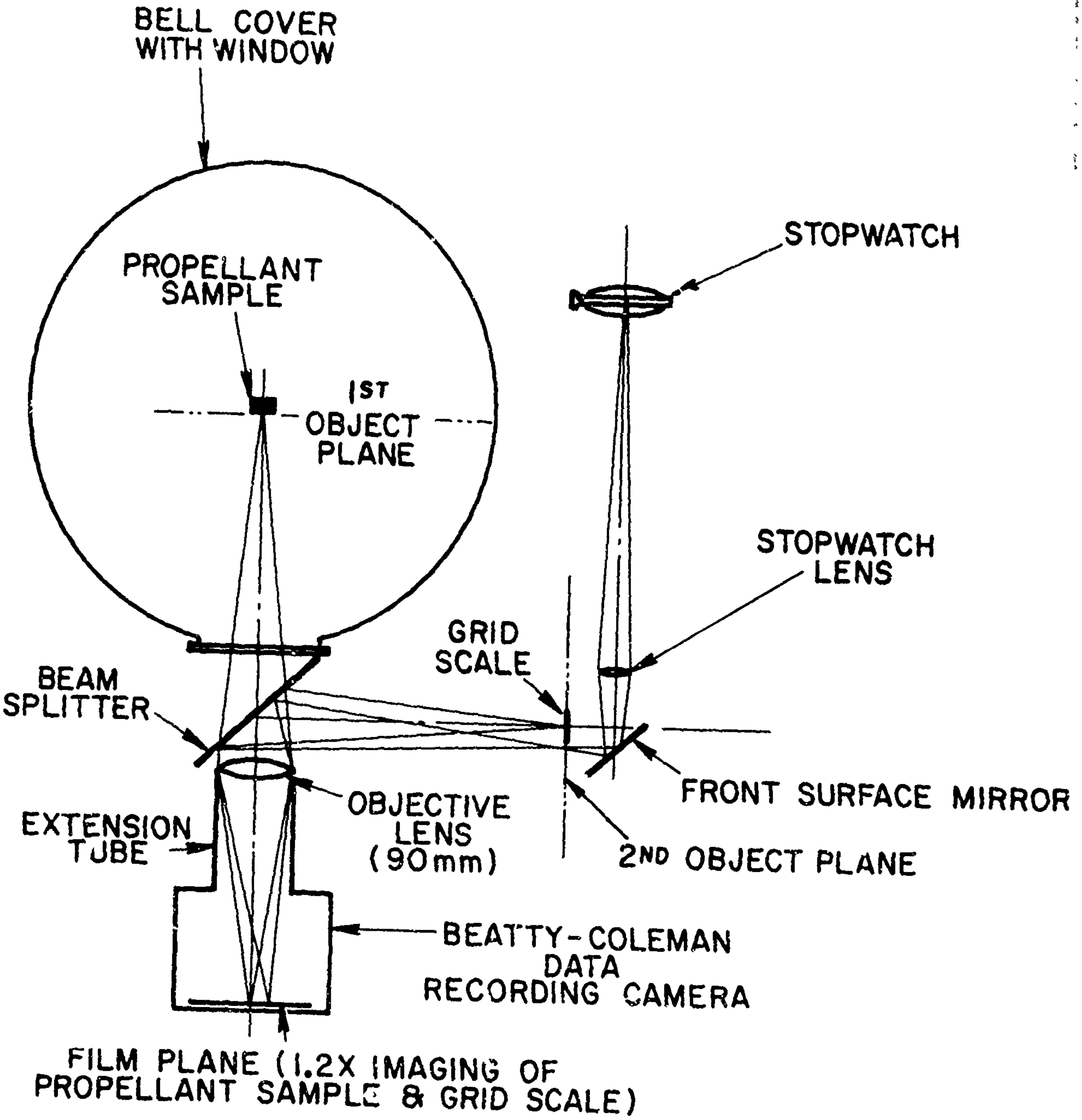


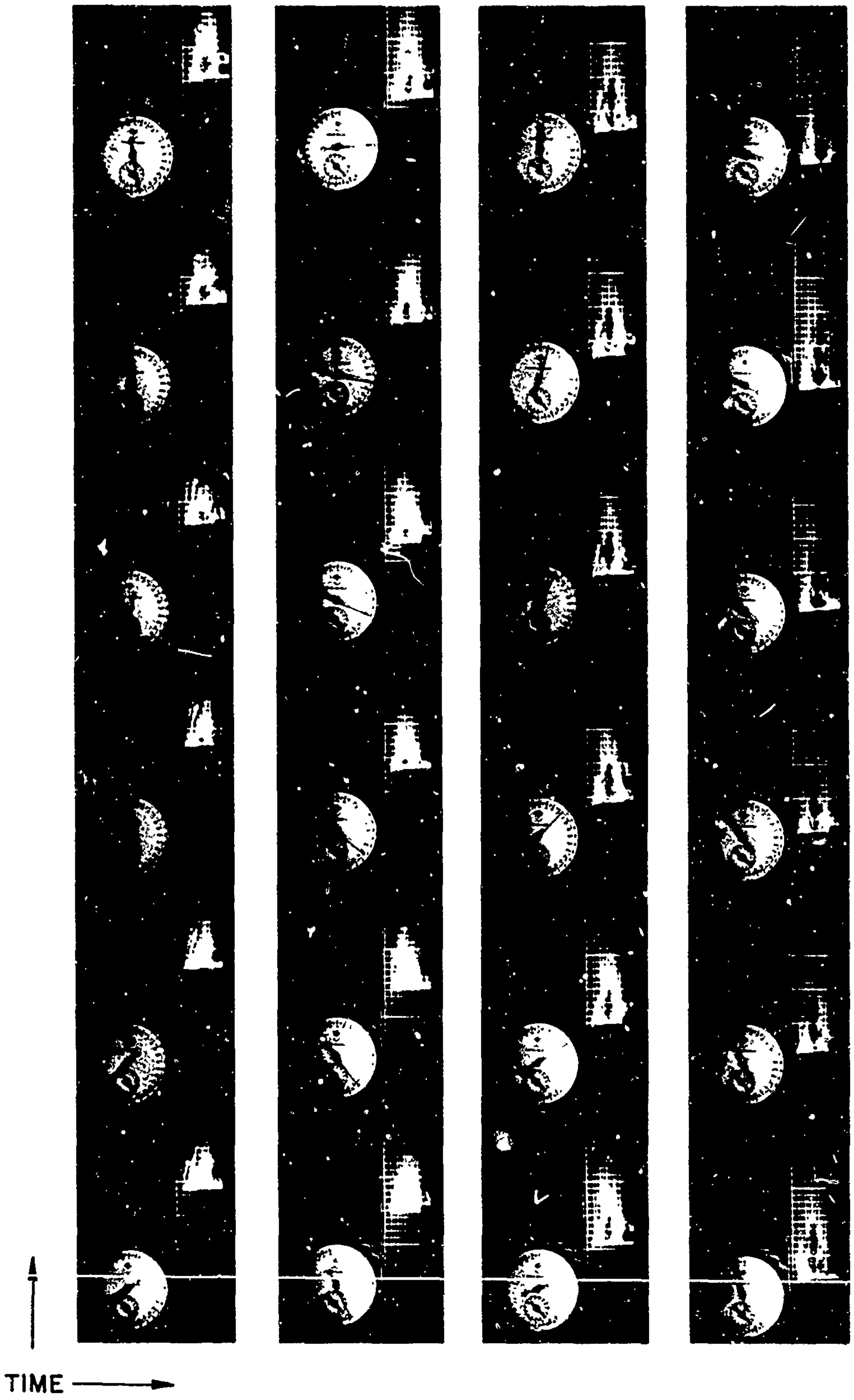
FIGURE 5



PHOTOGRAPHIC BURNING RATE MEASUREMENT
OPTICAL SYSTEM

JP19-4002-65

FIGURE 6



TYPICAL FILM RECORD USED FOR PROPELLANT
BURNING RATE DETERMINATION
(STOPWATCH FACE REVERSED DUE TO OPTICS)

FIGURE 7