Prediction of Detonation Hazard in Solid Propellants

by;
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Abstract

Classification of the detonation hazard after ignition of a large solid propellant rocket motor has in the past been based on sensitivity test methods which have little relationship to the actual conditions under which such an incident might occur. The development of a method by which prediction of such an occurence is possible is described in this paper.

Experimental work has shown that when a large mass of an explosive or propellant is burned in a closed system, a sharp change in slope of the burning rate/pressure curve occurs at a pressure which is specific for that material. This transition pressure is dependent on the initial temperature of the material. For explosives this transition pressure is in the range of 4-8000 psi and is related to the sensitivity of the explosive. For propellants, the transition pressure is somewhat higher and, this pressure as well as the slope of the transition curve appears to be related to the physical state and the energy level of the propellant.

From the transition pressure and the slope of the transition curve and from the physical configuration of a missile motor, the hazard of detonation may be determined.

To extend the range of measurements possible, a pressure vessel has been developed in which measurements of propellant burning rate at pressures as high as 250,000 psi can be made. This vessel has a unique design consisting of two concentric cylinders. Radial stresses are taken by the inner cylinder, which is replaceable if fracture should occur. Recording of pressure information precedes fracture of the inner vessel. The outer cylinder carries only axial stresses and is of sufficient strength to prevent fracture and retain fragments.

The development of this vessel has also made possible the examination of burning characteristics of cannon propellants for very high pressure applications. Results show that some standard cannon propellants have transition characteristics similar to those described for explosives and rocket propellants. This phenomenon explains some disastrous incidents resulting from very high pressure gun firings.

Introduction

In assessing the hazard involved in the use of a rocket motor there are a number of factors to be considered. First, the hazard of detonation while transporting the motor from its manufacturing site to place of launching in its shipping container. Second, the hazard of detonation of the propellant if the warhead should explode. Third, the hazard of detonation of propellant if struck by a high explosive bomb. Fourth, the hazard of detonation of the propellant if struck by bomb fragments or projectiles. Fifth, the hazard of detonation after a normal ignition during launching.

Actually, numbers 1 and 5 are essentially the same hazard - that is transition from burning to detonation, while 2, 3 and 4 are essentially shock initiation.

Concern with these latter three problems of shock initiation are generally recognized and most propellants are well characterized as to shock sensitivity by various booster sensitivity or pipe tests. The information obtained tells little about transition from deflagration to detonation (DDT). This brings us to items 1 and 5.

A major hazard from missile transportation and handling is accidental ignition. In the confined condition, will this result in a pressure blow of the missile case or will it result in transition to high order detonation? The difference for a large motor containing tons of solid propellant could be a good fire or a major disaster. If the possibility (or non-possibility) of transition could be predicted, a much more realistic approach to storage and handling could be adopted.

The hazard of transition to detonation after normal ignition on a firing stand could result from unknown defects which exist in a motor resulting from manufacture, aging or handling.

This report describes work which has been done thus far in an effort to classify explosives with respect to the possibility of DDT under the conditions and geometry which may actually exist in a solid propellant motor.

Theory

Kistiakowsky (1) described a mechanism for the development of detonation in a large mass of granular or crystaline explosive ignited thermally at a localized region within the bulk. As the explosive burns, the gases formed cannot escape between crystals and a pressure gradient develops. This increase in gas pressure causes an increase in burning rate which in turn causes an increase in pressure with constantly increasing velocity. This condition results in the formation of shock waves which are reinforced by the energy released by the burning explosive and they eventually reach an intensity where the entire energy of the reaction is used for propagation of the shock wave and a stable detonation front is produced. A critical mass exists for each material above which this deflagration can pass over into detonation under proper conditions. Below this mass the burning will first increase and then decrease as the material is consumed.

The transition to detonation is considered largely a physical process in which the linear burning rate of the bed of material increases to several thousand meters per second although the individual particles are consumed at the rate of only a few meters per second.

The validity of this mechanism has been demonstrated experimentally for granular propellants by a number of workers (2) (3) (4).

In the experimental work described here, it was believed that very similar conditions could be established if a large mass of explosive or propellant were burned in a closed chamber. It has been shown (5) (6) that for composite propellants, the highly elastic binder material will undergo brittle fracture when stress is applied at very high strain rates. When propellants or explosives are burned in a closed chamber the rate of pressure build up accelerates sufficiently to develop surface strains in the large grain at rates which exceed those needed to produce brittle fracture. Combine this with the embrittlement accompanying the high pressures involved and the thermal shock produced by the hot gases of combustion on the cold grain and a condition equivalent to that existing for granular material could exist. A further verification of this mechanism is the increased tendency of propellants to detonate when cooled to low temperatures. This problem is well known to anyone working with solid propellants both for rockets or cannons.

Basis for Experimental Studies

If the mechanism suggested by Kistiakowsky for granular and crystaline explosives could apply to solid propellants by the mechanism suggested above, then it should be possible to demonstrate the increase in burning surface for such materials by burning large pieces in a closed chamber in which the burning of the material produced the higher pressures for accelerated burning. The first indication that such a reaction actually might occur was found when a series of cannon propellants, which had caused guns to blow up when fired at temperatures of -20°F and -40°F were tested in a closed chamber (7). When records were made of rate of change of pressure vs. pressure, it was found that a sharp increase in rate occurred at a pressure which was fairly specific for each lot of propellant tested. If such a mechanism did exist, then it should be demonstrable for high explosives as well. Since the normal burning rate laws are known to hold for both propellants and explosives when burned under static pressure conditions (as in a strand burning rate bomb) a comparison of these two methods of burning would demonstrate the existance of the mechanism. Calculation of the linear burning rate of a cylinder of material under constantly changing pressure from the measurement of dp/dt vs. pressure is given in references (8) and (9). In this calculation the assumption is made that the cylinder is ignited uniformly on all surfaces and always burns normal to that surface. Experience with interrupted burning of propellant grains of even complicated geometry verifies this. If, however, cracking or crazing should occur, the calculated linear burning rate will be far in excess of the value expected and the increase in surface area can be calculated from this apparent increase in linear burning rate.

Experiments With Burning of High Explosives

Cylinders of TNT were prepared with diameters of 1" to 1¼" and lengths of 1" to 3". These cylinders were machined from solid blocks of TNT which had been carefully cast to prevent porosity or voids. All cylinders were machined from the same casting and were considered to have about the same crystaline structure. A series of these were fired at loading densities (weight of explosive, grams/volume of chamber, cc) of 0.11 to 0.387. In addition, in some tests the chamber was preloaded up to 10,000 psi by including some very fast burning mortar propellant which produced the preloading pressure before the TNT had a chance to burn appreciably. Figure 1 shows some of the typical oscillograms obtained. Strands were also cut from the block of TNT and were burned at pressures up to 20,000 psi in a Crawford strand burning rate bomb. Linear burning rate vs. pressure were calculated for all the results obtained and were plotted on a single log plot. Figure 2 shows the average curve obtained from this data. Note the change in slope that occurs for the closed bomb line at about 6,000 psi while the strand burner shows the normal burning rate/pressure relationship.

A calculation of increase in surface area with pressure is shown in Figure 3. This was done by substituting the burning rate obtained from the strand burner into the equation used for calculation of the closed bomb burning rate and solving for surface area at different values of pressure. Note that an increase in surface area of almost 20 times occurs. Figure 4 gives the ratio of calculated area/expected area for a typical cylinder of TNT.

Experiments of this same nature were made with Composition B which is a mixture of 60 percent of RDX with 40 percent of TNT with 1 percent of wax desensitizer added. Results similar to TNT were obtained although difficulty in obtaining uniform ignition required the use of preloading for all tests. Figures 5, 6, 7 and 8 show the data obtained for Composition B. This pretransition pressure appears to be somewhat lower than for TNT alone although detail in this area of the curve is lacking because of the preloading required.

Tests of Propellants

A number of experimental and high energy propellants were then tested using this same technique. These can only be described as composite and double base types because of security considerations. Results of these propellants are presented here, each one showing modifications of the same pretransition characteristics. The first propellant, a double base type with solid oxidizer, when fired in the closed bomb showed a somewhat exaggerated pre-transition effect as shown in Figure 9. A series of these tests were calculated to linear burning rate vs. pressure as for TNT and Composition B. The results are shown in Figure 10. Note that the transition which occurs at about 15,000 psi is even sharper than for the explosives and the slope of the curve is steeper. This is believed due to the larger amount of energy resulting from combustion of this propellant as compared with the explosives. Strand burning rated data was not available for this propellant at high pressure. Therefore, the low pressure curve was extrapolated. Calculation of changes in surface area shows increases up to 25 times for this material. Other samples of similar composition were tested in which changes were made in the plasticizer; both in the material used and the percentage. These changes were found to shift the pre-transition pressure up or down. No effort was made at this time to relate this shift to differences in physical properties. All these samples of propellant were detonable with a #6 blasting cap.

A second propellant-designated ARP, a high energy double base type, gave the results shown in Figure 11. The straight line burning rate curve was obtained with points from strand burning rate tests and closed bomb tests at loading densities up to 0.4. However, when a preloading of 15,000 psi was used in one test, a pre-transition change in slope in the curve resulted at about 40,000 psi. The pressure rate was so high that a large part of the trace was lost. Extensive damage also resulted to the bomb and further testing of this composition was stopped at this time to await the development of more suitable high pressure equipment.

A third type of propellant tested was a composite double base - Type QZ manufactured by Rohm & Haas. This propellant type was known to have undergone DDT when fired in a large motor which contained some porous propellant. Tests at 70°F did not show any transition point. However, when cooled to -60°F a typical pre-transition curve resulted (Figure 12). In addition to these propellants, a number of lower energy and less sensitive materials were tested in the bomb both with and without preloading. No indications of pre-transition could be found within the pressure limitations of our test equipment.

Design of Ultra-High Pressure Equipment

Because of the limitations of our test equipment (80,000 psi) the design of a vessel that would contain much higher pressures, was undertaken. The basic design concept utilized was based on the fact that for sufficiently high rates of loading, the inertia of the vessel walls would resist failure sufficiently long to permit measurement of the pressure time history. To make a practical unit, two concentric cylinders were used. The inner replaceable cylinder contained the high pressure while the outer massive cylinder held the end closures for the inner cylinder. A space between the cylinders was provided for expansion of the gases in case of failure of the inner cylinder. The outer cylinder also served as a confinement for fragments resulting from failure of the inner cylinder. All pressure on the end closures is transmitted axially to the outer cylinder which has sufficient strength to hold pressures in excess of 300,000 psi in the inner chamber. The seals between the inner cylinder and end caps were designed to expand as the outer cylinder stretched due to the pressure development. When the inner chamber did not break, it was found that the expansion of the seals maintained pressure on the end caps, making it impossible to open. Therefore, provision was made to recompress the seals with a hydraulic ram to release this pressure and permit opening of the bomb. After many difficulties with parts failures, a basic design shown in Figure 13 was evolved. An exploded view, of an early design, is given in Figure 14.

Actual detail of the final design of this vessel is not given here because it is still undergoing changes resulting from experience in its use. Suffice it to say, that when working with the dynamic pressures and high temperatures of the type encountered in this work, every conceivable type of failure has occurred. However, measurements of pressures as high as 250,000 psi have been made.

Measurement of pressures can be made in this vessel with any type of pressure transducer by suitably modifying the gage housing. In our initial testing, pressure/time measurements were made using a Kistler Gage Type 601 with a special hyperballistic probe. This gage is designed to measure pressures up to 300,000 psi. It is a piezoelectric type in which the charge that build up on a quartz crystal under compression is measured by means of a special electrometer circuit. The pressure is transmitted to the crystal through a small carefully ground piston which extends into the pressure chamber.

For interior ballistic work and for measurement of rate of change of pressure it is considered more desireable to obtain measurements of dp/dt vs. pressure rather than pressure time. However, at the time the work described below was done, such instrumentation was not available. Work being done at the present time is using such measurements.

<u>Measurement of High Pressure Characteristics of Cannon Propellants</u>

Following the reasoning and pre-transition characteristics described above for rocket propellants, it seemed reasonable to expect that a similar pre-transition mechanism might exist for cannon propellants.

Actually, over the past many years, numerous accidents in gun firings have occurred which have been difficult to explain in terms of anything other than propellant malfunction. Most frequently these have occurred in low temperature firing of propellants which function normally in average temperature conditions. Typical of this type of malfunction are low temperature mortar firings using

M9 propellant. High pressures developed under such conditions have, on some occasions, ruptured mortar tubes. M17 propellant has also been known to display erratic ballistic behavior at -40oF, and in 1958 a 76MM gun was blown up in such a malfunction.

It was during the investigation of this malfunction, that it was shown that certain lots of M17 propellant had the characteristic of developing a change in the burning rate/pressure curve (Reference 7). Under closed bomb tests it was possible to determine which lots of M17 propellant would actually develop this high pressure. Traces showing dp/dt vs. pressure of good and defective M17 propellants are given in Figure 15.

Up to this point, except for the low temperature tests, these transitions have only been noted in rocket propellants and explosives on an experimental basis. Cannon propellants have been used in these pressure ranges rather commonly with no such effects, except for occasionally unexplained malfunctions. One such malfunction occurred recently, when a gun designed for 86,000 psi max pressure was destroyed with T36 cannon propellant when an increase in charge weight of about 2 percent to increase pressure above 70,000 psi, caused an increase in max pressure of over 100 percent.

With the development of the ultra high pressure closed bomb, capable of testing propellants at much higher pressures than previously, it became possible to determine if the same type of behavior demonstrated for rocket propellants and explosives could be shown cannon propellants at high pressures. A M17 propellant of 0.045 web was loaded into this new bomb at a loading density of .40. A maximum pressure of 105,000 psi was anticipated. Figure 16 is the pressure/time trace obtained. Careful examination shows that at the end of this pressure rise (about 92,000 psi) there is a vertical rise of indefinite magnitude before the trace returns to low pressure. This is indicative of transition to detonation having taken place after 90 percent of the propellant has been burned. Other evidence of the detonation inside the bomb was the fracture of the inner cylinder which had been calculated to hold in excess of 150,000 psi, and a definite spalling condition existing in some of the fragments of the inner cylinder. The massive end plug of the bomb was also cracked all the way through.

After repairs were completed to the apparatus, tests were then made of T28 propellant using the same conditions. Figure 15 shows the pressure/time trace. While the burning time was much shorter, a maximum pressure of 105,000 psi was obtained with no unusual incident in the bomb to indicate a transition effect. T28 propellant has been fired at .40 loading density a number of times to verify this. At the time of these tests only pressure/time information was available. For future work it is expected that dp/dt vs. pressure will be available.

These results fit in very well with the mechanism stated previously. M17 propellant and T28 propellant are very similar in energy level. Their basic difference is in compressive strength and the difference in the homogeniety of their structure. M17 propellant is notoriously poor as far as compressive strength is concerned although with some modification in processing, improvement has been made as with T36 propellant.

It is interesting to note that in high pressure gun firings with M17 propellant, the transition effect of T36 which originally was demonstrated above 70,000 psi was found for M17 propellant to begin at 50,000 psi.

The very sketchy nature of the work presented here is the result of a very limited study of cannon propellant burning under very high pressure conditions. However, we believe it is significant enough to be reported at this time.

Conclusions

In the work presented herein, there is definite evidence that the process of transition from deflagration to detonation for explosives and propellants is a continuous reaction consisting of first - ignition; second - under confined conditions (such as might exist in a large mass of material or porous material) a pre-detonation reaction consisting of accelerated burning due to a physical breakdown of the surface resulting from the pressure, rate of change of pressure and temperature gradient; third - development of an accelerating shock front; fourth - detonation if sufficient mass of material is available.

It is believed that any material which can be detonated should exhibit this pre-detonation reaction. In the case of very sensitive primary explosives the level of controlling parameters required to start detonation is so low that they cannot be measured by present techniques. For "non-detonable" propellants the pressures required for the pre-detonation reaction to occur are so high that for all practical purposes, they cannot be attained.

It is considered practical that this technique can be used for the classification of the detonation hazard for a particular motor configuration if the pre-transition pressure and slope of the burning rate pressure curve of the propellant used is known. Thus, for example, if a defect or void should exist in a propellant, which might conceivably ignite on firing, by considering such an ignition as an interior ballistic system the pressure and rate of pressure rise can be calculated to determine if pre-detonation conditions could develop before tensile failure of the grain occurred. If such reaction can occur then the accelerated pressure rise could develop the shock front necessary for transition to detonation.

REFERENCES

1. Kistiakowsky, G. B., Initiation of Detonation in Explosives, Third Symposium on Combustion Flame and Explosion Phenomena Williams and Wilkins, 1949.

2. Hyndman, J. R., et al, Rohm and Hass Co. Ballistics Section Program Report #67, October 1957.

3. Mason, C. M. et al, (U. S. Dept. of Interior, Bureau of Mines) Final Summary Report #3734 Investigation of Susceptibility to Detonation of Propellants.

4. Macek, A. (Naval Ordnance Laboratory) NAVORD 6105, Sensitivity of Explosives VII. Transition from Slow Burning to Detonation: A Model for Shock Formation in a Deflagrating Solid, 3 February 1958.

5. Jones, J. W., Sagers, D. L., and Nolan, E. J., Fracture Mechanics of Solid Propellants, Progress Report No. ELab-A-19, 16 February 1959-15 February 1960, Eastern Laboratory, E. I. duPont de Nemours & Company (Confidential)

6. Jones, J. W., Prediction of Catastrophic Rocket Motor Explosion Conditions from Broad Spectrum Mechanical Property Analysis. Preprints of Sixteenth Meeting, JANAF Solid Propellant Group, Vol. 5.

7. Russell, K. H., Goldstein, H. M., Investigation & Screening of M17 Propellant Production for Lots Subject to Poor Low Temperature Ballistic Performance, Technical Report DB-TR 7-61 Ammunition Group, Picatinny Arsenal, Dover, N.J., June 1961

8. Pallingston, A. O., Weinstein, M., Method of Calculation of Interior Ballistic Properties of Propellants from Closed Bomb Data, Picatinny Arsenal Technical Report #2005, June 1954.

9. Wallace, W. F., New Formulas for Rapid Calculation of Linear Burning Rates of Solid Propellants. Picatinny Arsenal Technical Report #2488, April 1958.

10. Wachtell, S., McKnight, C. E., A Method for Determination of Detonability of Propellants & Explosives, Third Symposium on Detonation, ONR Symposium Report ACR-52, Also Picatinny Arsenal Technical Report DB-TR 3-61.

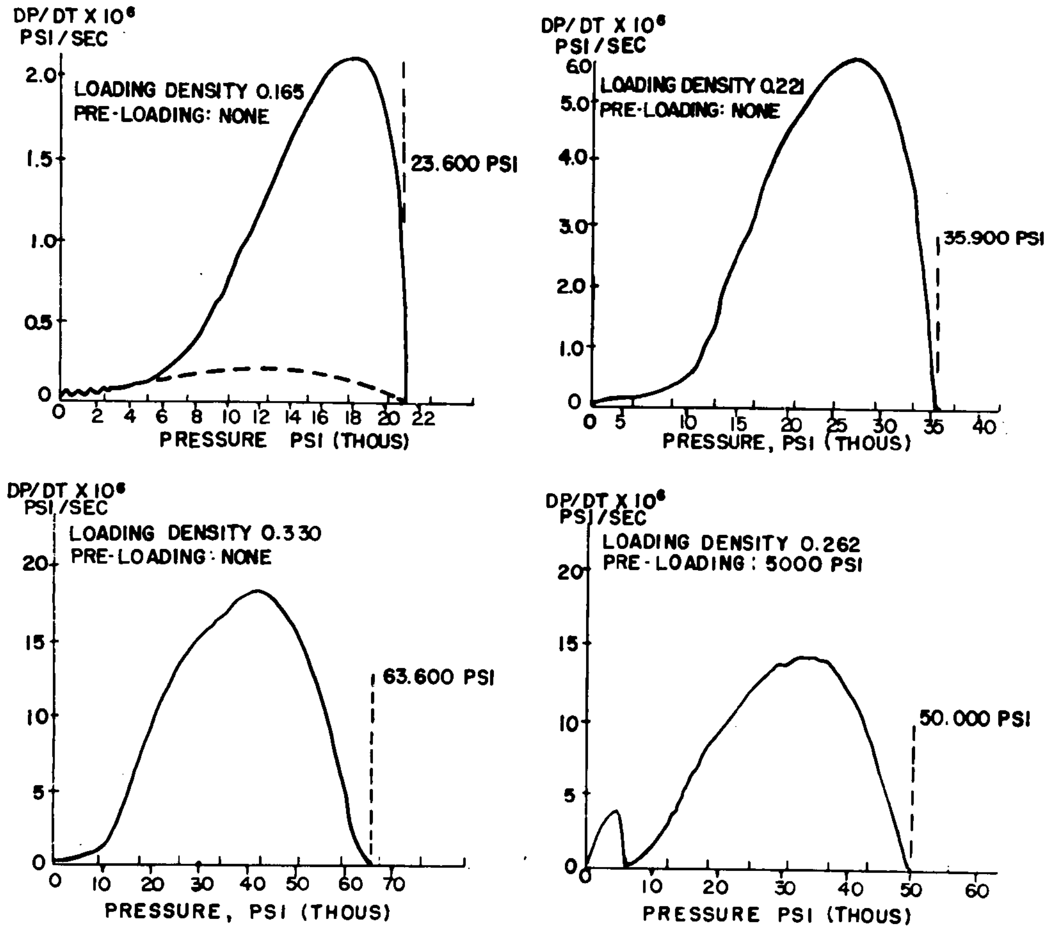


Figure 1 . Closed Bomb Test TNT

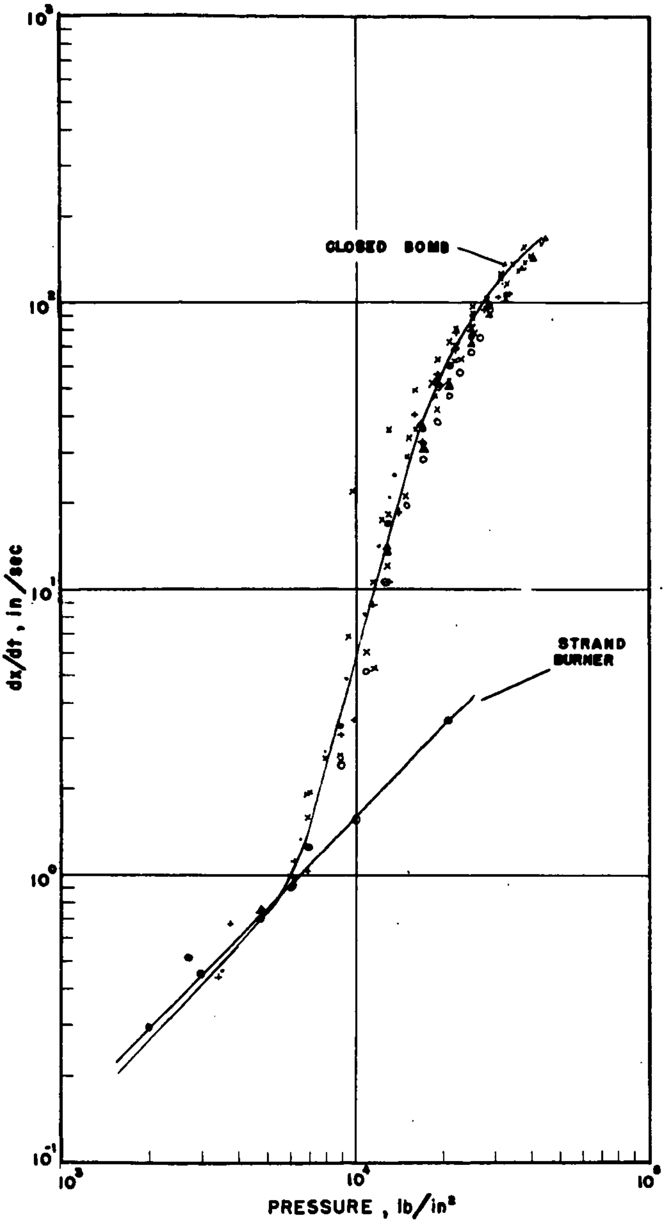
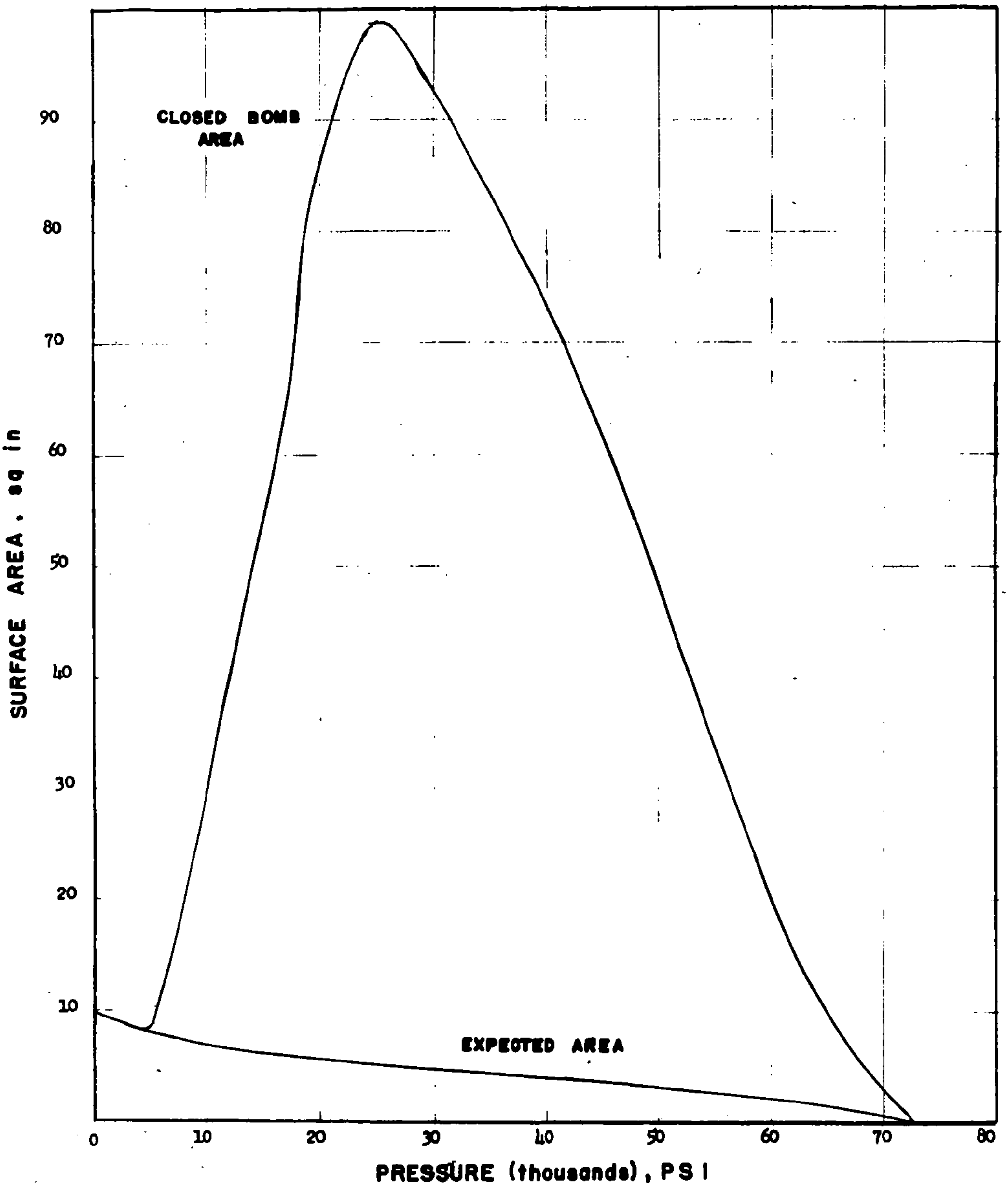
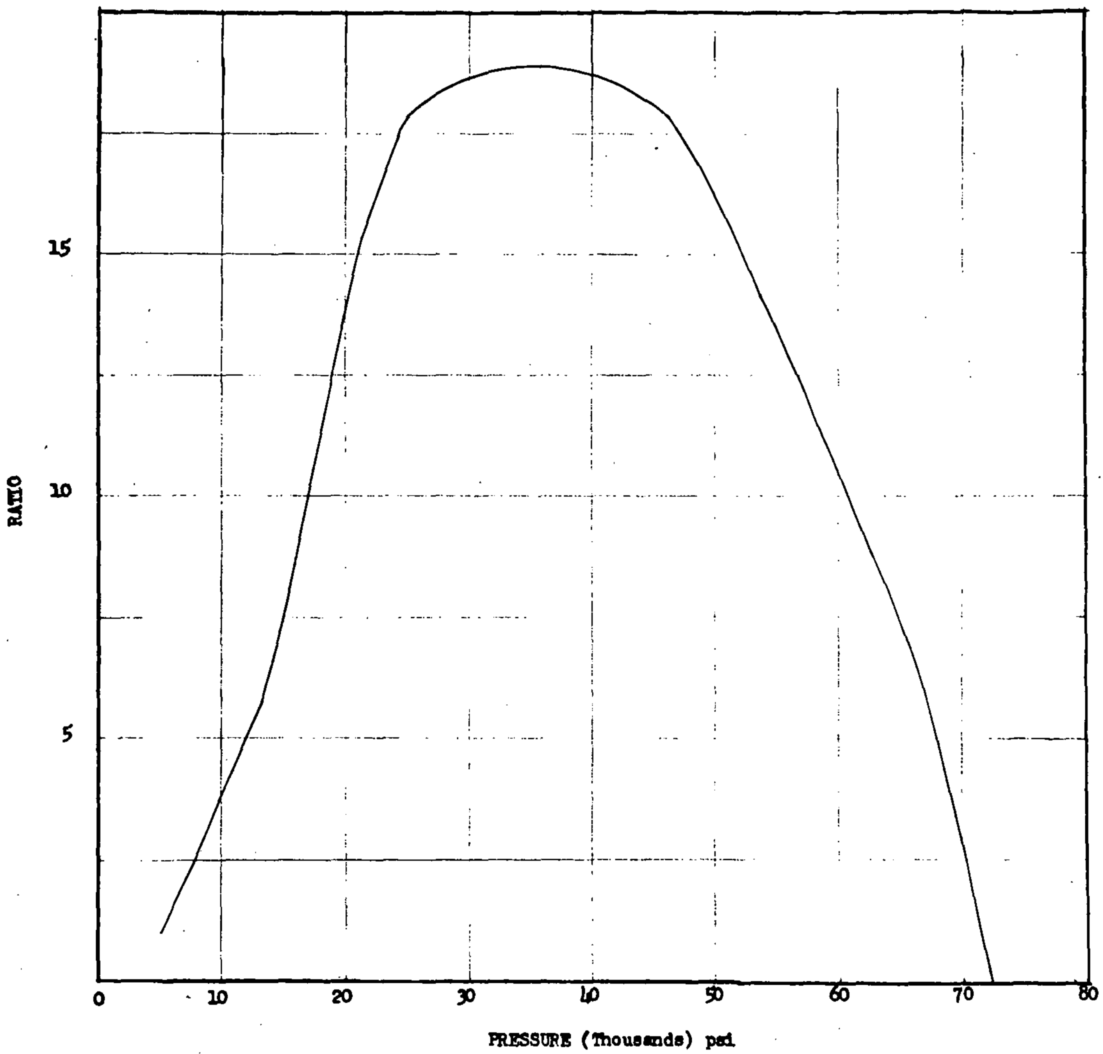


Figure 2. Linear Burning Rates of TNT Obtained with Closed Bomb and Strand Burner



EXPECTED SURFACE AREA VS ACTUAL AREA OBTAINED FOR TNT CYLINDER BURNED IN CLOSED BOMB

FIGURE 3



RATIO OF EXPECTED AREA TO ACTUAL AREA
FOUND FOR TNT CYLINDER

FIGURE 4

CLOSED BOMB TEST
COMPOSITION B

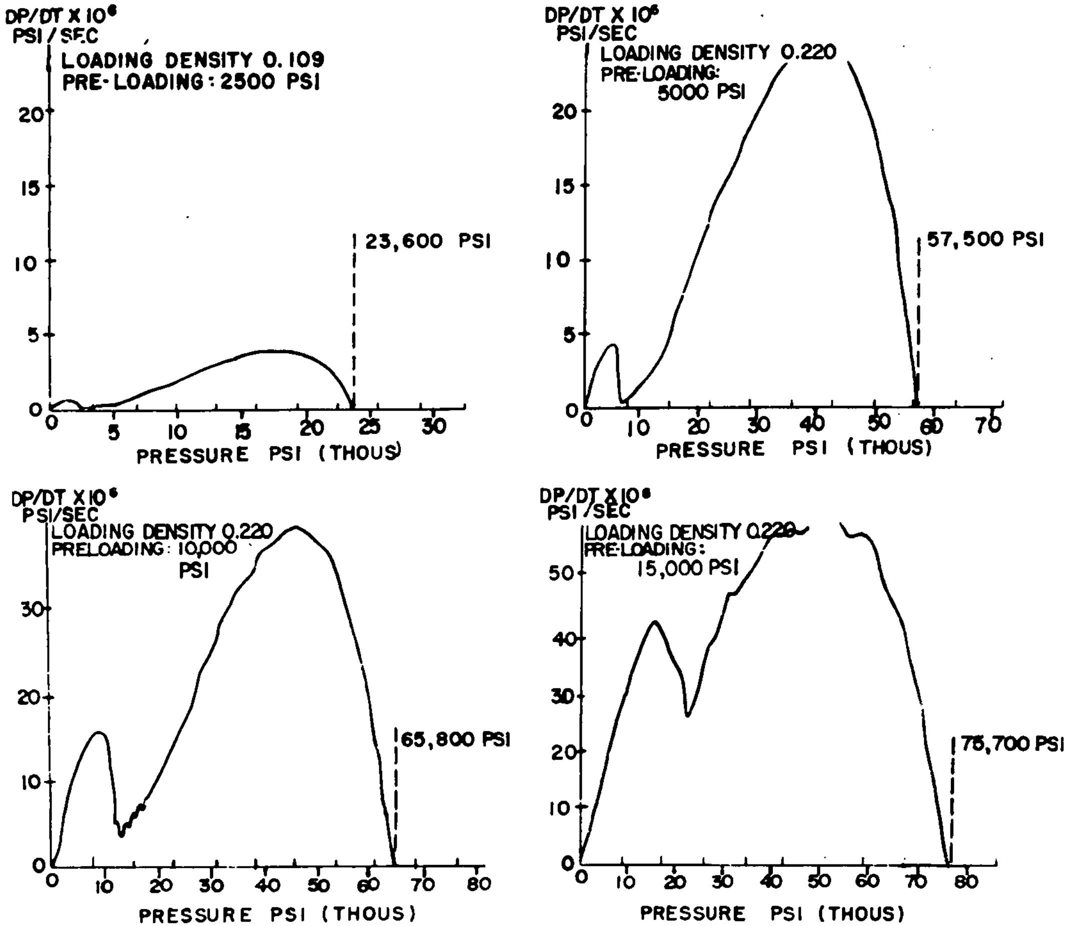
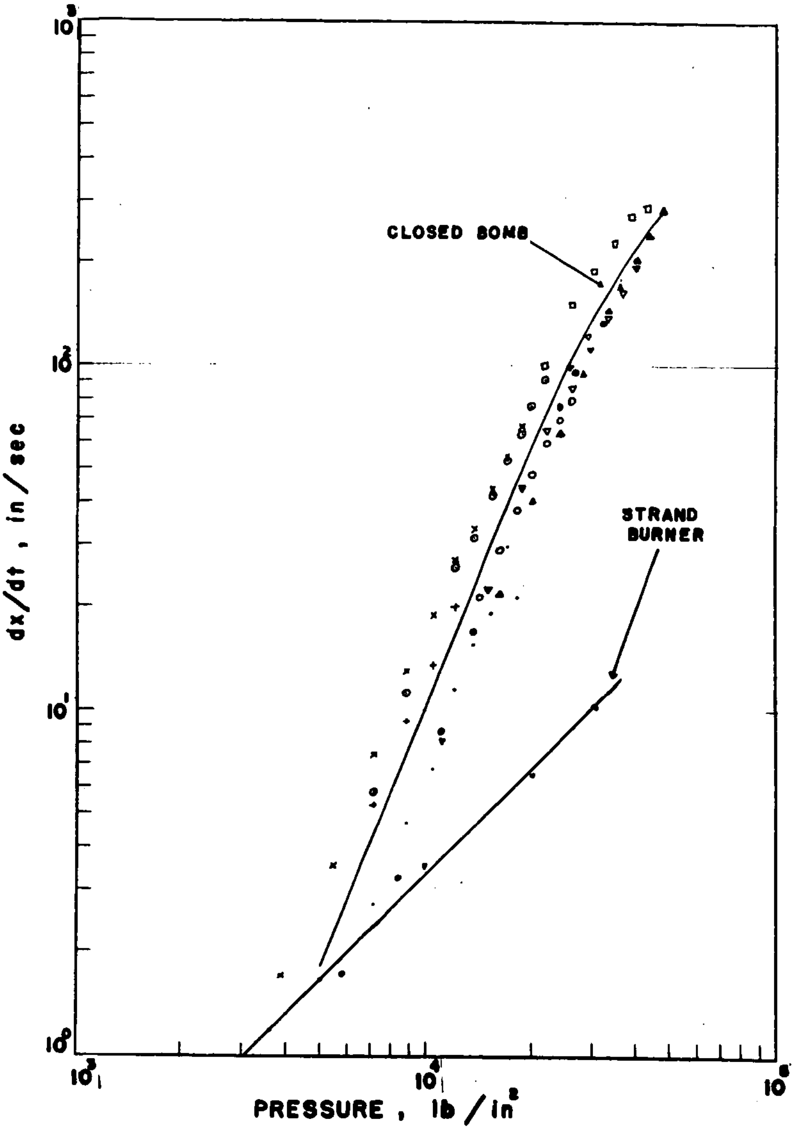
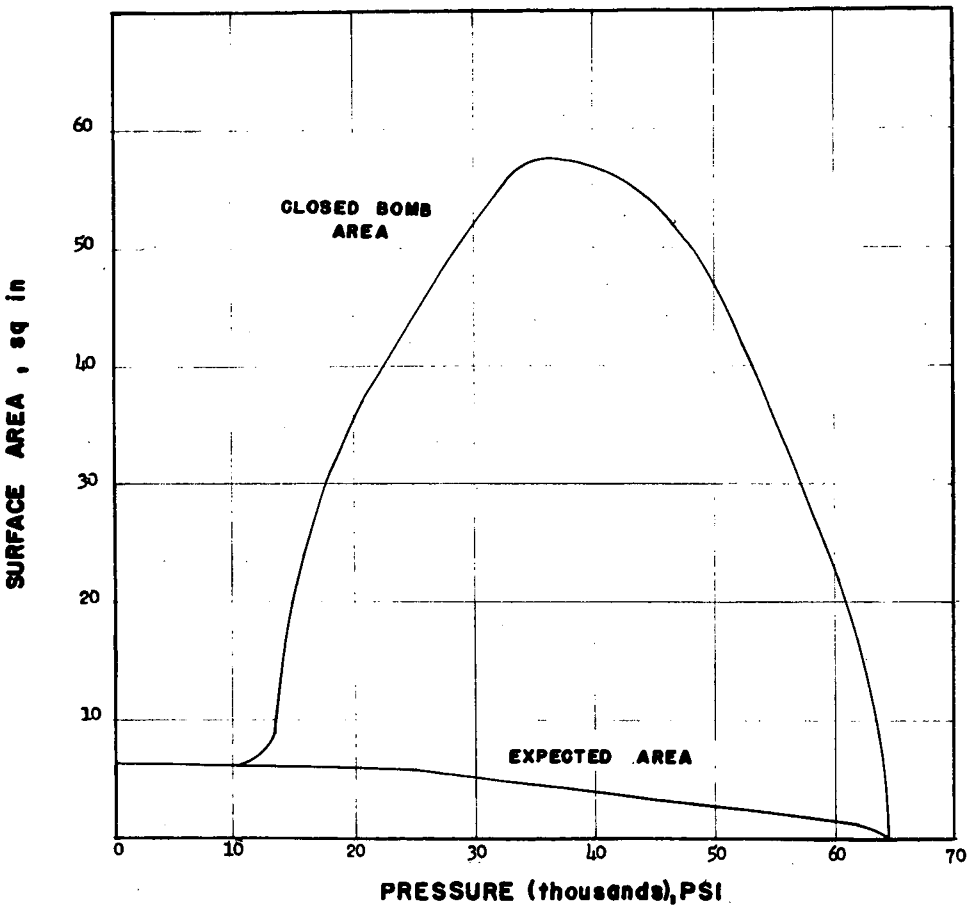


FIGURE 5



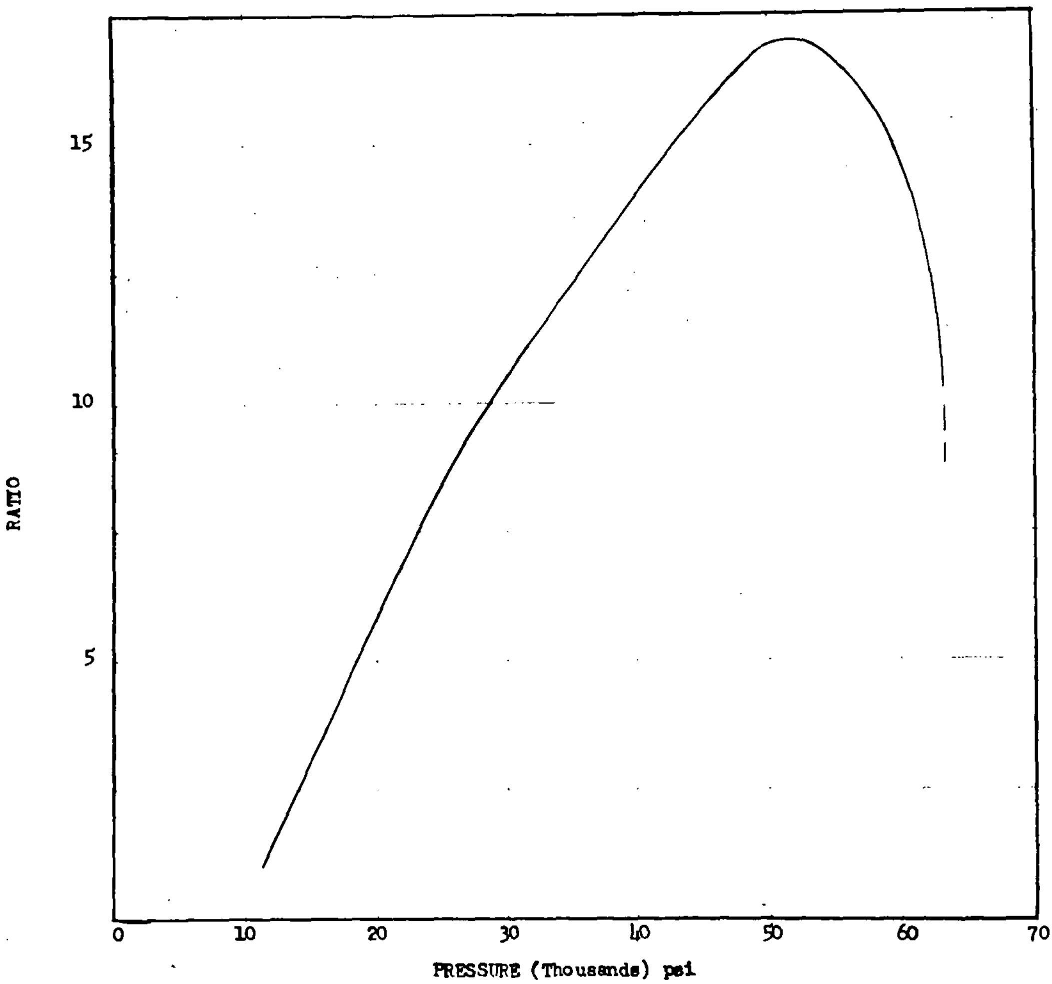
LINEAR BURNING RATES OF COMPOSITION B OBTAINED WITH CLOSED BOMB AND STRAND BURNER

FIGURE 6



EXPECTED SURFACE AREA VS ACTUAL AREA OBTAINED FOR COMPOSITION B CYLINDER BURNED IN CLOSED BOMB

FIGURE 7



RATIO EXPECTED AREA TO ACTUAL AREA FOUND
FOR COMPOSITION B CYLINDER

FIGURE 8

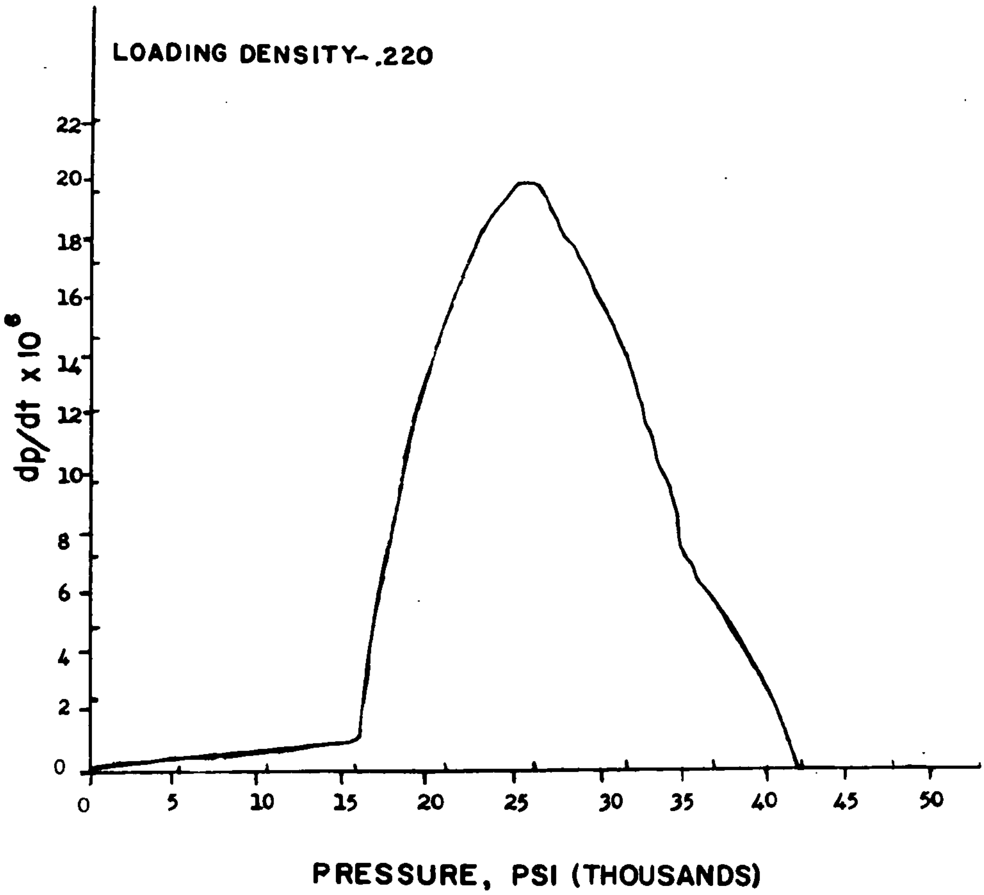


Figure 9. Closed Bomb Test Experimental Propellant

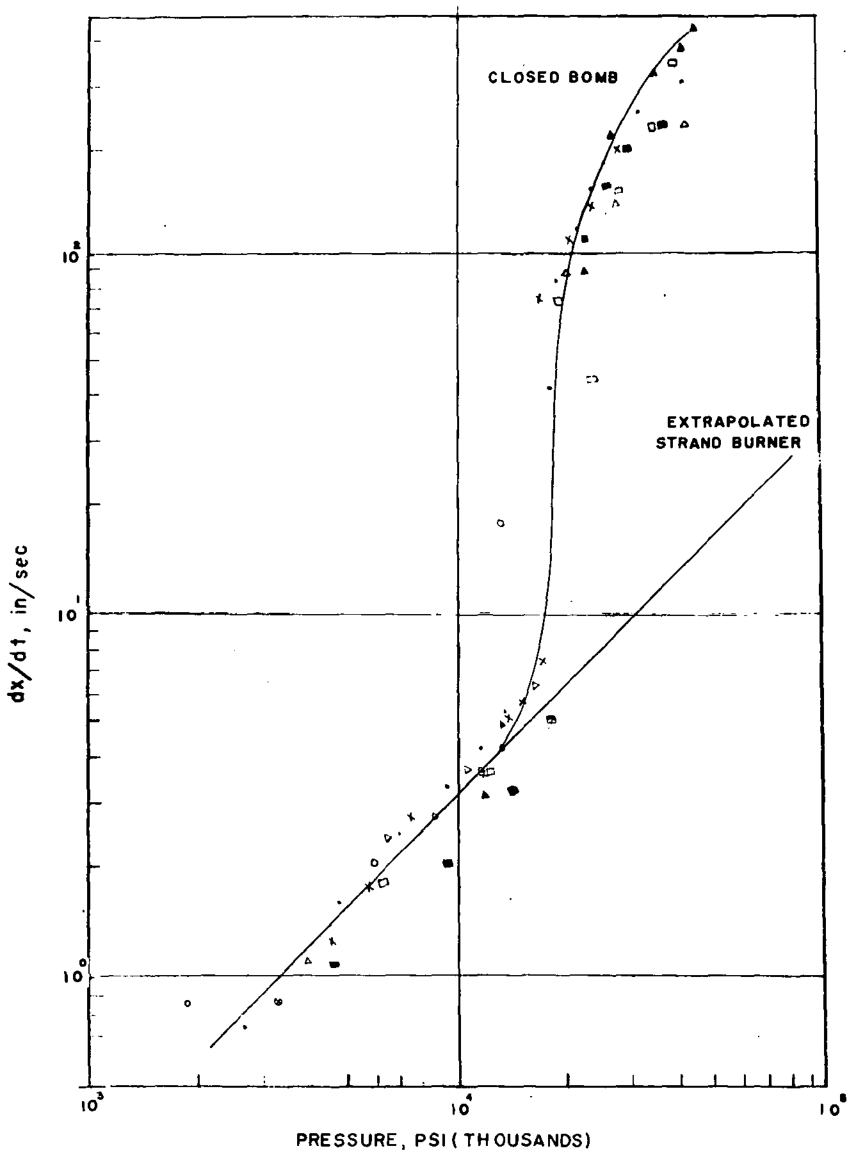
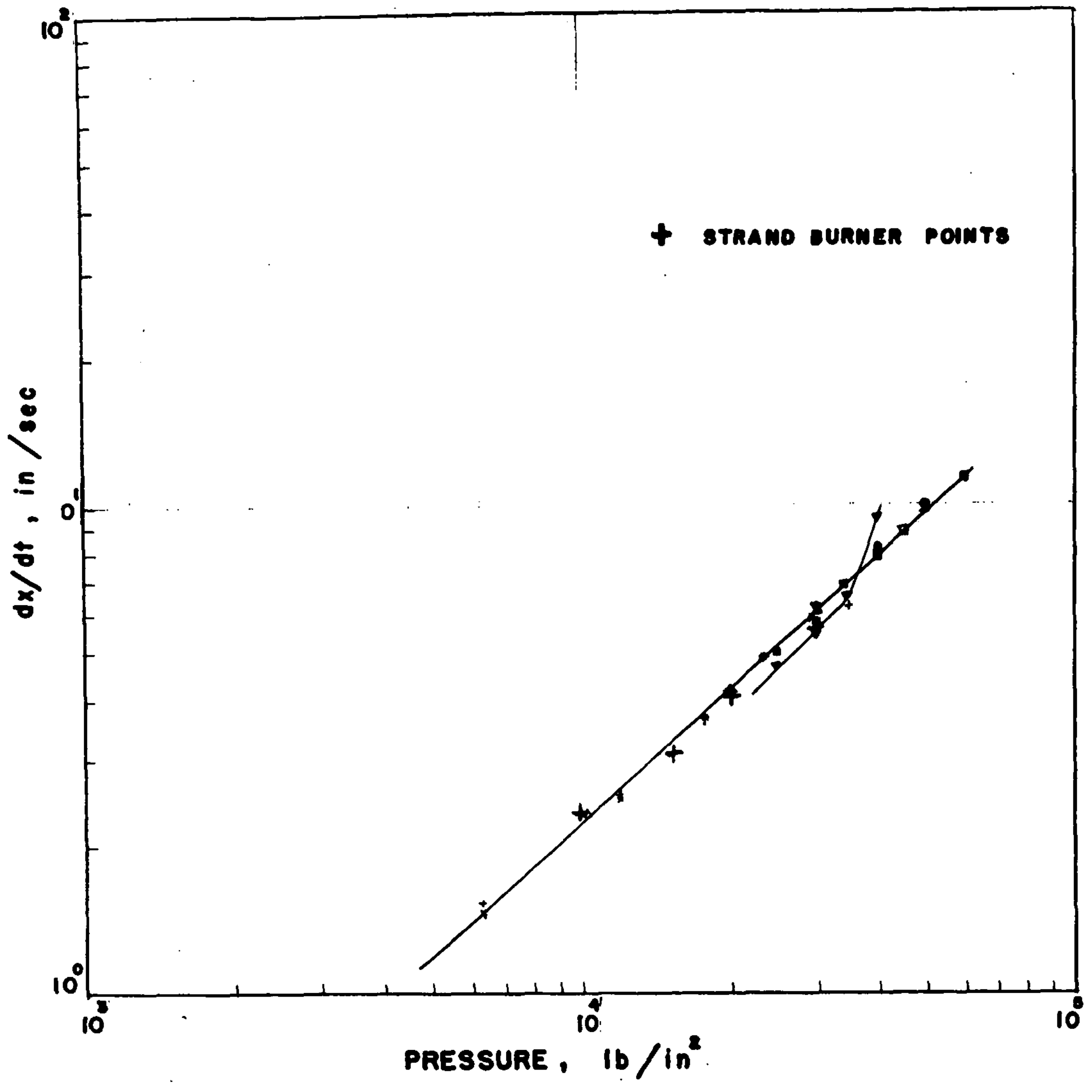


Figure 10 Linear Burning Rate of Experimental Propellant Obtained with Closed Bomb



LINEAR BURNING RATES OF ARP PROPELLANT OBTAINED WITH CLOSED BOMB AND STRAND BURNER

FIGURE 11

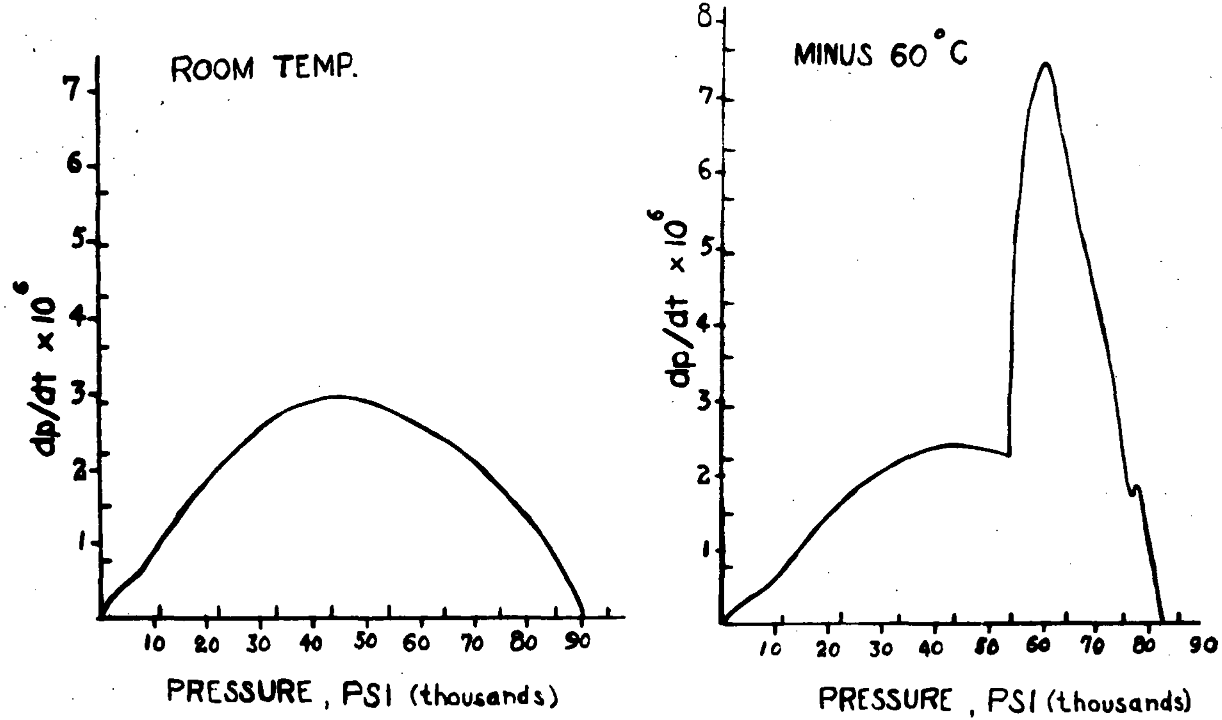
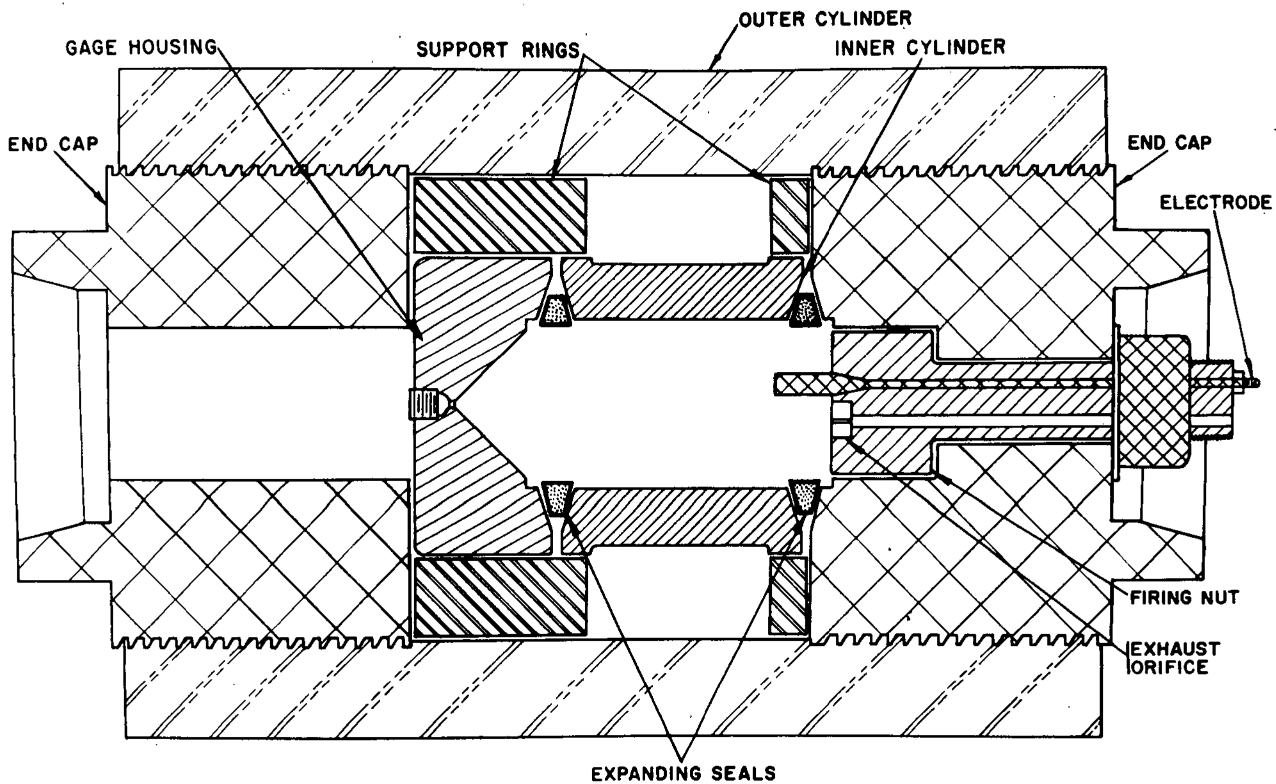


Figure 12 Closed Bomb Test Rohm and Haas Propellant Composition QZ



ULTRA-HIGH PRESSURE VESSEL FOR PROPELLANT TESTING

FIGURE 13

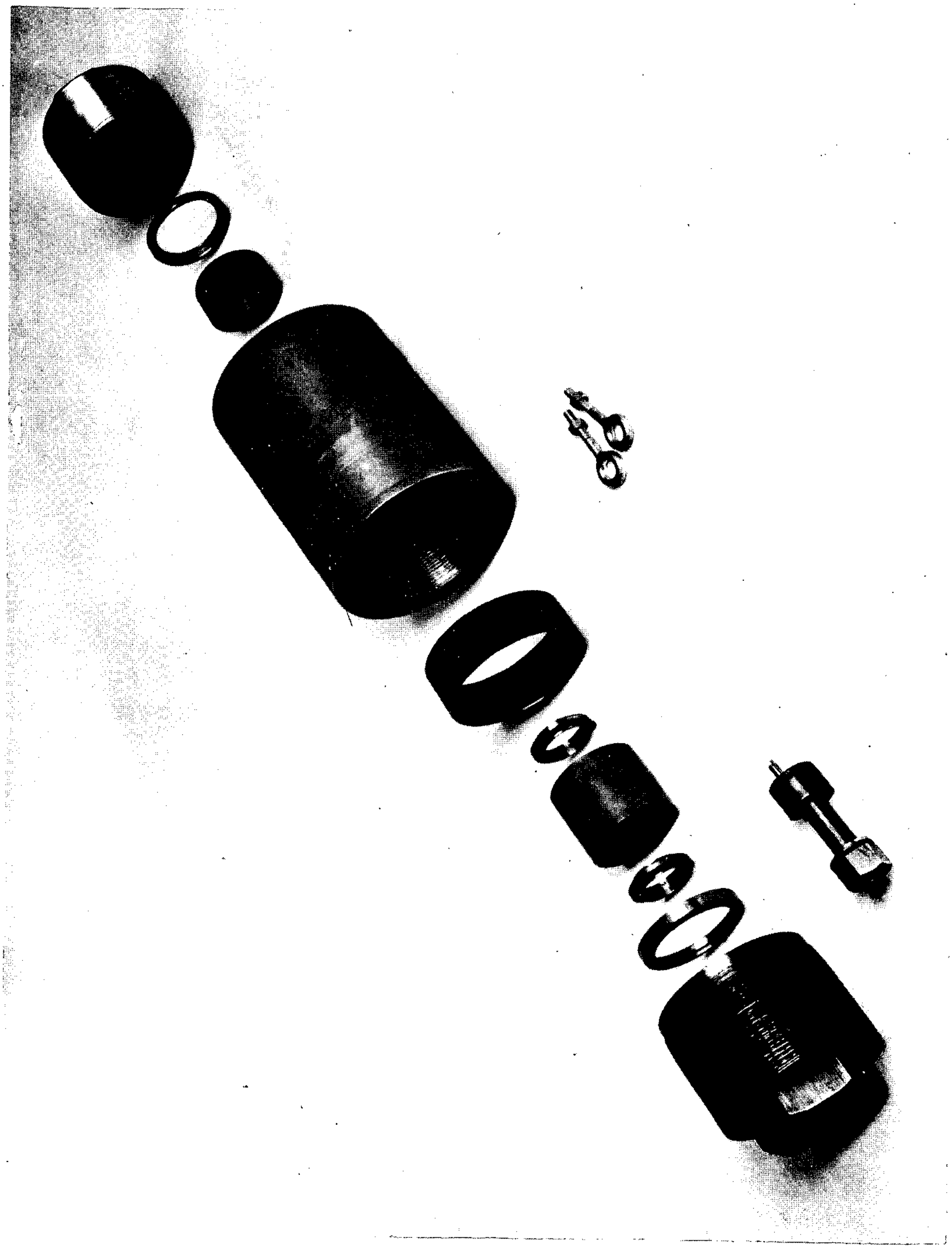
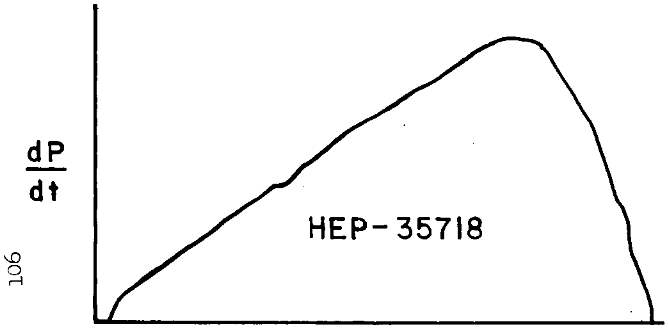
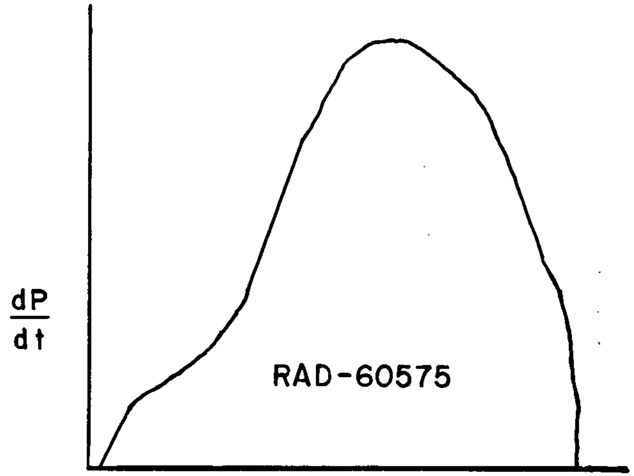


FIGURE 14 ULTRA-HIGH PRESSURE VESSEL, EXPLODED VIEW FROM FIRING END



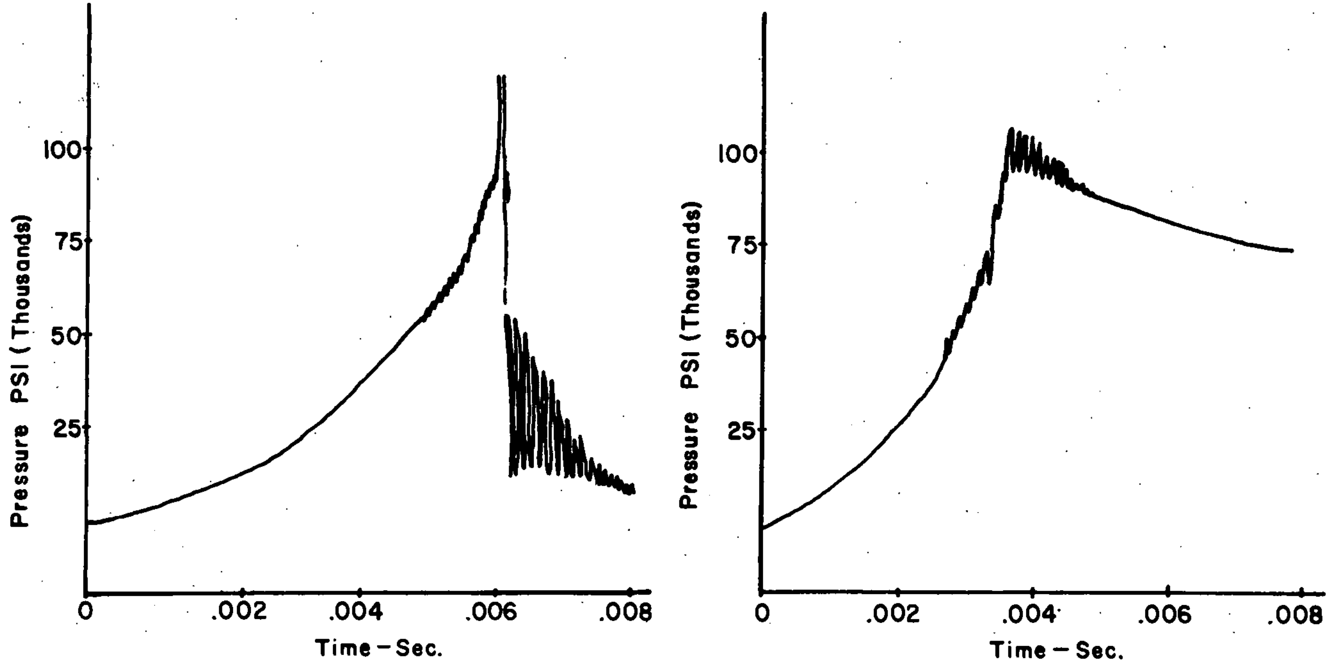
A sample trace classified as "OK", based on closed bomb firing at −40° F.



A sample trace classified as "bad", based on closed bomb firing at −40° F.

TESTS OF M17 PROPELLANTS SHOWING GOOD AND DEFECTIVE LOTS

FIGURE 15



M17 PROPELLANT
Lot SUN-62815
0.4 Loading Density

T28E1 PROPELLANT
0.4 Loading Density

HIGH PRESSURE CLOSED BOMB TESTS OF CANNON PROPELLANTS

Figure 16