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U. S. NAVAL AMMUNITION DEPOT - CRANE, INDIANA

DEPARTMENT OF THE NAVY
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INVESTIGATION OF THE BURNING CHARACTERISTICS OF THE LEAD DIOXIDE-CUPRIC OXIDE-SILICON STARTER COMPOSITION

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INVESTIGATION OF THE BURNING CHARACTERISTICS OF THE LEAD DIOXIDE-CUPRIC OXIDE-SILICON STARTER COMPOSITION

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ABSTRACT

A study is made of the burning characteristics of a statistical family of 16 fuel-rich combinations of the lead dioxide-cupric oxide-silicon starter mix system. Factors that determine the behavior and predictability of the system are defined and investigated by calorimetry, pressure-time curve studies and other techniques. The burning characteristics required for optimum performance as a starter composition are considered.

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INTRODUCTION

1. The object of the present investigation has been to acquire a better understanding of the fundamental factors that control the behavior of the lead dioxide-cupric oxide-silicon starter composition so that an adequate specification could be written covering it. The investigation began when it was observed that the heat of reaction for the system as experimentally determined in the calorimeter was more than 95% of the theoretical thermodynamic value calculated--when a certain chemical reaction mechanism was assumed--from the following relationship:

$$\Delta H = q_p = \sum H_{products} - \sum H_{reactants}$$

If it were possible to predict the heat of reaction, this indicated that the reaction mechanisms assumed to occur between the three components of the system were valid. Thus, the investigation began on a firm conviction that the basic thermochemistry of the system was understood.

2. The first problem with which the investigation was concerned, then, dealt with the behavior of the reacting system and with the factors that governed that behavior. This involved determining the effect that varying such factors had on the burning characteristics, and the extent that the effect of such changes could be predicted.

3. The first phase of the investigation treats the various types of data developed on the behavior of the reacting system, the methods and instrumentation used to develop the data, and the interpretation of the significance of the data. The second phase of the investigation involves a study of the range of acceptable burning characteristics of the starter composition currently used in the Mk 25 Mod 2 Marine Location Marker. Formerly, the Mk 25 Signal employed a formula consisting of 5 parts by weight of lead dioxide, 6 parts of cupric

oxide, and 7 parts of silicon (5L-6C-7S). This formula apparently worked well for awhile, but malfunctions due to failure of ignition or excessive delay times finally forced a change to a less energetic system consisting of 2 parts by weight of lead dioxide, 3 parts of cupric oxide, and 5 parts of silicon (2L-3C-5S). In March 1962, the Quality Evaluation Laboratory conducted a statistically designed experiment on the Mk 25 Marine Marker. The first experiment investigated eight factors at three levels involving the performance of 505 specially prepared signals. One of these factors was the formula, and one of the levels was the formula 2L-3C-5S. In May 1962, a follow-up experiment was conducted involving three factors, one of which was formula. This time 80 signals were prepared and tested. One of the conclusions of these two experiments was that the 2L-3C-5S formula was superior in performance to the 5L-6C-7S formula. In other words, the formula that burned slower, developed less pressure, and had a lower calorific output was superior in performance to the more energetic formula.

4. During the latter months of 1963, this present investigation began testing all production batches of Mk 25 starter composition in a new apparatus which measured the rate of pressure change that occurred as the starter composition burned in a closed bomb. One objective of these tests was to develop data from which the range of acceptable burning characteristics could be established.

5. A third objective of this investigation was to determine the feasibility of using a single starter composition for the various phosphorus signals. Since all available information indicates that the 2L-3C-5S formula is required for the Mk 25 Mod 2 signal, the question now to be answered is whether this formula will perform satisfactorily in other phosphorus signals such as the Mk 6-3 Marine Location Marker which currently employs a 5L-6C-7S formula. No data has to the present been developed on this problem.

6. Finally, the fourth objective of this study was to write a specification based upon all the known data for the starter composition. Such a specification would cover all aspects of the preparation and performance of the starter composition to assure consistent, reliable, and predictable behavior characteristics of the starter composition. This specification is being prepared concurrently with this report.

DESIGN OF THE EXPERIMENT

1. The experiment was designed with the objective of developing data on the effect of a variety of factors, acting alone as well as interacting with each other, on the burning characteristics of the starter composition.

2. The following factors were selected:

   a. The fuel-to oxidizer ratio.

   b. The lead dioxide-to-cupric oxide ratio.

   c. The effect of the particle size of the three components.

   d. The effect of using components from different suppliers.

   e. Processing variations.

   f. Density or degree of packing.

   g. Miscellaneous factors that arose during the investigation, including particle size distribution of the silicon, contaminants in the silicon, moisture (humidity), and crystal type of the silicon.

3. The following characteristics of the starter composition were investigated:

   a. Heat of reaction (calorific output).

   b. Pressure-time curve.

      (1) Slope of curve.

      (2) Maximum pressure developed.

      (3) Time from ignition to peak (or peaks).

      (4) Time to normal cooling curve.

      (5) Pressure at normal cooling curve.

      (6) Height above where normal cooling curve is established.

   c. Heat transfer characteristics.

   d. Ignitability.

4. A statistical family of 16 formulas was prepared covering the range of fuel-rich combinations considered as even remotely practical as starter compositions. This family of formulas, shown in Tables I and II, contains four levels of fuel-oxidizer combinations varying from 30% fuel--70% oxidizer to 60% fuel-40% oxidizer. Within each of these four levels are four variations of the lead dioxide-cupric oxide ratio, being 1:4 at one extreme and 4:1 at the other extreme. Thus, the effects of progressively changing the fuel-oxidizer ratio can be observed, as well as the effects of varying the PbO_2-CuO ratio within each fuel-oxidizer level. Under these conditions, the effect of each component on the burning characteristics of the starter composition can be determined.

5. Calorific values, pressure-time curves, and heat transfer curves for two levels of silicon were obtained on each combination within this statistical family of formulas. This data, which will be treated in the section that follows, appears in Tables III-XIII.

6. The effects of silicon particle size variation on the pressure-time curve were studied for nine silicon samples ranging in average particle size from 1.65 microns to 19.0 microns. These sample components were from various suppliers. Data on all the different silicon samples were obtained on the 2L-3C-5S formula currently used in the Mk 25 Mod 2 Marine Marker and appears in Table X.

7. The effects of lead dioxide and cupric oxide particle size variation on pressure-time curves for two levels of silicon are shown in Tables XI and XII. Again, the composition used is the 2L-3C-5S formula of the Mk 25 Mod 2 Marine Location Marker.

8. Table XIII shows some variations of the pressure-time curves obtained on 2L-3C-5S composition made from components obtained from different suppliers.

9. Table XIV shows data on the ignitability of the statistical family of formulas using a black powder fuze such as is used in the Mk 6-3 Marine Location Marker.

FACTORS DETERMINING THE HEAT OF REACTION

1. It was assumed at the beginning of this study that the probable reaction mechanism of the lead dioxide-cupric oxide-silicon system in any fuel-rich combination would be as follows:

$$PbO_2 + Si = Pb + SiO_2 + \text{heat}$$

$$2\,CuO + Si = 2\,Cu + SiO_2 + \text{heat}$$

In order to verify that the equations represented the true reaction, the theoretical thermodynamic value for the heat of reaction of the system was calculated. In the case of the 2L-3C-5S formula used in the Mk 25 the calculations would proceed in this way:

$$\begin{array}{l} \text{2 grams} \qquad\qquad\quad \text{Y grams} \\ PbO_2 + Si = Pb + SiO_2 \\ 239.2 \qquad\qquad\qquad\quad 60 \end{array}$$

or Y = 0.5017 grams of SiO_2 formed

2. At the reacting temperature the heat of formation is given by the literature as 67,100 cal/mol for PbO_2 and 218,000 cal/mol for SiO_2. We can now calculate the free energy which will be evolved under these conditions:

$$PbO_2 + Si = Pb + SiO_2$$

$$\frac{\text{2 grams}}{\text{239.2 M.W.}} \times 67{,}000 \text{ cal/mol} = 561.0 \text{ cal as the heat of formation of 2 grams } PbO_2$$

and

$$\frac{\text{0.5017 grams}}{\text{60 M. W.}} \times 218.900 \text{ cal/mol} = 1830.4 \text{ cal as the heat of formation of 0.5017 grams } SiO_2$$

therefore

$$\begin{array}{r} 1830.4 \text{ cal} \\ \underline{-561.0 \text{ cal}} \\ 1269.4 \text{ cal} \end{array}$$

This says that in a 10 gram sample of 2L-3C-5S starter composition the 2 grams of PbO_2 will react with an excess of silicon and evolve 1269.4 cal of free heat for 10 grams of composition, or 126.9 cal for one gram of composition.

3. In exactly the same way, we calculate the free heat liberated by three grams of CuO reacting with an excess of silicon in the following reaction:

3 grams						Z = 1.13 grams
2CuO	+	Si	=	2Cu	+	SiO_2
159.1						60
1548.5 cal						4122.6 cal

$$\begin{array}{r} 4122.6 \text{ cal} \\ \underline{-1548.5 \text{ cal}} \\ 1574.1 \text{ cal/3 grams CuO in 10 grams sample} \\ \text{or } 257.4 \text{ cal/gram} \end{array}$$

Adding

Free heat for PbO_2-Si system = 126.9 cal/g
Free heat for CuO-Si system = 257.4 cal/g
Theoretical heat of reaction = 384.3 cal/g for 2L-3C-5S

4. The experimental value in this instance is 97.7% of the predicted theoretical value, so that it is very highly probable that the assumed reactions are actually the real reactions. Further work shows that the heat of reaction can be predicted with a high degree of accuracy for any fuel-rich combination of the starter mix components. Tables III and IV show the comparison between the theoretical heat of reaction values and the experimental calorific values obtained for the entire statistical family of 16 combinations based on 6.0 micron silicon, and for four random samples based on 8.0 micron silicon.

5. Table XIII shows the calorific value ($\triangle$H) obtained using components from different suppliers. These chemicals were procured under existing Federal Specifications with purity and particle size requirements. Again, the Mk 25 formula was used. In this basic formula, components from different suppliers were substituted one by one. No significant variation occurs. Since each of these chemicals had already passed the specification requirement for purity, no variation was really anticipated.

6. Table XII shows the calorific value of the 2L-3C-5S formula as the particle size of the various components are varied. Only in the sample using Hummel

silicon with an average particle size of 13.6 microns did a minor variation occur. Here the calorific value is 93.1% of theoretical whereas all the other samples of this particular formula were approximately 97.5% of theoretical.

7. It is evident, then, from these considerations that the composition is the primary factor determining the heat of reaction of a starter composition. It is, of course, assumed that the components are of a purity that meets requirement. Otherwise, the source of the chemical components had no significant effect on the heat of reaction. Variations in the particle size of the oxidizers had no significant effect on the calorific value, except that the introduction of silicon containing particles of relatively large sizes caused a slight decrease in the calorific value in one instance. It might be theorized that this low calorific value is caused by incomplete combustion due to the nonuniformity of particle distribution due to the large difference in the size of many of the silicon particles compared to the size of the particles of the oxidizers.

DETERMINATION OF THE PRESSURE-TIME CURVE

1. It has been accepted that the burning characteristics--the heat evolved, the quantity of gas, the rate of heat evolution, the type of clinker formed, etc.--vary considerably from formula to formula and even within different production batches of the same formula. Furthermore, it has been assumed that certain burning characteristics are more desirable than others. For example, practical experience has shown that more signal malfunctions occur in the Mk 25 Mod 2 Marine Marker when the 5L-6C-7S formula is used than when the 2L-3C-5S formula is used. Consequently, general and somewhat arbitrary requirements have been set up in the past for the performance of the various starter compositions.

2. It has been one of the objectives of this investigation to determine the important aspects of the burning characteristics for a statistical family of 16 starter composition formulas. At the same time a large number of production samples have been tested using various techniques, and the results of these tests have been analyzed in order to determine which tests are most significant and what performance limits within such tests are acceptable.

3. One of the most promising tests utilized in this study of burning characteristics has been the "pressure-time curve." This curve depicts the change in pressure due to the ignition, burning, and cooling of the starter composition within a closed bomb as a chart moves at an appropriate rate.

APPARATUS FOR DETERMINING RATE OF PRESSURE CHANGE

1. Figure 1 is a photograph of the instrument used to obtain the pressure-time curves utilized in this study. It consists of a Honeywell recorder equipped with a 25 psi transducer installed in a bomb of 90 ml air capacity when loaded with a sample holder containing 12 grams of the sample that has been tamped four times. The aluminum sample holder is one inch high by 1.75 inches O.D. with a wall and bottom thickness of 0.125 inch. Ignition of the sample is by means of a 22.5 volt transformer which heats a 10 cm length of Parr ignition wire to incandescence. The wire just touches the center of the sample. Changes of pressure are recorded on the chart which moves at two seconds per inch.

2. Figure 2 is a drawing which represents the pressure bomb in which the sample is burned.

PROCEDURE

1. The procedure for obtaining a pressure-time curve for a starter composition is relatively simple. A 12 gram sample, weighed to the nearest 0.05 gram, is placed in the aluminum sample holder. The aluminum sample holder is then tapped four times and positioned in the bomb. A 10 cm length of Parr ignition wire is fitted into the small holes on each of the electrodes projecting down from the bomb lid. A loop is bent in the wire so that the bottom of the loop just touches the center of the sample. Hot wire ignition is entirely preferable over ignition using a squib or an electric match since the latter may blow the powdered sample out of the cup or into an unsymmetrical configuration. Reproducibility of results requires that the degree of packing, the geometry of the sample, and the point of ignition be very nearly the same in every test run. Fortunately, this is not too difficult to achieve once the procedure has been established.

The lid is next placed into position on the "O" ring with the ignition wire just touching the sample. The toggle clamps are then adjusted to fasten the lid of the bomb securely into place. The bomb must be pressure-tight and this condition will usually be indicated when the lid is fastened by the appearance of an increase in pressure on the recorder. Finally, the chart is started and the sample fired within the bomb. The change in pressure appears as a curved line on the chart.

EXAMPLES OF PRESSURE-TIME CURVES

1. Because of the large number of samples used in this study, it is not practical to include all the pressure-time curves obtained. Instead, numerical values which describe various characteristics of the curves will be used. However, it will be desirable to show some actual curves of typical as well as unusual test results. Figure 3 shows a typical Mk 25 Mod 2 starter composition curve. The various notations assigned to the various aspects of the curve are defined.

2. Although all of the aspects of the pressure-time curve are reported for each test run, they are not all utilized in this study. In Figure 3, ignition occurs to the right side of the curve, the pressure climbing steadily to the first peak, faltering, then climbing again to the maximum peak, after which--more or less abruptly depending on conditions--it falls until a consistent cooling curve is established.

3. Figures 4-7 show other types of curves obtained.

EFFECTS OF COMPOSITION ON THE PRESSURE-TIME CURVE

1. Tables V and VI show data for two levels of silicon on pressure-time curves of a statistical family of 16 formulas. Tables I and II show the composition of each of these formulas. The changes that occur in these pressure-time curves depend entirely on changes in the composition and on no other factor. All other factors are held constant. Table V shows the results of pressure-time analysis of curves obtained using 8 micron silicon, whereas Table VI contains data for the atypical 6.0 micron silicon. Both tables are based on results obtained from formulas using lead dioxide with an average particle size of 2.23 microns and cupric oxide with an average particle size of 3.4 microns.

2. Two factors interact in these changing compositions to determine their burning characteristics: first, the fuel to oxidizer ratio; and second, the lead dioxide to cupric oxide ratio. We will now examine the data in order to define any general tendencies that are apparent in the behavior of the starter composition.

3. On each of four levels, with the fuel-oxidizer ratio held constant, the reaction rate of the samples increased as the ratio of lead dioxide to cupric oxide increased. Bear in mind that the calorific value actually decreases as the ratio of lead dioxide over cupric oxide increases. Consequently, the burning rate and the heat of reaction are not necessarily directly related to each other. The increased reaction rate is revealed by the change in various characteristics of the pressure-time curves:

   a. The slope of the curve is progressively steeper.

   b. The maximum pressure progressively increases.

   c. The time to the maximum pressure peak progressively decreases.

4. From this it may be concluded that on each of the four levels in which the fuel-oxidizer ratio is held constant while the PbO_2-CuO ratio changes, as the proportion of lead dioxide increases (and the cupric oxide decreases) the

reaction rate and maximum pressure increase, although the calorific value decreases. In sample 13, another significant effect of the PbO_2-CuO ratio is demonstrated. This sample, with only 8% lead dioxide to 32% cupric oxide, could not be ignited by the usual methods (fuze, hot wire, squib) whereas sample number 16 with 32% lead dioxide and 8% cupric oxide was readily ignited. The lead dioxide not only controls the rapidity of the burning rate but also determines the ease of ignition.

5. We conclude, then, that both the cupric oxide and the lead dioxide are essential to the control of the behavior of the composition. A composition composed of 50% lead dioxide and 50% silicon would burn explosively fast, whereas a composition composed of 50% cupric oxide and 50% silicon would not burn at all. A composition with 20% lead dioxide, 30% cupric oxide, and 50% silicon has burning characteristics that make it useful as a starter composition. Furthermore, this understanding of the effects of the two oxidizers on the system allows some control over production batches with questionable or unacceptable pressure-time curves. If a batch is found, for whatever combination of reasons, to burn sluggishly or be difficult to ignite, it could be reblended in such a way that the ratio of PbO_2 to CuO is increased while the ratio of oxidizer to fuel remains the same. Or a batch that burns too rapidly could be brought to the desired performance in the rate of pressure-rise apparatus by reblending it so that the ratio of CuO to PbO_2 is increased, while the oxidizer to fuel ratio remains the same.

6. Tables V and VI also indicate the effect upon the system when the PbO_2-CuO ratio is held constant and the oxidizer-fuel ratio is varied. If we examine the data on the pressure-time curves for each of the four ratios of PbO_2:CuO, we at once see that the group of formulas with 70% oxidizer to 30% fuel are in a class by themselves. Figure 8 shows the effect of increasing the per cent of oxidizer on the maximum pressure for four formulas in which the PbO_2-CuO

ratio is held constant at 1:1.5. As the per cent of oxidizer is increased, the pressure increases almost linearly up to 60% oxidizer-40% fuel. The pressure rise for formulas beyond 60% oxidizer then increases exponentially. We may say then that the oxygen balance of this system becomes critical somewhat beyond 60% oxidizer with burning characteristics that approach being explosive in violence.

7. Where neither of the oxidizers is in large excess over the other--e.g., in samples 2, 6, 10, and 14, and samples 3, 7, 11, and 15--the effect of progressively decreasing the oxidizer can be seen. First, the calorific value decreases from 530.7 cal/g to 298.3 cal/g so there will be less heat evolved. The maximum pressure can be seen progressively to drop. However, the burning rate as indicated by the time to the maximum pressure peak changes somewhat erratically. The reaction rate generally decreases from number 2 through numbers 6, 10, and 14, and from number 3 through numbers 7, 11, and 15. However, toward the middle group, the change is practically negligible--7.88 secs for number 6 to 7.38 secs for number 10, 5.5 seconds for number 7, and 5.5 seconds for number 12.

8. It will be noted that some pressure-time curves have two peaks. The appearance of these two peaks indicates that the reaction between the silicon-lead dioxide system and the silicon-cupric oxide system does not proceed at the same rate. A study of the pressure-time curves in Tables V and VI reveals the following factors that appear to favor the appearance of two peaks.

a. The existence of a substantial amount of lead dioxide in the formula.

b. A balance between the amount of PbO_2 and the amount of CuO.

c. A balance between the total oxidizer and the fuel, in which a ratio of 50% fuel to 50% oxidizer gave two peaks with three out of four of the ratios of PbO_2 to CuO used.

d. Moderation of the intensity of the reaction by an excess of silicon.

In other words, two peaks do not appear in highly energetic and rapidly burning samples, and they appear more frequently in samples containing 60% silicon than in samples containing 40% silicon.

9. In conclusion, the occasion of two peaks in a pressure-time curve is determined by factors that favor the appearance of the two independent and distinct chemical reaction mechanisms that are occurring simultaneously. The PbO_2-Si reaction is more rapid than the CuO-Si reaction, and it causes the first peak while the slower CuO-Si reaction is responsible for the second peak. However, both of these reaction rates are dependent upon temperature, and perhaps pressure, so that when the reaction is sufficiently energetic, as it is in formulas containing 70% oxidizer, only one sharp peak appears (Figure 4) and there is no distinction between the rate of the PbO_2-Si reaction and the CuO-Si reaction. On the other extreme, two peaks do not appear in samples with a large excess of CuO over PbO_2 or where there is a combined effect of a deficiency of PbO_2 and an excess of silicon fuel as in number 14.

10. Thus, either the extreme of a very fast burning formula or that of a very slow burning formula will not give a pressure-time curve with two peaks. Nor would these extremes appear to be desirable as practical starter compositions. Some compositions with an excess of PbO_2 over CuO give pressure-time curves with two peaks in which the first peak is higher than the second peak, e.g., sample number 12. But the burning rate is too fast, or the maximum pressure too high, so that these formulas also do not afford practical starter compositions. Experience and experimental data indicate that a starter mix formula with two approximately equal pressure-time peaks, in which the second peak is slightly higher than the first, is a moderate burning, easily ignited, and relatively gasless formula that has been shown to function reliably in the Mk 25 Mod 2 Marine Location Marker. It is quite possible, although not supported by

experimental data as yet, that a formula with such a pressure-time curve would also function reliably in other signals employing this starter system to ignite phosphorus composition.

EFFECTS OF PARTICLE SIZE ON THE PRESSURE-TIME CURVE

1. Effects of Particle Size Variation of Silicon on the Pressure-Time Curve

a. Table X presents data on the pressure-time curves of nine silicon specimens from various suppliers ranging in average particle size from 1.65 microns to 19.0 microns. Only the 1.65 micron silicon is of the amorphous type; all the other specimens are of the cubical crystalline form. Figure 9 shows the maximum pressure recorded on pressure-time curves plotted against the average particle size of the silicon as determined on the Fisher Subsieve Sizer. The effects of several factors can be seen:

(1) The combined factors of small particle size and amorphous form of silicon cause the most extreme deviations. This type of silicon is clearly to be avoided.

(2) The effect of particle size only in which there is a general decrease in maximum pressure from 9.56 psi for 4.6 micron silicon to 6.25 psi for 19 micron silicon. Eight micron silicon of the cubical form runs about 8.0 psi.

(3) One silicon sample, which is the cubical form and has an average particle size of 6.0 microns, behaves in an atypical manner (see Figure 7), having a maximum pressure of 12.75 psi. It is tentatively believed that dissolved impurities in the silicon--chromium and/or manganese--are responsible for the unusual behavior of this silicon. This effect is not associated with particle size.

b. The effect of the particle size on the burning rate is also shown by the value tP_{max} derived from the pressure-time curve data shown in Table X. This value represents the time in seconds from ignition to the maximum pressure peak. In the normal cubical silicon form, it ranges from 3.5 seconds for 4.6 micron silicon to 9.5 seconds for 19.0 micron silicon. For 8 micron silicon, the value for the maximum peak is 7.38 seconds, and for the first peak, five seconds.

Also, the slope of the curve drops from 76° for the 4.6 micron silicon to 33° for the 19.0 micron silicon.

c. It can be concluded then that the average particle size of the silicon has a demonstrable effect on the reaction rate and the maximum pressure generated. On the other hand, other properties of the silicon--such as the crystal form and the presence of contaminants--can have an even greater influence on its behavior as a starter composition than the particle size.

2. Effects of the Particle Size of the Oxidizers on the Pressure-Time Curve

a. Table XI contains data derived from pressure-time curves obtained on three different particle sizes of both the oxidizers. Curves are obtained on samples all of which were made from the same 8.0 micron silicon using the same 2L-3C-5S formula.

b. Figure 10 shows three levels of particle sizes for each of the two oxidizers plotted against the maximum pressure obtained for each from Table XI. These slopes indicate that the pressure change is inversely related to the particle size change within the limits covered, i.e., between 0.65 microns and 2.23 microns for the lead dioxide, and between 1.41 microns and 5.1 microns for the cupric oxide.

c. In Table XI, number 4 shows a combination of the two largest particle sizes for the oxidizers and number 6 shows the smallest. The maximum pressure varies from 7.00 psi for the large particle size combination to 9.5 psi for the small particle size combination. Normal Mk 25 production batches of starter mix rarely exceed these limits, although occasionally a batch will burn at slightly below 7.00 psi. If a batch burns and generates a pressure in excess of 9.5 psi, there is usually something wrong. Variations in reaction time also appear where, for example, the angle of the slope varies from 61° for the largest average particle size for each oxidizer (number 4) to 68° for the smallest (number 6).

d. We may conclude, then, that the burning time and the maximum pressure are related to the particle size of the two oxidizers such that, within limits, as the average particle size decreases the maximum pressure increases, while the angle of the slope also increases. Furthermore, the effect of the particle size is cumulative, being a combination not only of both the oxidizers but also of the fuel as well.

EFFECTS OF OTHER FACTORS ON THE PRESSURE-TIME CURVE

1. Moisture-Humidity

a. During a rainy period in which the relative humidity of the atmosphere exceeded 90%, it was observed that the maximum pressure of the Mk 6-3 starter composition prepared by production went up from an average of about 11.0 psi to about 13.0 psi. An investigation showed that all the components were identical and that the batches were prepared by the same operator in the same way.

b. An experiment was set up in the laboratory to test the effect of high atmospheric humidity on the pressure-time curve. One portion of a production batch was placed over water in a closed vessel; the control portion of the same batch was placed over magnesium perchlorate in a desiccator. After 24 hours, pressure-time curves were obtained on these two samples. The ability of the starter composition to absorb water on the surface of its particles and the effect of this absorbed water on the pressure-time curve is shown in Figures 11 and 12.

c. It will be seen that a difference of only 0.55% moisture between the two samples accounted for a difference of 2.1 psi--i.e., the adsorption of 0.55% moisture raised the maximum pressure from 11.8 psi to 13.9 psi, which would be considered unusually high. When the sample was redried and retested, the maximum pressure was found to have returned to normal.

2. Impurities.

a. The appearance during this investigation of a silicon specimen with unusual burning properties has already been mentioned. This silicon was supplied by the Hummel Chemical Company and had an average particle size of 6.0 microns. When used as a component in the Mk 25 formula (2L-3C-5S), the maximum pressure was 12.75 psi (Figure 7), whereas a normal 8.0 micron silicon gave a P_{max} of about 8.0 psi (Figure 3). Various explanations were advanced and tested in an effort to account for this large variation. To begin with, difference in pressure is all out of proportion to the difference in the average particle size. This has already been indicated in Figure 9. Nor was the elevated pressure due to adsorbed moisture on the 6.0 micron silicon; after drying the pressure remained high. The crystal form was identified as cubical and the particle size distribution, when compared to other silicon samples of 8.0 microns and 4.6 microns, was normal. However, effluorescence spectroscopy indicated the existence of manganese and chromium impurities which were dissolved within the silicon crystals. These elements were not found in the other silicon specimens tested.

b. Since these impurities could not be removed from the silicon without destroying it, nor readily added to other silicon specimens, it remains uncertain that this is the cause of the unusual burning characteristics of this silicon. No other silicon of the cubical type, whatever the average particle size, has shown these unusual burning characteristics.

3. Crystalline Form

a. With one exception, all the silicon specimens used in this study were of the adamantine or cubical form. The one exception was an amorphous silicon specimen. Figures 9 and 11 indicate the more energetic activity of amorphous silicon. This is also shown by calorimetric runs on 2L-3C-5S starter composition prepared from amorphous silicon which yields 416 cal/g as compared with 375 cal/g for cubical silicon. Consequently, amorphous silicon is not suitable for ordinary starter compositions.

4. Suppliers

a. With the exception of the atypical 6.0 micron silicon supplied by the Hummel Chemical Company, all the chemical components employed in this study performed in a generally normal and predictable manner. These components had all previously passed one or more of the existing Government Specifications. Of the many silicon shipments supplied by the Hummel Chemical Company that have been investigated by the laboratory, this is the only one recorded that has shown such unusual burning properties. Apparently, whatever the factor that causes this 6.0 micron silicon to perform in an unusual way, the factor does not normally appear in either Hummel silicon or silicon from other suppliers.

5. Density

a. Generally, it was found that packed samples burn somewhat faster than loose samples due to the increased intimacy of the reacting particles. However, this line of investigation was not pursued any further because the starter mix is loaded loose in production and then packed slightly by tamping. In experimental work in the laboratory, this method of loading starter mix samples into the bomb for pressure-time curve studies gave good reproducibility of results. As long as this technique is continued on the production line, it does not seem to be a significant factor.

HEAT TRANSFER CHARACTERISTICS

1. The object of this part of the investigation was to determine the intensity and rate of heat evolved and transferred to the phosphorus signal--or, in the case of the actual experiment, to the sensing and recording device. It was believed that different formulas might exhibit different heat transfer characteristics due to the fact that they would have different burning characteristics as well as clinkers with different compositions. Consequently, heat transfer data was obtained on two levels of silicon for the statistical family of sixteen formulas. This data appears in Tables VIII and IX.

2. This data does not, however, appear to contribute any new insight into the burning characteristics of the various formulas studied. Most of the characteristics revealed by other techniques simply reappear here. In general, this data indicates that as the per cent of oxidizer decreases, the burning time increases while the temperature intensity decreases. If the oxidizer to fuel ratio is held constant, any increase in the ratio of lead dioxide over cupric oxide is accompanied by an increase in the temperature intensity as well as an increase in the burning rate (i.e., it burns hotter and faster). The value t_i, which represents the time the temperature of the burning starter composition exceeds 600°C and is therefore above the ignition point of the phosphorus composition, is of some interest. In most cases, the time at which the starter composition is hotter than 600°C exceeds 20 seconds. This is greater than the required delay time for ignition of the signal, which is 15 seconds for the Mk 25 Mod 2 Marine Marker. However, with the one high energy formula reported, the time fell to 8.00 seconds indicating the rapidity with which the heat is generated and dissipated. Moreover, the value for t_i tends to decrease as the fuel to oxidizer ratio increases and as the lead dioxide to cupric oxide ratio increases.

3. The apparatus used in this study consisted of a Sargent recorder equipped with a thermocouple and appropriate cold junction. The chromel-alumel thermocouple was an inconel sheathed "ceramo" type[1] and was fitted into the center of an aluminum sample-holder through a hole in the bottom. The aluminum sample-holder was 1.75" I.D., 1.125" in height, with 0.1" thick walls, and a bottom and top thickness of 0.375". Twelve grams of sample are ignited by an electric match introduced through a hole in the top of the sample-holder.

4. Figures 13, 14, and 15 show three heat transfer curves. Figure 13 is an example of a high energy formula (sample number 3, Table I) and Figure 14 is an example of a relatively low energy formula (sample number 13, Table I). Figure 15 represents the heat transfer curve for the Mk 25 Mod 2 starter composition formula.

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[1] Thermocouple supplied by Technical Equipment Corporation, Denver, Colorado, Catalogue Number F 2007.

IGNITABILITY OF STARTER COMPOSITIONS

1. The ease or difficulty of the ignition of the statistical family of sixteen formulas was investigated. The sixteen formulas were made of the same components used throughout this study: 2.23 micron lead dioxide, 3.4 micron cupric oxide, and 8.0 micron silicon. Approximately 12 grams of each of the sixteen formulas were tested in a M2 [illegible] phenolic cup equipped with the customary nitrocellulose cap and black powder fuse. Tests were conducted in the open air. Table XIV shows a summary of the results obtained under the test conditions.

2. No attempt is made here to apply a relative degree of ease of ignitability. The table merely shows which formula had ignition failures that could be repeated. Generally, however, it can be said that ease of ignition depends on these factors:

a. Average particle size of the components.

b. Per cent of lead dioxide present.

When the particle size of the three components is relatively small, the ease of ignition of the resulting composition is increased. Also, a larger ratio of lead dioxide gives a composition that ignites easily.

CONCLUSION

1. The attempt has been made in this investigation to establish the relationship between the burning characteristics of the system and the factors that determine those characteristics. It is now possible, on the basis of data obtained, to analyze the "burning characteristics" into three primary effects:

   a. The quantity of heat generated.

   b. The rate at which the heat is generated.

   c. Maximum pressure and rate of pressure decline.

We should now examine each of these "effects" as to the causes that determine them.

The Quantity of Heat Generated

1. This aspect of the behavior of the system has been shown to depend almost entirely upon the composition in any fuel-rich combination of the three components and is to a high degree predictable. All other factors studied, including average particle size of the components, contaminants, traces of moisture, supplier, density, etc., had no significant effect upon the quantity of heat liberated by the burning composition.

The Rate at Which Heat Is Generated

1. The concept "burning rate" has generally been used to denote the rate at which the flame front moves through the composition. However, the study of pressure-time curves affords a more pertinent and sophisticated description of the reaction occurring in the burning system. The double peaks appearing in so many moderate burning formulas indicate the existence of two reaction mechanisms proceeding simultaneously but not at the same speed--the PbO_2-Si system proceeding much more rapidly than the CuO-Si system. In high energy formulas, the two peaks are indistinguishable, showing that as the temperature

of the burning system increases the speed of the two reactions becomes more nearly the same. However, this is true only in the most vigorously burning formulations. Surprisingly enough, in almost all formulas except the most energetic, the heat of reaction and the reaction rate are not directly related. For example, formula number 5 in Table V has a theoretical heat of reaction of 489.9 cal/g, but the value $t\frac{1}{2}P_{max}$ is 5.38 seconds and the angle $\Theta = 38°$; whereas in formula number 12, which has a theoretical heat of reaction of only 339.0 cal/g, the value $t\frac{1}{2}P_{max}$ is 0.94 seconds and the angle $\Theta = 82°$. Number 12 obviously has a much faster burning rate although the heat evolved is much less.

2. For moderately energetic formulas, suitable as starter compositions, four factors have been found which control the reaction rate:

   a. The composition.

   b. The average particle size of the components.

   c. The crystalline form of the silicon.

   d. The presence of impurities in the silicon (although this has not been conclusively demonstrated).

If the behavior of the composition is to be controlled, these factors must be controlled.

3. The composition factor can itself be analyzed further into two factors: the fuel to oxidizer ratio and the PbO_2 to CuO ratio. Of these, it is the PbO_2 to CuO ratio that exerts the most significant influence over the burning rate of the system. Increase the PbO_2 on any fuel to oxidizer level and the rate and vigorousness of the reaction is increased; decrease the PbO_2 and the rate and vigorousness of the reaction is decreased. These same tendencies hold true with ease of ignitability. In general, the results of this study indicate that a balance between the fuel to oxidizer ratio and the lead dioxide to cupric oxide ratio produces a starter composition with the most desirable qualities:

easily ignited but not touchy or dangerous; sufficient heat of reaction[2] without being enough to vaporize the elemental lead formed during the reaction and thus kick up the internal pressure unduly during the first few seconds after ignition; a reaction rate moderate enough to allow both the PbO_2:Si system and the CuO:Si system to proceed independently thus stretching out the time during which the reacting composition is actually generating peak energy (this is perhaps the best argument for supporting the superiority of the two-peaked system); a moderate maximum pressure which allows some variation either up or down without approaching any critical limits; a clinker that is firm and slightly plastic when hot, and which holds together because of the low gassing of the composition and the moderate heat of reaction. Of course, the perfect balance--theoretically speaking--between oxidizer and fuel would be a 1:1 ratio or 50% of each, and between the PbO_2 and the CuO a 1:1 ratio or 25% of each. The Mk 25 Mod 2 starter composition with the 2L-3C-5S formula is so close to this balance that to argue over the difference would be pedantic.

4. In general, the burning rate and the maximum pressure are inversely related to the average particle size of the components. In Table X, the column of figures for the values $t\frac{1}{2}P_{max}$ and Θ show progressive changes as the average particle size of the silicon becomes larger. With the exception of the 6.0 micron atypical silicon, number 4, the values for P_{max} show a regular decrease as the average particle size of the silicon increases. Table XI shows similar tendencies for the two oxidizers. Figure 10 demonstrates the predictable relationship between the change in the A.P.S. of each of the oxidizers and the maximum pressure. Figure 9 shows the effect of different particle sizes of silicon on the value P_{max}. Note that between 8 and 14 microns A.P.S., the P_{max} value hardly changes at all. We may conclude, then, that the A.P.S. of the

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[2] Cf. Q. E. Laboratory Memo 3541A:re of 16 March 1962 et seq.

silicon should be in the range of 8-14 microns; the A.P.S. of the lead dioxide in the range of approximately 1-3 microns; and the A.P.S. of the cupric oxide in the range of approximately 1.5-5.0 microns. Components now procured for the Mk 25 Mod 2 starter composition almost always fall within these limits.

5. Concerning the crystalline form of silicon, it need only be said that amorphous silicon will not do, and that the silicon used in starter compositions for phosphorus candles should always be cubical or adamantine silicon.

6. Concerning the 6.0 micron atypical silicon sample from Hummel Chemical Company, very little can be said. Effluorescence spectroscopy indicates traces of manganese and chromium dissolved within the silicon crystals. As far as is known, this condition--and indeed this silicon sample--is unique. The phenomenon has been encountered only once. In all other known respects the silicon is normal. But as a component in a starter composition, it is extremely reactive, the P_{max} value for 2L-3C-5S jumping from about 8 psi to about 13 psi, and the $t\frac{1}{2}P_{max}$ value dropping from 2.75 seconds to 1.62 seconds. Compare Tables V and VI. Attempts to add contaminants to normal silicon and thereby reproduce these unusual burning characteristics have so far failed.

Maximum Pressure and Rate of Pressure Decline

1. The maximum pressure is determined primarily by the interaction of three factors:

  a. The amount of heat evolved.

  b. The rate of heat evolution.

  c. The amount and type of materials volatilized.

Concerning the amount and rate of heat evolution, let it suffice to say that the rate of heat evolution has more influence on the maximum pressure than does the amount of heat evolved. In Table VI, compare P_{max} for sample number 5 (ΔH = 488.9 cal/g) with the P_{max} for sample number 16 (ΔH = 271.2 cal/g).

Number 5 has a P_{max} value of only 12.3 psi compared to 21.5 psi for number 16.

2. The amount and nature of materials that will volatilize also affect the maximum pressure as well as the rate of pressure decline after the peak has been reached (i.e., after reaction has ceased). There are primarily two materials in the starter mix that will vaporize and thus influence the maximum pressure and the rate of pressure decline: elemental lead formed during the reaction

$$PbO_2 + Si = Pb + SiO_2$$

and adsorbed moisture.

3. The amount of PbO_2 and the high heat of reaction account for the extraordinary size of ΔP in samples numbers 1-4 in both Tables V and VI. High values for ΔP are undesirable because the explosive expansion of lead vapor disperses the sample and clinker, often with considerable violence. Observe in Figure 3 the low value for ΔP for the Mk 25 Mod 2 starter formula: 1.3 psi.

4. Figures 11 and 12 show the effect of humid conditions on the Mk 6-3 starter composition. The 0.55% of absorbed moisture raised the value of P_{max} from 11.8 psi to 13.9 psi and ΔP from 3.05 psi to 4.30 psi. Thus, adsorbed volatiles have the effect of producing a pressure-time curve which is essentially the same as that of a more energetic formula. It would also appear that the moisture content of the starter composition can be significantly increased in humid weather simply by exposure to the atmosphere. The moisture content of the components and the adsorption of moisture by the composition under extremely humid conditions are factors that should be controlled insofar as is practicable.

Acceptable Range of Burning Characteristics For Mk 25 Mod 2 Starter Composition

1. A second objective of the present investigation has been to determine from the accumulated data an acceptable range of burning characteristics for the starter composition used in the Mk 25 Mod 2 Marine Location Marker.

2. It will be remembered that mention was made in the introduction of the statistically designed experiment performed on the Mk 25 Mod 2 Marine Markers by the Q. E. Laboratory in 1962. One of the significant factors affecting the number of signal failures was the composition or formula used. The most energetic formula (6L-6S-8C) was involved in the most failures (51/135), while the least energetic formula (2L-3C-5S) was involved in the least failures (4/135). The formula used up to that time--and still used in the Mk 6-3 Marine Location Marker--the 5L-6C-7S formula, was involved in 23 failures out of 135 test signals. There seems to be little doubt, therefore, that the present formula exhibits superior properties and that the acceptable range of burning characteristics for the Mk 25 Mod 2 starter composition is precisely the normal burning characteristics of the 2L-3C-5S formula.

3. To define "normal range of burning characteristics" we will review the laboratory data obtained in this study and develop from them a set of criteria which can then be tried against the behavior of production batches of Mk 25 starter composition.

4. The study of pressure-time curve data on the 2L-3C-5S formula covers the following range of variable factors:

a. Crystalline silicon, A.P.S. from 8.0 u to 14.0 u, JAN-S-230A, Type I, Grade A, Class 6.

b. Lead dioxide, A. P. S. from 0.65 u to 2.23 u, MIL-L-376A, Grade A.

c. Cupric oxide, A. P. S. from 1.4 u to 5.1 u, MIL-C-13600 (ORD).

d. Moisture, 0.2 maximum.

e. Contaminants which alter the burning properties of the silicon, none.

f. Density, composition placed in aluminum cup and tapped four times.

g. Supplier, indifferent.

The ranges of burning characteristics exhibited by the above factors are as follows:

Burning Characteristic	Symbol	Value Range
a. Burning rate	Θ	55°--68°
b. Maximum pressure	P_{max}	6.75-9.65 psi
c. Reaction time	tP_{max}	6.1-7.9 secs

5. Table XV shows the values for these three characteristics for 48 production batches manufactured at NAD Crane during late 1963. Only three samples fall outside these limits, all of which are on the low side: batches 408, 425, and 427. All have slow burning rates, and two have low P_{max} values, indicating a probable deficiency in PbO_2.

6. Finally, the heat of reaction should be 95% of the theoretical value of 385 cal/g--in other words, 365.7 cal/g minimum. This value is determined on the Paar Model 1200 adiabatic calorimeter under 25 atmospheres of argon gas. While calorimetry was not performed on these production batches, since this is a time consuming operation, future batches falling outside the proposed pressure-time curve limits should be further tested by calorimetry as well as chemical analysis to determine the cause of the deficiency and then reblended to meet the requirements.

Feasibility of Using Mk 25 Mod 2 Starter Composition In Other Phosphorus Signals

1. Work has not yet been done to determine the feasibility of using the 2L-3C-5S formula in other signals using the phosphorus composition such as the Mk 6-3 Marine Location Marker. This will require the manufacture and testing of completed signals.

Specification for the Mk 25 Mod 2 Starter Composition

1. A specification for the Mk 25 Mod 2 starter composition, covering component requirements, processing, and performance of the finished composition, is to be written based upon the findings set forth in this report.

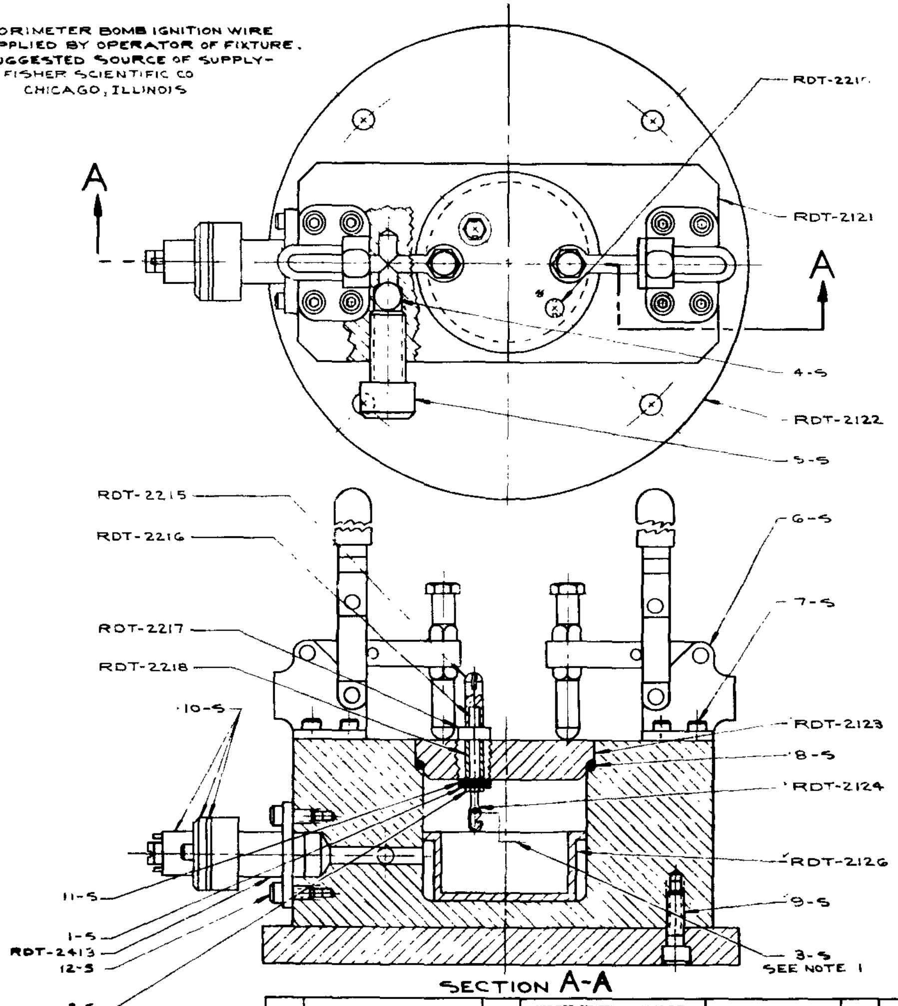
FIGURES

FIGURE 1

Apparatus for Determining Rate of Pressure Change

NOTES:

1. PARR CALORIMETER BOMB IGNITION WIRE TO BE SUPPLIED BY OPERATOR OF FIXTURE. SUGGESTED SOURCE OF SUPPLY-
FISHER SCIENTIFIC CO
CHICAGO, ILLINOIS



AMT.	PIECE NO.	NOMENCLATURE
1	RDT-2121	HOUSING
1	RDT-2122	BASE
1	RDT-2123	COVER
2	RDT-2124	ELECTRODE
1	RDT-2126	CUP
1	1-S	$\frac{3}{32}$ ID x $\frac{7}{16}$ OD x $\frac{1}{32}$ THICK STAINLESS STEEL WASHER
2	2-S	№ 3(.099) 48 NC-2B HEX NUT (STAINLESS STEEL)
AR	3-S	PARR CALORIMETER BOMB IGNITION WIRE
1	4-S	.375 DIA STAINLESS STEEL BALL
1	5-S	.500-13UNC-2A x 1 SOC HD CAP SCR
2	6-S	WESPO № 301 TOGGLE CLAMP
14	7-S	№ 8(.164)-32 NC-2A x $\frac{1}{2}$ SOC HD CAP SCR
1	8-S	$2\frac{3}{8}$ x $2\frac{1}{8}$ x $\frac{1}{8}$ "O" RING PARKER № 2-229 MS9021-229
4	9-S	.250-20UNC-2A x $\frac{3}{4}$ SOC HD CAP SCR
ONE ASS'M	10-S	PRESSURE TRANSDUCER - CONSOLIDATED ELECTRODYNAMICS TYPE 4-312
5	11-S	$\frac{1}{2}$ OD x $\frac{3}{16}$ ID x $\frac{1}{32}$ THICK MICA WASHER
6	12-S	№ 8(.164)-32 NC-2A x $\frac{3}{4}$ SOC HD CAP SCR
1	RDT-2215	CAP
1	RDT-2216	CONNECTOR
1	RDT-2217	SPACER
1	RDT-2218	GROMMET
1	RDT-2219	GROUND PLUG
1	RDT-2413	TRANSDUCER ADAPTER

RDT-2120

LTR.	DESCRIPTION	DATE
	REVISIONS	

UNLESS OTHERWISE SPECIFIED
REMOVE ALL BURRS AND SHARP EDGES
DIMENSIONS ARE IN INCHES
TOLERANCE ON FRACTIONS ±
DECIMALS ± ANGLES ±
DO NOT SCALE THIS DRAWING
MATERIAL
SPECIFICATIONS OF LATEST ISSUE APPLY

R & D APPROVAL		DATE
ENGINEER		
DESIGNED BY		
CHECKED BY	MARTIN	6-18-63
DRAWN BY	M. WOODS	6-7-63

APPROVED: 19
DIRECTOR

TEST FIXTURE, PRESSURE
FOR
MARKER, LOCATION, MARINE MK25
STARTER COMPOSITION

SCALE $\frac{1}{1}$

U.S.
NAVAL AMMUNITION DEPOT
CRANE, IND.
RESEARCH & DEVELOPMENT
DEPARTMENT

R & D DRAWING NO.
RDT-2120

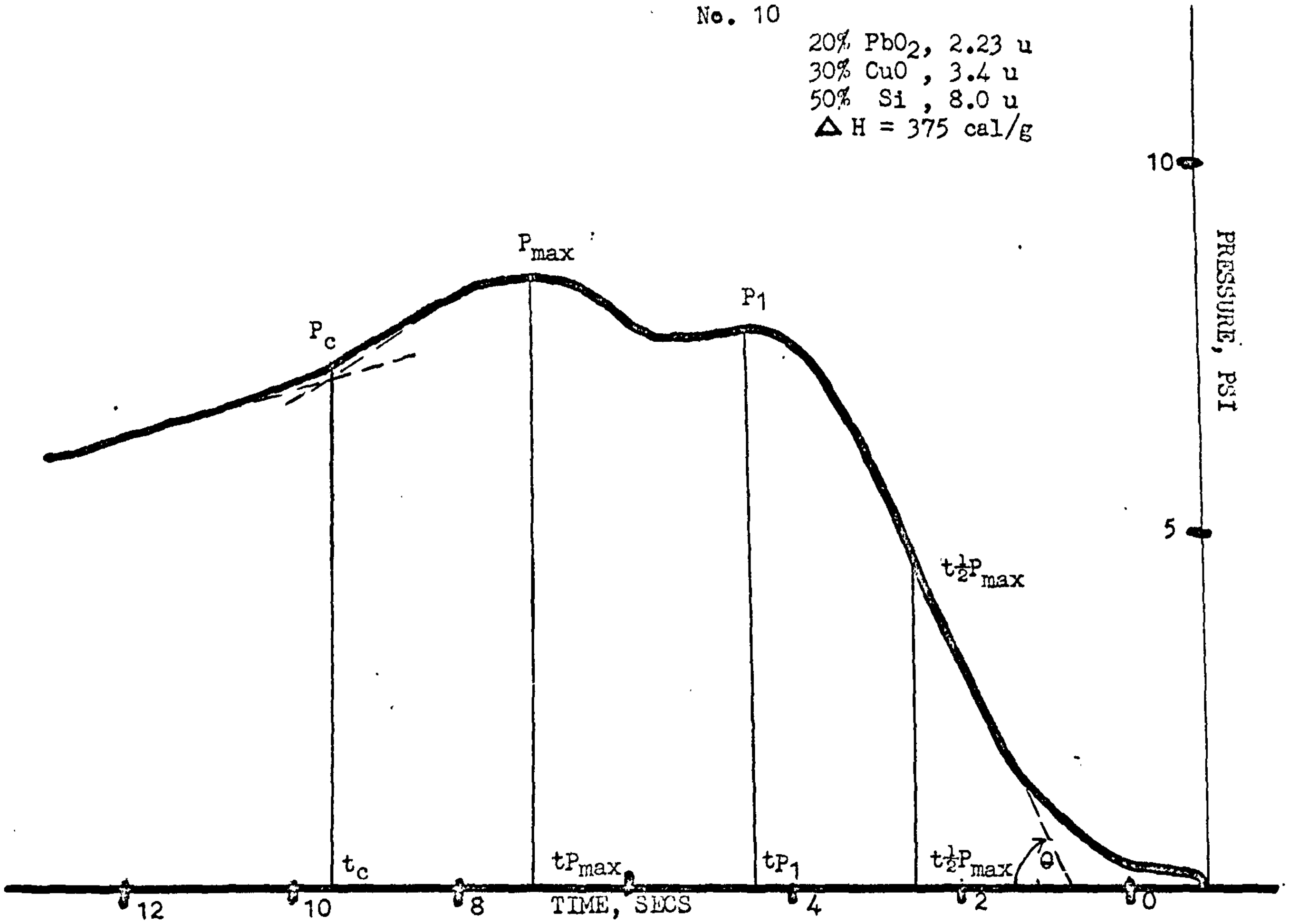


FIGURE 3. A PRESSURE-TIME CURVE OF A TYPICAL MK 25 MOD 2 STARTER COMPOSITION

$t_{\frac{1}{2}P_{max}}$ = 2.75 secs = the time at which one half of the maximum pressure is attained.

θ = 64° = the slope of the curve at $t_{\frac{1}{2}P_{max}}$.

tP_1 = 5 secs = time to the first peak, in the event there is more than one peak.

tP_{max} = 7.38 secs = time to the maximum pressure peak.

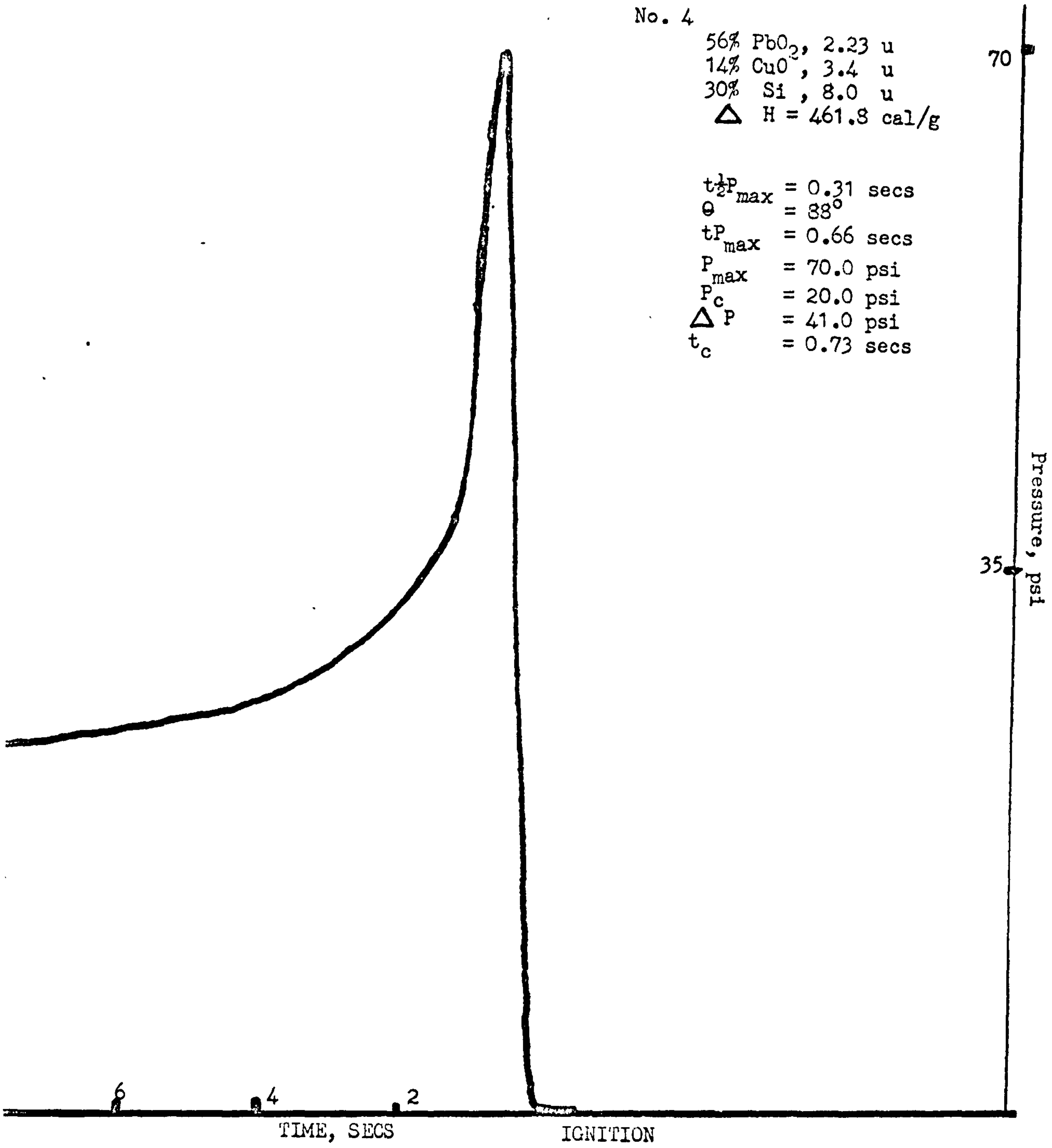
P_{max} = 8.5 psi = maximum pressure in psi.

P_c = 7.2 psi = pressure at which the normal cooling curve of the system is established.

ΔP = 1.3 psi = the difference between P_{max} and P_c.

ΔH = 375 cal/g = the heat of reaction. This value is not derived from the pressure-time curve, but from calorimetric determinations. It is included with the other data for convenient reference.

t_c = 10.5 secs = time until normal cooling cuve is established.



No. 4

56% PbO_2, 2.23 u
14% CuO, 3.4 u
30% Si, 8.0 u
$\Delta H = 461.8$ cal/g

$t_{\frac{1}{2}}P_{max} = 0.31$ secs
$\theta = 88^{\circ}$
$tP_{max} = 0.66$ secs
$P_{max} = 70.0$ psi
$P_c = 20.0$ psi
$\Delta P = 41.0$ psi
$t_c = 0.73$ secs

FIGURE 4. A PRESSURE–TIME CURVE OF A RAPID BURNING HIGH ENERGY STARTER COMPOSITION

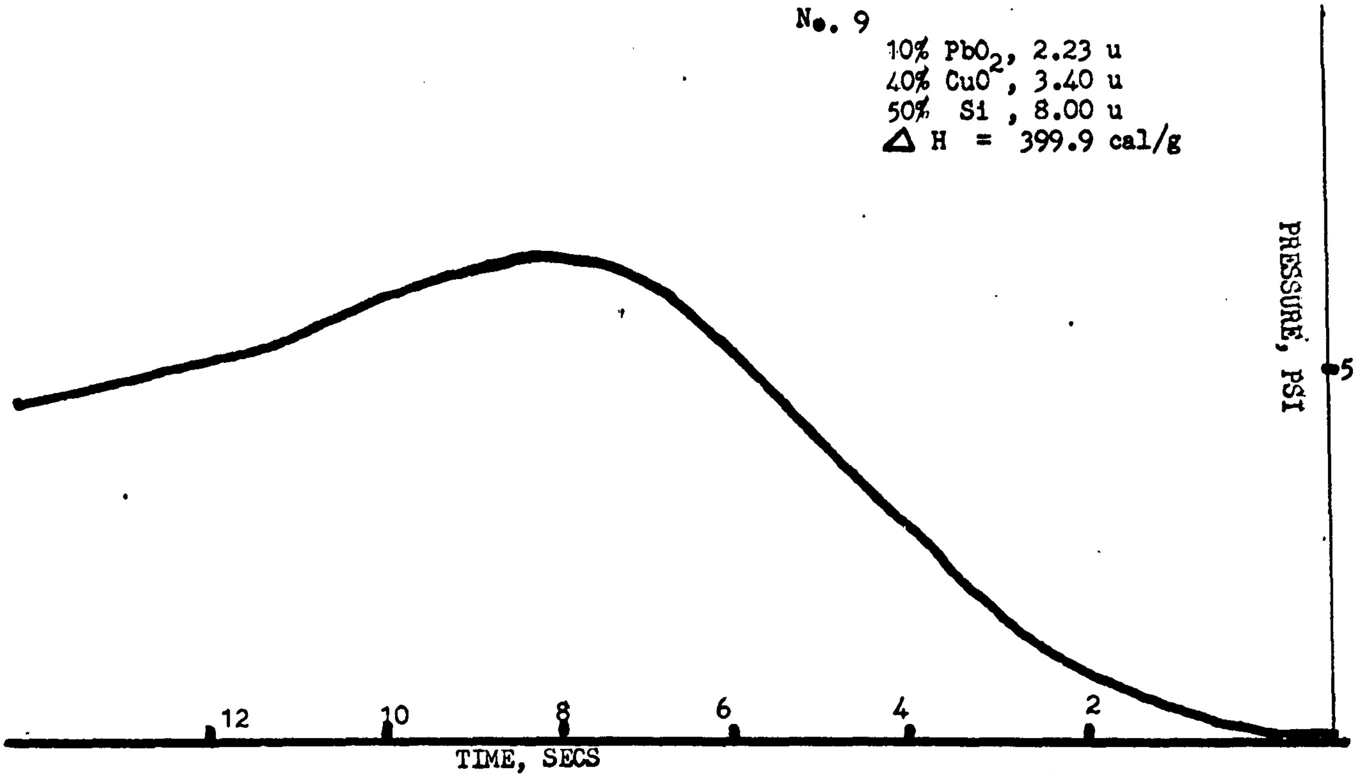


FIGURE 5. A PRESSURE–TIME CURVE OF A HIGH–CuO, LOW– PbO_2 COMPOSITION

$t_{\frac{1}{2}}\,P_{max}$ = 4.75 secs

θ = 45°

tP_{max} = 8.38 secs

P_{max} = 6.45 psi

P_c = 5.88 psi

ΔP = 0.57 psi

t_c = 10.5 secs

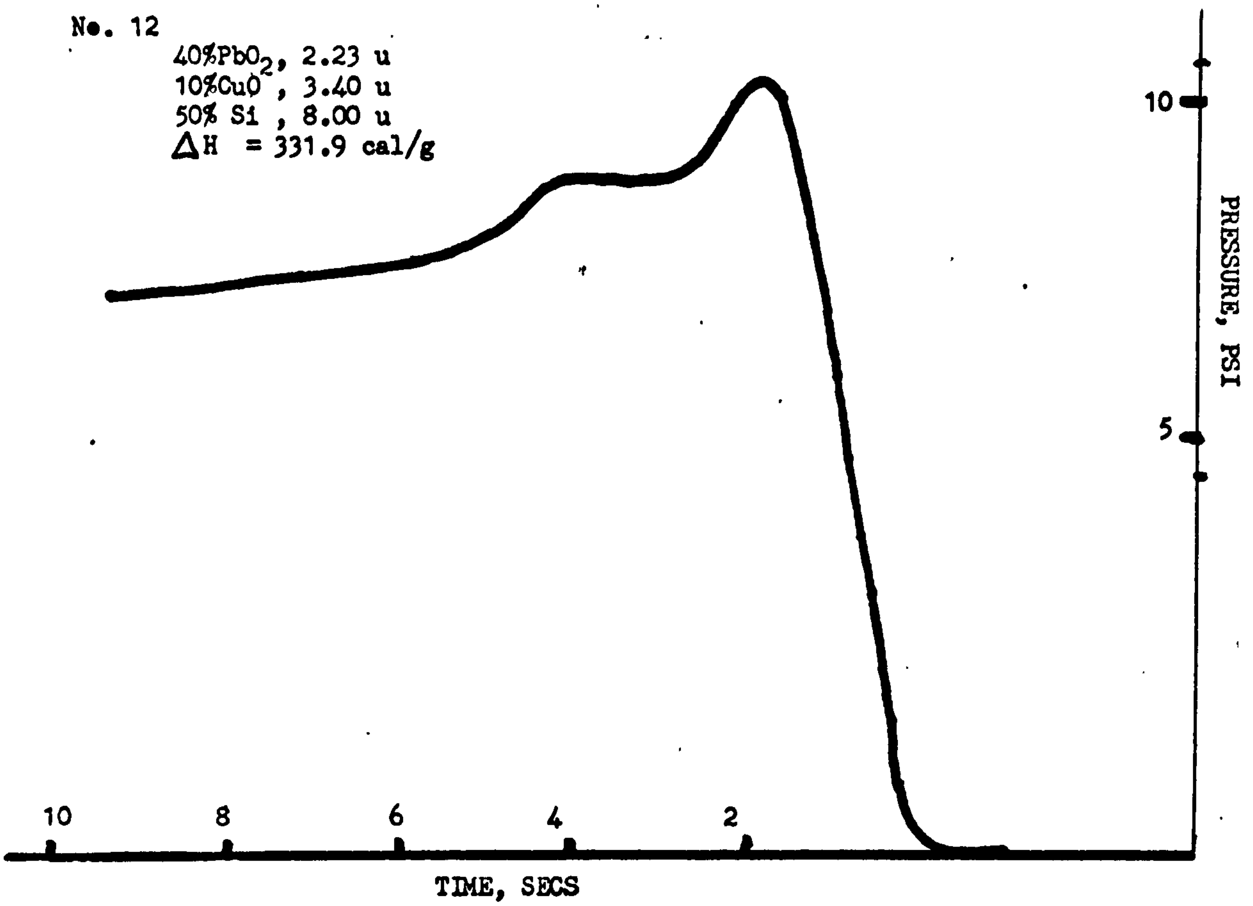


FIGURE 6. A PRESSURE - TIME CURVE OF A HIGH- PbO_2, LOW- CuO STARTER COMPOSITION

$t_{\frac{1}{2}P_{max}}$ = 0.94 secs

θ = 82°

tP_{max} = 2.0 secs

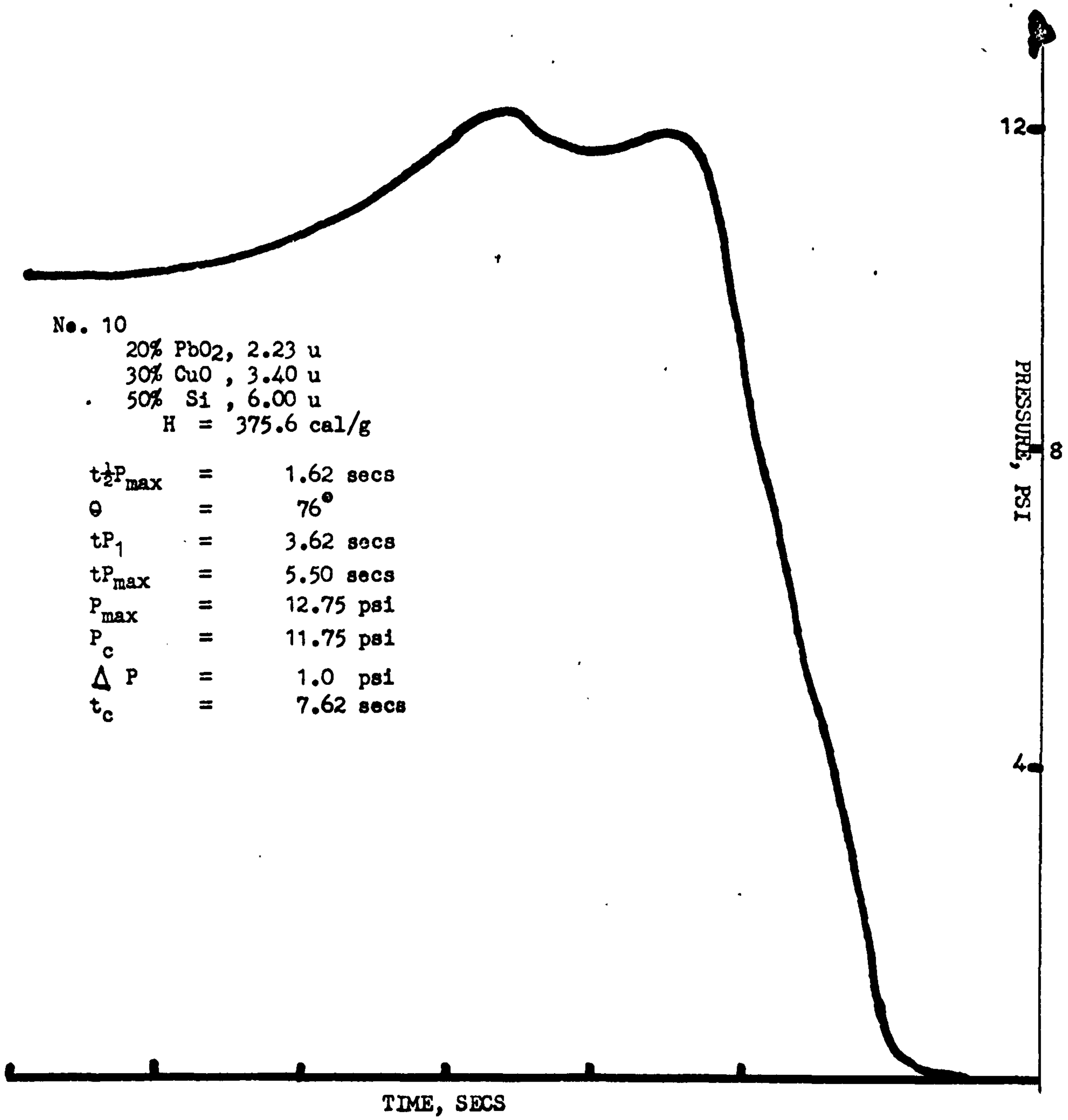
tP_2 = 4.4 secs

P_{max} = 10.4 psi

P_c = 7.75 psi

ΔP = 2.65 psi

t_c = 5.9 secs



No. 10

20% PbO_2, 2.23 u
30% CuO , 3.40 u
50% Si , 6.00 u
H = 375.6 cal/g

$t_{\frac{1}{2}}P_{max}$ = 1.62 secs
θ = 76°
tP_1 = 3.62 secs
tP_{max} = 5.50 secs
P_{max} = 12.75 psi
P_c = 11.75 psi
ΔP = 1.0 psi
t_c = 7.62 secs

FIGURE 7. PRESSURE–TIME CURVE OF MK 25 MOD 2 STARTER COMPOSITION MADE WITH AN ATYPICAL SILICON

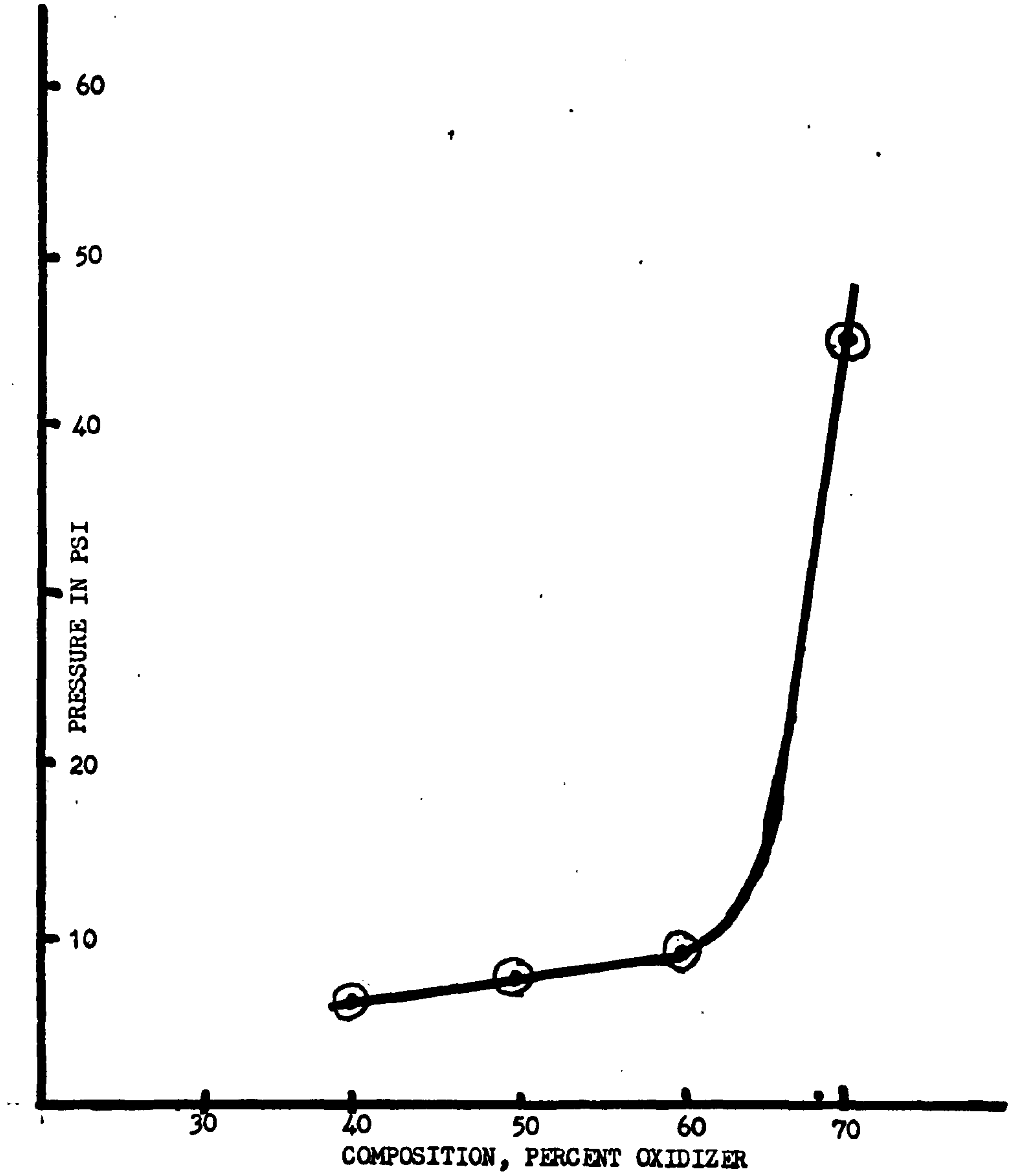
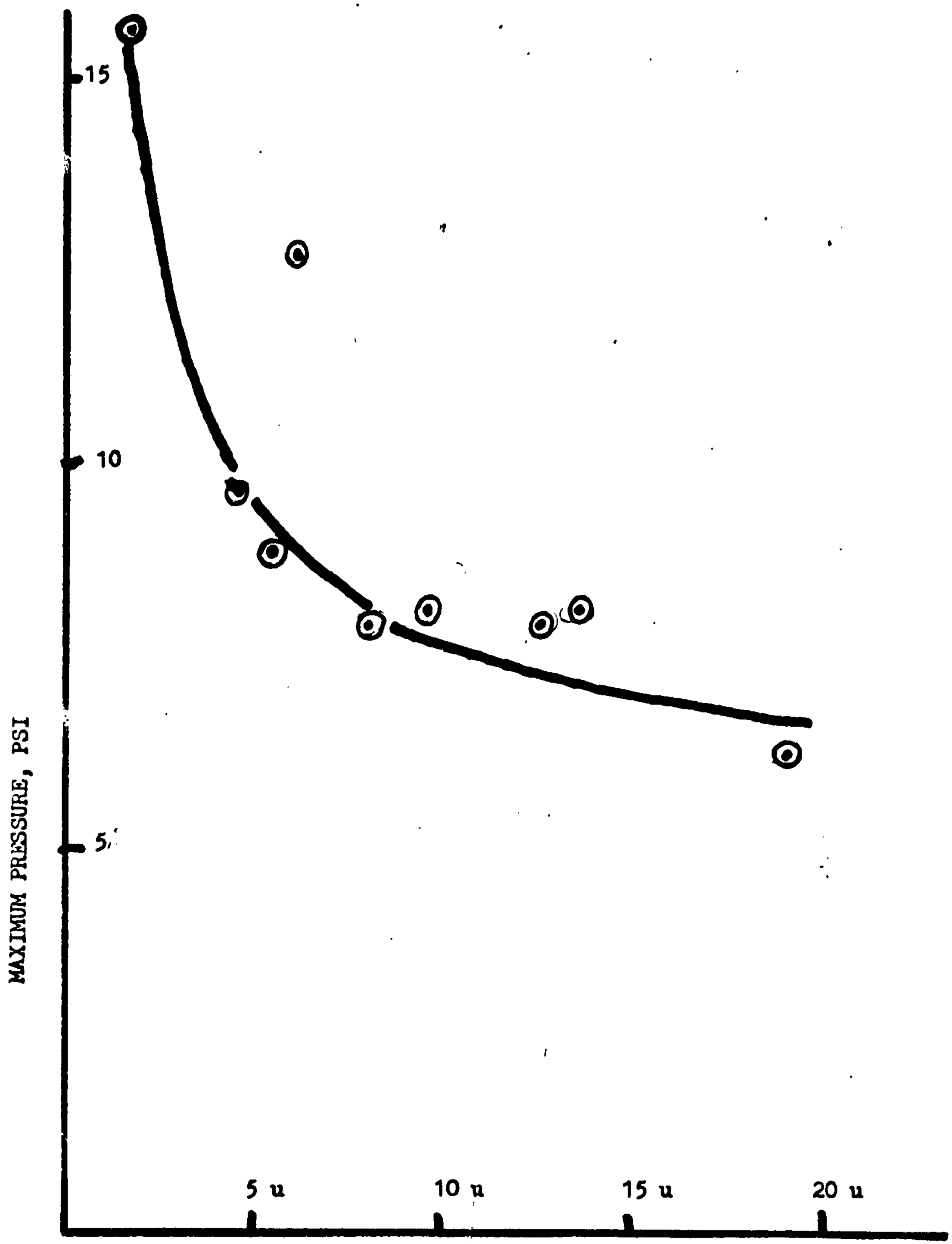


FIGURE 8. GRAPH SHOWING INCREASE IN PRESSURE AS PERCENT OXIDIZER INCREASES
(RATIO OF PbO_2 to CuO is 1:1.5 in all instances)



SILICON AVERAGE PARTICLE SIZE, MICRONS

FIGURE 9 EFFECT OF SILICON PARTICLE SIZE VARIATION ON P_{max} OF PRESSURE-TIME CURVE FOR 2I - 3C - 5S FORMULATION

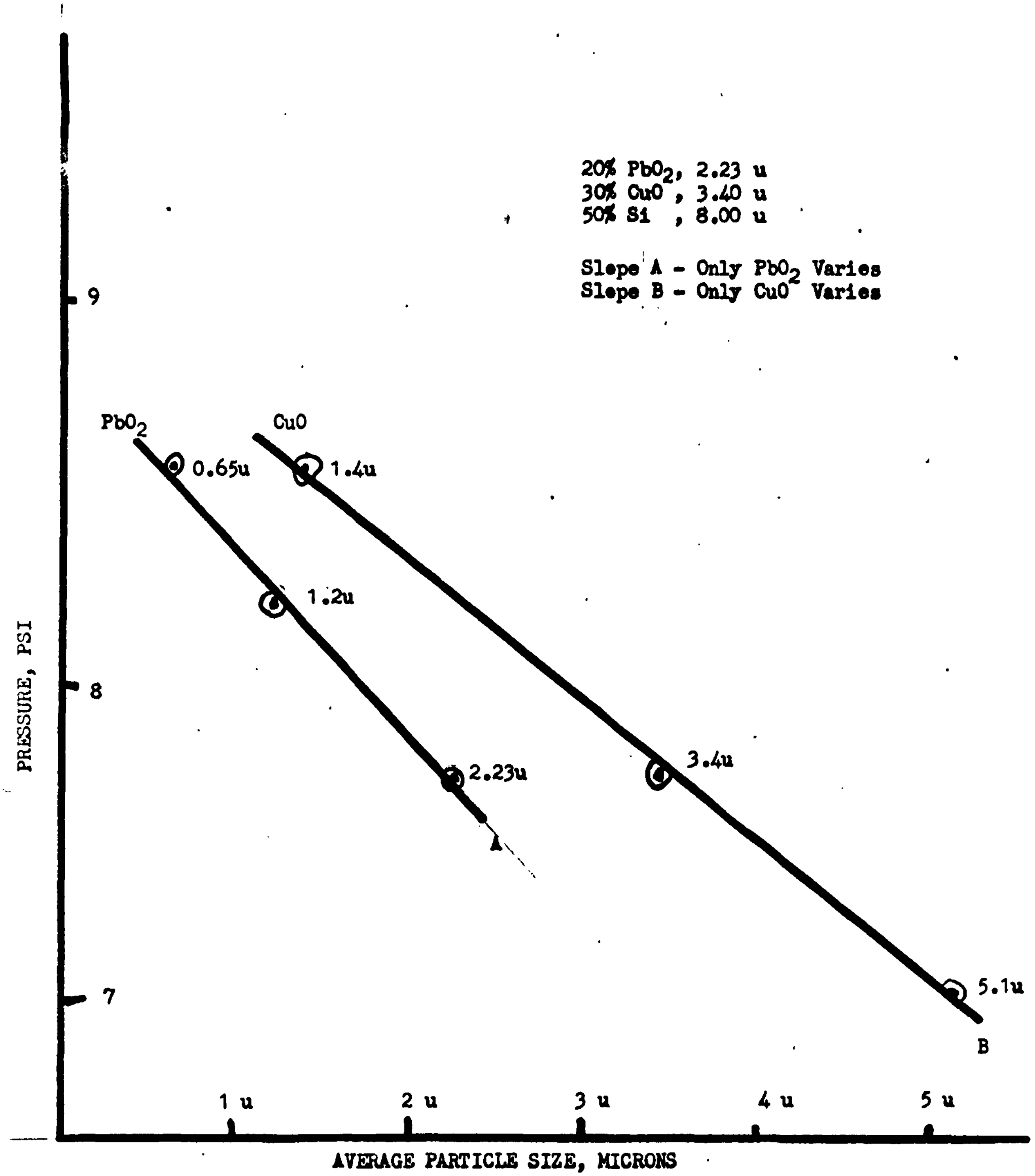
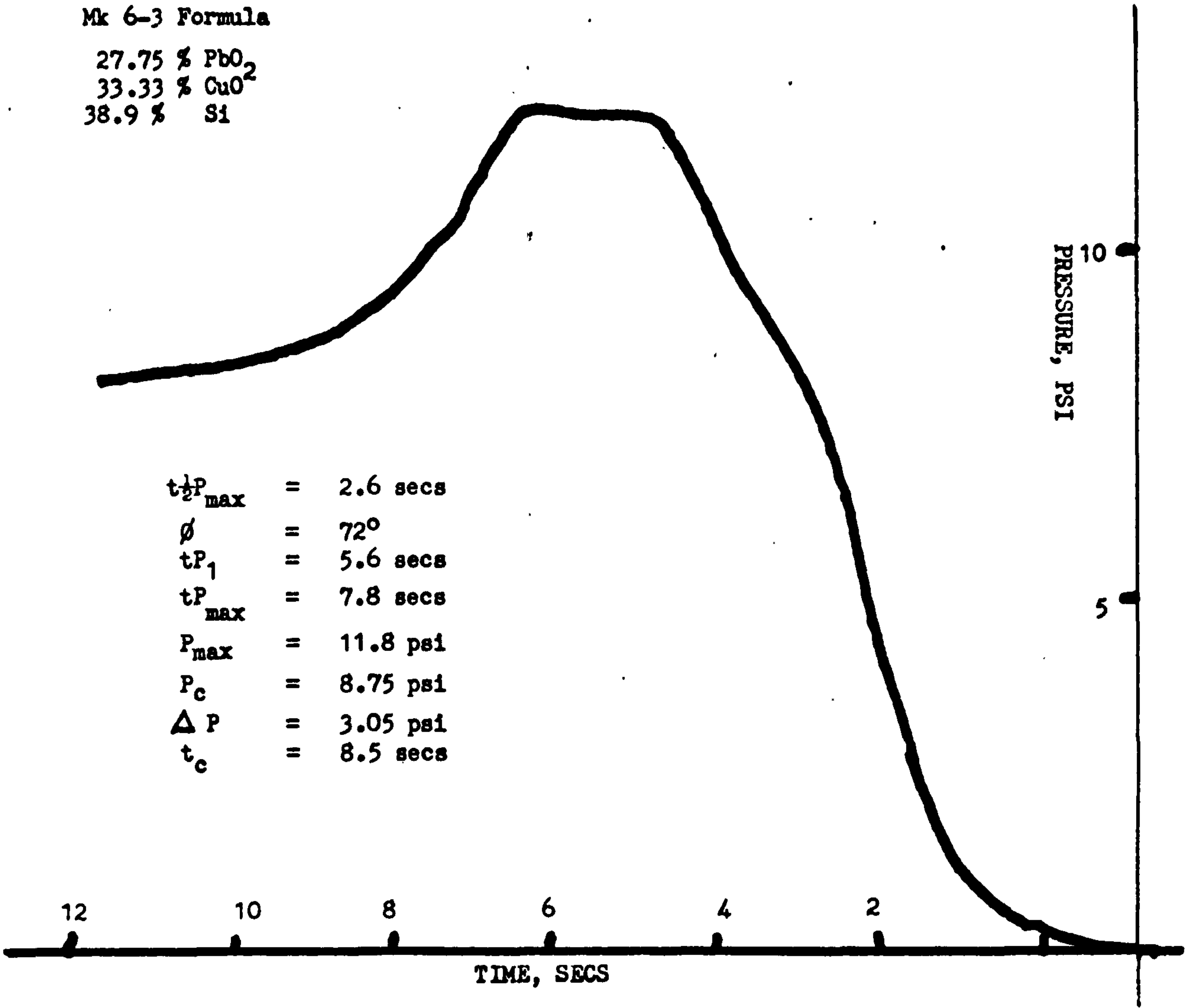


FIGURE 10. EFFECT OF PbO_2 and CuO PARTICLE SIZE VARIATION ON P_{max} OF PRESSURE-TIME CURVE FOR 2L - 3C - 5S FORMULATION

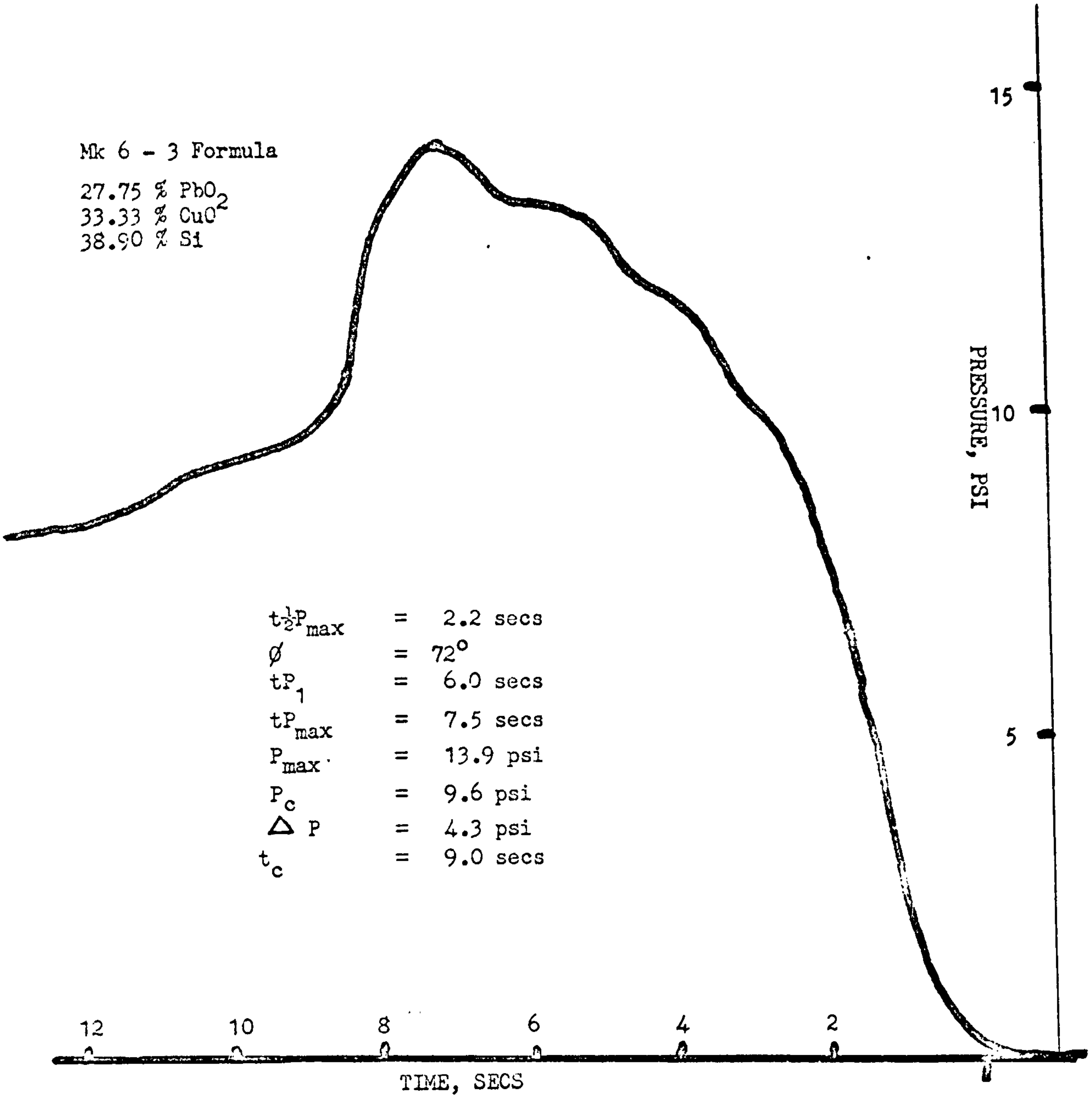


Mk 6-3 Formula

27.75 % PbO_2
33.33 % CuO
38.9 % Si

$t_{\frac{1}{2}P_{max}}$ = 2.6 secs
ϕ = 72°
tP_1 = 5.6 secs
tP_{max} = 7.8 secs
P_{max} = 11.8 psi
P_c = 8.75 psi
ΔP = 3.05 psi
t_c = 8.5 secs

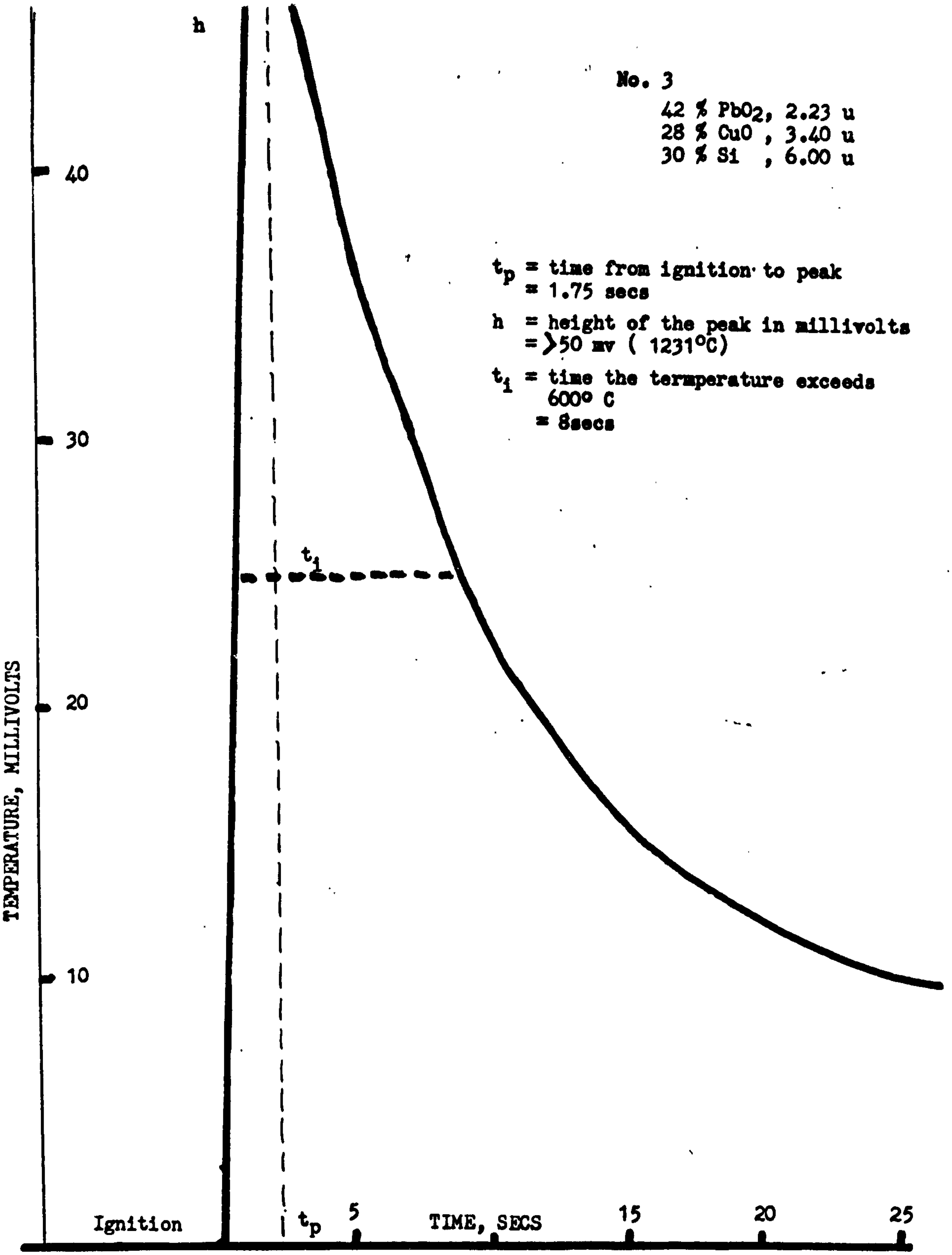
FIGURE 11. PRESSURE – TIME CURVE OF MK 6 – 3 STARTER COMPOSITION AFTER DRYING IN THE DESICCATOR FOR 36 HOURS


Mk 6 - 3 Formula

27.75 % PbO_2
33.33 % CuO
38.90 % Si

$t\frac{1}{2}P_{max}$ = 2.2 secs
Ø = 72°
tP_1 = 6.0 secs
tP_{max} = 7.5 secs
P_{max} = 13.9 psi
P_c = 9.6 psi
ΔP = 4.3 psi
t_c = 9.0 secs

FIGURE 12. PRESSURE-TIME CURVE OF MK 6 - 3 STARTER COMPOSITION AFTER 36-HOUR EXPOSURE TO HIGH ATMOSPHERIC HUMIDITY



No. 3
42 % PbO_2, 2.23 u
28 % CuO , 3.40 u
30 % Si , 6.00 u

t_p = time from ignition to peak
= 1.75 secs

h = height of the peak in millivolts
= >50 mv (1231°C)

t_i = time the termperature exceeds
600° C
= 8secs

FIGURE 13. HEAT TRANSFER CURVE OF A HIGH ENERGY STARTER COMPOSITION

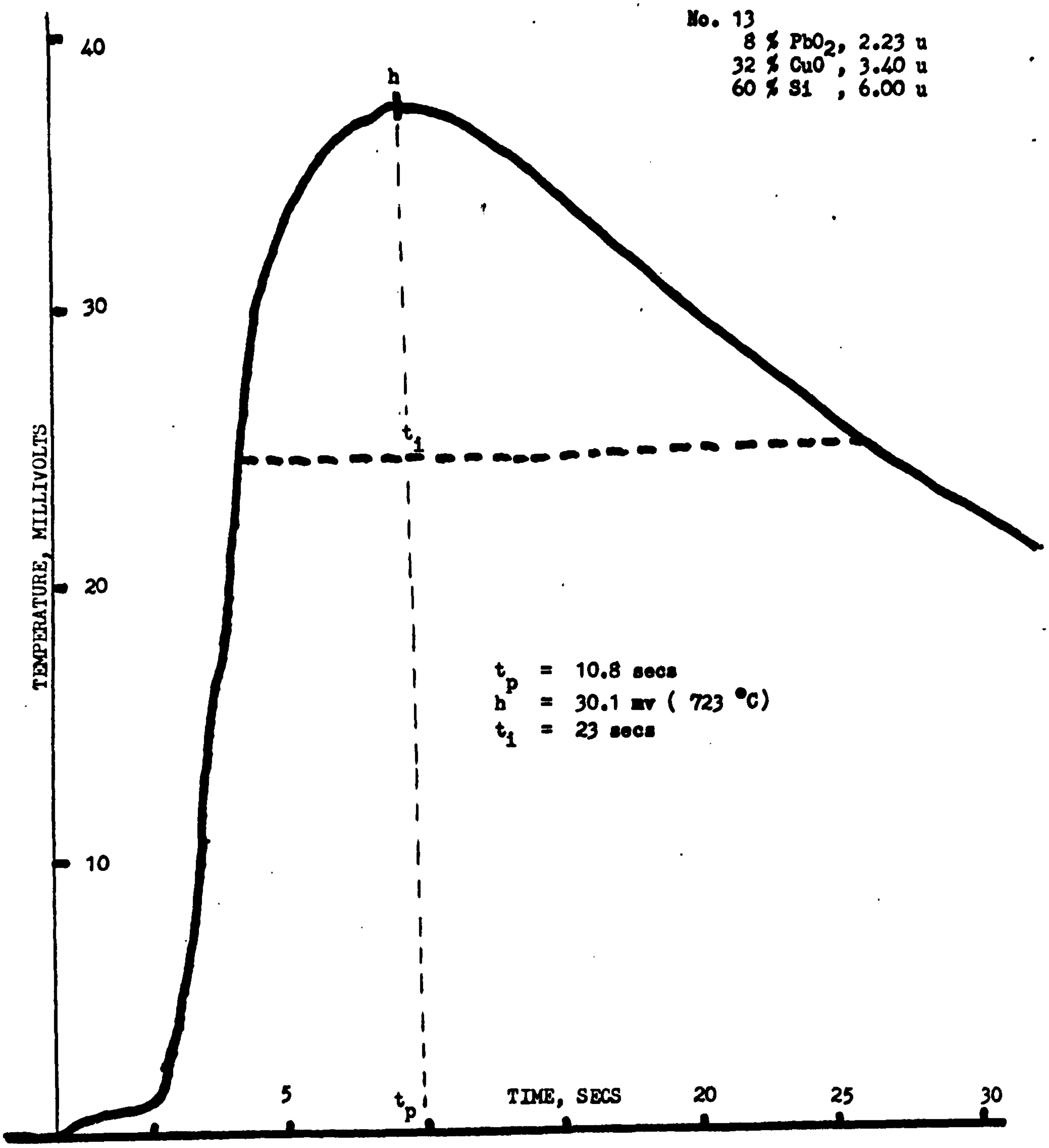
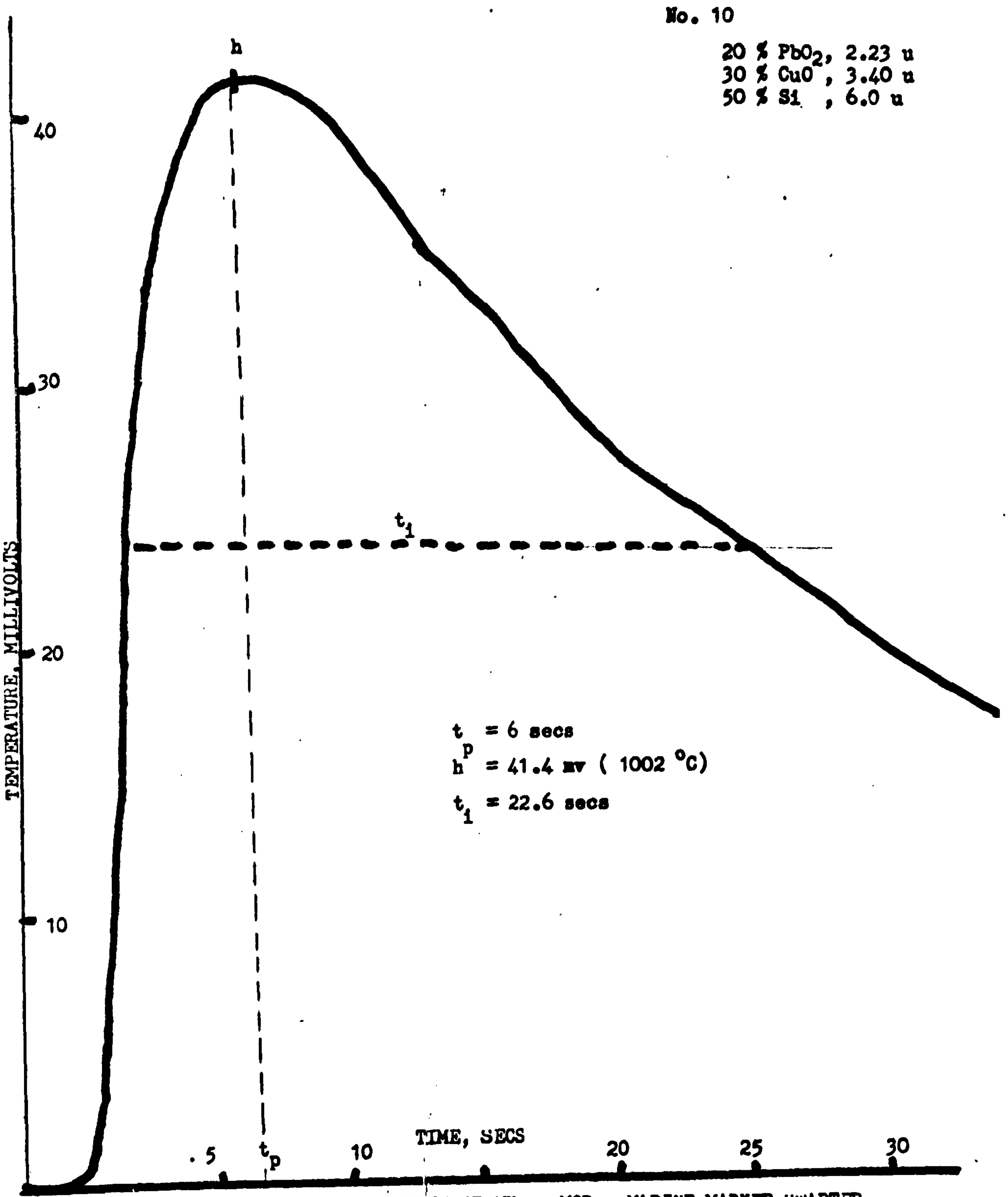


FIGURE 14. HEAT TRANSFER CURVE OF LOW ENERGY STARTER COMPOSITION



No. 10

20 % PbO_2, 2.23 u
30 % CuO , 3.40 u
50 % Si , 6.0 u

t_p = 6 secs
h_p = 41.4 mv (1002 °C)
t_i = 22.6 secs

FIGURE 15. HEAT TRANSFER CURVE OF MK 25 MOD 2 MARINE MARKER STARTER COMPOSITION

APPENDIX

TABLE I

BASIC STATISTICAL FAMILY OF STARTER MIX COMBINATIONS USED IN THIS STUDY

Si : PbO_2-CuO RATIO		PbO_2 : CuO RATIO			
		1 : 4	1 : 1.5	1.5 : 1	4 : 1
1 : 2.33	Si = 30 %	No. 1 PbO_2=14% CuO =56%	No. 2 PbO_2=28% CuO =42%	No. 3 PbO_2=42% CuO =28%	No. 4 PbO_2=56% CuO =14%
1 : 1.5	Si = 40 %	No. 5 PbO_2=12% CuO =48%	No. 6 PbO_2=24% CuO =36%	No. 7 PbO_2=36% CuO =24%	No. 8 PbO_2=48% CuO =12%
1 : 1	Si = 50%	No.9 PbO_2=10% CuO =40%	No.10 PbO_2=20% CuO =30%	No. 11 PbO_2=30% CuO =20%	No. 12 PbO_2=40% CuO =10%
1.5 : 1	Si = 60 %	No. 13 PbO_2=8% CuO =32%	No. 14 PbO_2=16% CuO =24%	No. 15 PbO_2=24% CuO =16%	No. 16 PbO_2=32% CuO =8%

TABLE II

BASIC STATISTICAL FAMILY OF STARTER MIX COMBINATIONS USED IN THIS STUDY

FUEL TO OXIDIZER RATIO = 1 : 2.33						
No.	SILICON		LEAD DIOXIDE		CUPRIC OXIDE	
	%	Ratio	%	Ratio	%	Ratio
1.	30	2.14	14	1.0	56	4.0
2.	30	1.07	28	1.0	42	1.5
3.	30	1.07	42	1.5	28	1.0
4.	30	2.14	56	4.0	14	1.0
FUEL TO OXIDIZER RATIO = 1 : 1.5						
5.	40	3.33	12	1.0	48	4.0
6.	40	1.67	24	1.0	36	1.5
7.	40	1.67	36	1.5	24	1.0
8.	40	3.33	48	4.0	12	1.0
FUEL TO OXIDIZER RATIO = 1 : 1						
9.	50	5.0	10	1.0	40	4.0
10.	50	2.5	20	1.0	30	1.5
11.	50	2.5	30	1.5	20	1.0
12.	50	5.0	40	4.0	10	1.0
FUEL TO OXIDIZER RATIO = 1.5 : 1						
13.	60	7.5	8	1.0	32	4.0
14.	60	3.75	16	1.0	24	1.5
15.	60	3.75	24	1.5	16	1.0
16.	60	7.5	32	4.0	8	1.0

TABLE III

CALORIMETRY ON STATISTICAL FAMILY OF 16 STARTER MIX COMBINATIONS
(For 6 Micron SILICON)

SAMPLE NO. *	HEAT OF REACTION		
	EXPERIMENTAL	THEORETICAL	% OF THEORETICAL
1.	575.5 cal/g	570.0 cal/g	100.9 %
2.	530.7	538.6	98.5
3.	495.1	506.4	97.8
4.	461.8	474.4	97.3
5.	456.0	488.9	93.3
6.	436.4	461.6	94.5
7.	410.1	434.4	96.0
8.	390.6	406.8	96.0
9.	399.9	407.4	98.2
10.	375.6	384.3	97.7
11.	355.7	362.0	98.3
12.	331.9	339.0	97.9
13.	no fire	—	—
14.	298.3	307.8	96.9
15.	280.3	289.6	96.8
16.	264.3	271.5	97.3

TABLE IV

CALORIMETRY ON FOUR RANDOM SAMPLES OF 16 STARTER MIX COMBINATIONS
(For 8.0 Micron SILICON)

3.	493.3	506.4	97.4
7.	413.2	434.4	95.1
10.	374.6	384.3	97.4
16.	267.0	271.5	98.3

Note: All samples made with 2.23 micron PbO_2 and 3.40 micron CuO.

*** Refer to Table I for composition of each sample number.**

TABLE V

PRESSURE - TIME CURVE DATA FOR 8.0 MICRON SILICON

** No.	$t_{\frac{1}{2}}P_{max}$	Ø	tP_1	tP_{max}	P_{max}	P_c	ΔP	t_c
1.	0.5 sec	84.5°	---	1.6 sec	36.5 psi	20.5 psi	16.0 psi	2.88 se
2.	0.75	83.0	---	1.38	45.5	25.0	20.5	2.25
3.	0.5	86.0	---	1.12	48.0	23.5	24.5	1.62
4.	0.37	88.0	---	0.75	56.0	22.5	33.5	1.37
5.	5.38	38.0	---	11.75	8.75	7.94	0.81	15.75
6.	3.68	56.0	---	7.88	9.75	8.94	0.81	9.38
7.	2.55	65.0	---	5.5	9.88	8.25	1.63	7.12
8.	0.88	86.0	1.75 sec	2.12	16.75	8.50	8.25	4.38
9.	4.75	45.0	---	8.38	6.45	5.88	0.57	10.5
10.	2.75	66.0	5.0	7.38	7.90	6.75	1.15	9.31
11.	1.75	74.0	5.50*	3.25*	8.38	7.13	1.25	7.75
12.	0.94	82.0	4.40*	2.00*	10.40	7.75	2.65	5.90
13.	Composition too insensitive to be ignited by normal means.							
14.	3.25	47.0	---	8.75	6.50	5.50	1.00	11.00
15.	2.25	68.0	3.38	7.00	6.88	6.00	0.88	8.75
16.	1.50	77.0	5.50*	2.38*	7.83	6.95	0.88	7.00

* Note: Indicates that the maximum peak is now the first peak instead of the second peak.

All samples made with 2.23 micron PbO_2 and 3.40 micron CuO.

See Figure 3 for explanation of terms.

** Refer to Table I for composition of each sample number.

TABLE VI

PRESSURE - TIME CURVE DATA FOR 6.0 MICRON SILICON

**No.	$t_{\frac{1}{2}}P_{max}$	Ø	tP_1	tP_{max}	P_{max}	P_c	ΔP	t_c
1.	0.59sec	86.0°	---	1.16sec	60.5 psi	30.0psi	30.5psi	2.08sec
2.	0.69	87.0	---	1.39	60.3	30.3	30.0	1.94
3.	0.44	88.0	---	1.00	70.0	28.5	41.5	1.50
4.	0.31	88.0	---	0.66	70.0	29.0	41.0	0.73
5.	4.00	56.5	---	8.50	12.3	11.25	1.05	10.00
6.	1.56	80.3	5.60*	3.38*	15.3	12.40	2.90	7.25
7.	0.63	85.0	---	2.25	17.9	12.50	5.40	5.25
8.	0.38	88.0	---	1.00	20.6	13.10	7.50	3.70
9.	3.40	66.0	---	8.00	11.9	11.3	1.30	11.5
10.	1.62	76.0	3.62	5.50	12.8	11.8	1.00	7.62
11.	1.00	84.0	5.12*	2.12*	15.3	12.5	2.75	7.75
12.	0.50	87.6	1.25	3.25	21.4	13.1	3.90	5.75
13.	Composition too insensitive to be ignited by normal means.							
14.	2.88	69.0	---	8.38	15.3	13.9	1.40	10.00
15.	1.69	79.0	---	5.50	18.3	17.3	1.00	8.40
16.	1.63	82.5	---	4.13	21.5	20.3	1.20	7.25

* Note: Indicates that the maximum peak is now the first peak instead of the second peak.

All samples made with 2.23 micron PbO_2 and 3.40 micron CuO.

** Refer to Table I for composition of each sample number.

TABLE VII

VISUAL BURNING TIME OF BASIC STARTER MIX COMBINATIONS FOR 6.0 MICRON SILICON

Burning time in seconds of 12 grams pressed in a 0.75" I.D. X 2" length steel body under a dead load weight of 2.5 kg to expel air.

(1) ** *	(2) *	(3) *	(4) *
(5) 11.0 secs 11.3 10.5 12.5 12.4 12.4 10.0	(6) 7.5 secs 7.4 7.6	(7) 4.5 secs 4.6 4.6	(8) 2.9 secs 2.9
(9) 10.0 secs 9.2 9.8	(10) 6.8 secs 6.8 7.4 6.8 6.5 6.7 6.9	(11) 4.8 secs 4.8	(12) 3.4 secs 3.7
(13) 21.9 secs 21.2 19.0	(14) 12.4 secs 11.8 12.0 11.8 10.5	(15) 7.9 secs 7.6 7.7 7.8	(16) 5.4 secs 5.6 5.9 5.8

* Note: Burns explosively.

** Refer to Table I for composition of each sample number.

TABLE VIII

HEAT TRANSFER DATA ON STARTER MIX STATISTICAL FAMILY FOR 6.0 MICRON SILICON **

(1)* h = 44.6 mv t_p = 3.0 secs t_i = 14.75 secs	(2)*	(3)* $>$ 50 mv 1.75 secs 8.00 secs	(4)*
(5) = 40.5 mv = 5.6 secs = 26.2 secs	(6) 41.2 mv 4.97 secs 20.1 secs	(7) 43.5 mv 4.37 secs 16.8 secs	(8) 46.5 mv 3.2 secs 14.9 secs
(9) = 36.7 mv = 8.0 secs = 23.6 secs	(10) 40.5 mv 7.0 secs 22.1 secs	(11) 43.0 mv 5.6 secs 21.2 secs	(12) 47.5 mv 4.2 secs 19.2 secs
(13) = 36.2 mv = 10.9 secs = 21.4 secs	(14) 37.6 mv 6.3 secs 19.5 secs	(15) 38.9 mv 5.5 secs 17.9 secs	(16) 37.5 mv 5.1 secs 18.5 secs

h = the peak height in millivolts.
t_p = the time interval to the peak.
t_i = the time the temperature of the burning and cooling sample exceeds 600° C.

* Note: Explosive burning.

** Refer to Table I for composition of each sample number.

TABLE IX

TIME ABOVE 600 °C AS DETERMINED ON THE HEAT TRANSFER APPARATUS FOR 8.0 MICRON SILICON ***

(1) *	(2) *	(3) *	(4) *
(5) **	(6)	(7)	(8)
22.75 secs 23.00 secs	26.00 secs 26.25 secs	22.00 secs	17.50 secs
(9) **	(10)	(11)	(12)
17.75 secs 15.25 secs	22.50 secs	18.50 secs 19.75 secs 23.80 secs	18.25 secs
(13) **	(14) **	(15)	(16)
	18.00secs 16.75 secs	19.50 secs	16.00 secs 16.25 secs

*Note: Burns explosively.

**Note: Difficult to ignite with an electric match.

*** Refer to Table I for composition of each sample number.

TABLE X

EFFECT OF SILICON PARTICLE SIZE VARIATION ON THE PRESSURE - TIME CURVE

No.	$t_{\frac{1}{2}}P_{max}$	ϕ	tP_{max}	P_{max}	P_c	ΔP	t_c	ΔH
1.	0.5 sec	87.0°	2.0 sec	15.6 psi	10.8 psi	4.9 psi	4.4 sec	416cal/g
2.	1.2	76.0	3.5	9.56	7.63	1.9	7.5	---
3.	1.6	72.0	5.5	8.80	7.60	1.2	7.8	---
4.	1.8	75.0	4.3	12.8	10.8	2.0	7.9	375.0
5.	2.8	63.0	7.4	7.90	6.8	1.1	9.3	374.6
6.	2.7	60.0	6.3	8.1	7.3	0.8	9.6	373.7
7.	2.5	65.0	7.3	7.9	7.1	0.8	9.8	---
8.	3.0	57.0	7.1	8.1	7.7	0.4	11.0	358.0
9.	4.5	33.0	9.5	6.3	4.9	1.4	17.0	372.6

No. 1 = P.A. 562 amorphous silicon, average particle size 1.65 microns.
No. 2 = Hummel cubic silicon, a. p. s. 4.6 u.
No. 3 = Hummel cubic silicon, a. p. s. 5.1 u.
No. 4 = Hummel cubic silicon, a. p. s. 6.0 u.
No. 5 = Glidden cubic silicon, a. p. s. 8.0 u.
No. 6 = Glidden cubic silicon, a. p. s. 9.4 u.
No. 7 = Hummel cubic silicon, a. p. s. 12.4 u.
No. 8 = Hummel cubic silicon, a. p. s. 13.6 u.
No. 9 = Hummel cubic silicon, a. p. s. 19.0 u.

Note: All samples made from 2.23 u PbO_2 and 3.40 u CuO. All samples are the 2L - 3C - 5S formula.

TABLE XI

EFFECT OF LEAD DIOXIDE AND CUPRIC OXIDE PARTICLE SIZE VARIATION ON PRESSURE - TIME CURVES FOR 8.0 MICRON SILICON

No.	$t\frac{1}{2}P_{max}$	ϕ	tP_1	tP_{max}	P_{max}	P_c	ΔP	t_c
1.	2.4 sec	64.0°	4.5 sec	6.6 sec	7.6 psi	7.0 psi	0.6 psi	9.3 sec
2.	2.6	66.0	5.4	8.0	8.1	6.5	1.6	9.8
3.	2.6	62.0	4.6	6.4	8.5	8.1	0.4	8.5
4.	2.9	61.0	- -	7.0	7.0	6.1	0.9	8.9
5.	2.4	67.0	4.9	7.3	8.5	7.5	1.0	9.4
6.	2.5	68.0	5.3	7.8	9.5	8.4	1.1	9.1

No. 1 = 8 u Si; 3.4 u CuO; 2.23 u PbO_2.
No. 2 = 8 u Si; 3.4 u CuO; 1.2 u PbO_2.
No. 3 = 8 u Si; 3.4 u CuO; 0.65 u PbO_2.
No. 4 = 8 u Si; 5.1 u CuO; 2.23 u PbO_2.
No. 5 = 8 u Si; 1.4 u CuO; 2.23 u PbO_2.
No. 6 = 8 u Si; 1.4 u CuO; 0.65 u PbO_2.

Note: All samples are the 2L - 3C - 5S formula.

TABLE XII

PRESSURE - TIME CURVE DATA ON COMPOSITIONS WITH DIFFERENT PARTICLE SIZES

No.	$t_{\frac{1}{2}P_{max}}$	∅	tP_{max}	P_{max}	P_c	ΔP	t_c	ΔH
1.	2.75sec	66.0°	7.4 sec	7.9 psi	6.8 psi	1.1 psi	9.3 sec	375 cal/g
2.	1.62	76.0	5.5	12.8	11.8	1.0	7.6	375.6
3.	2.50	60.0	6.3	8.1	7.3	0.8	9.6	373.7
4.	3.00	57.0	7.1	8.1	7.7	0.4	11.0	358.0
5.	1.78	74.0	5.8	12.9	11.0	1.9	8.9	377.0
6.	2.03	75.0	6.9	14.2	12.0	2.2	9.2	375.2
7.	1.88	68.5	8.4	12.6	11.2	1.4	8.4	373.5
8.	1.99	71.5	7.2	14.4	12.2	2.2	8.2	374.2

No. 1 = 8 u Si; 3.4 u CuO; 2.23 u PbO_2.
No. 2 = 6 u Si; 3.4 u CuO; 2.23 u PbO_2.
No. 3 = 9.4 u Si; 3.4 u CuO; 2.23 u PbO_2.
No. 4 = 13.6 u Si; 3.4 u CuO; 2.23 u PbO_2.
No. 5 = 6 u Si; 5.10 u CuO; 2.23 u PbO_2.
No. 6 = 6 u Si; 1.41 u CuO; 2.23 u PbO_2.
No. 7 = 6 u Si; 3.4 u CuO; 1.2 u PbO_2.
No. 8 = 6 u Si; 3.4 u CuO; 0.65 u PbO_2.

Note: All samples have the 2L - 3C - 5S formula.

TABLE XIII

PRESSURE - TIME CURVE DATA ON COMPOSITIONS MADE FROM COMPONENTS FROM VARIOUS SUPPLIERS*

No.	$t_{\frac{1}{2}P_{max}}$	ϕ	tP_{max}	P_{max}	P_c	ΔP	t_c	ΔH
1.	2.62 sec	68.5°	8.4 sec	13.2 psi	11.8 psi	1.4 psi	9.3 sec	375.5cal/g
2.	2.25	77.5	8.1	14.6	12.2	2.4	9.1	379.2
3.	2.62	75.0	7.3	14.6	12.8	1.8	10.7	374.2
4.	1.75	75.0	6.9	14.4	12.1	2.3	8.3	375.2
5.	2.72	65.0	8.2	8.1	7.3	0.8	9.6	373.7
6.	3.50	59.0	7.8	8.9	7.7	1.2	10.6	358.0

No. 1 = Baker & Adamson PbO_2 with average particle size of 1.2 u.
No. 2 = Shepherd 2.5 u PbO_2.
No. 3 = Eagle-Pitcher 0.65 u PbO_2.
No. 4 = Calumet 1.4 u CuO.
No. 5 = Glidden 9.4 u silicon.
No. 6 = Hummel 13.6 u silicon.

* Note: All samples have the 2L - 3C - 5S formula. One component in the basic composition is varied at the time; the component which is varied is shown above. The basic composition utilized these components: 6.0 u Hummel silicon; 3.4 u Glidden cupric oxide; and 2.23 u lead dioxide identifiable only as P. A. 245.

TABLE XIV

IGNITABILITY OF STATISTICAL FAMILY OF 16 STARTER MIX COMBINATIONS

(For 8.0 u Silicon)*

(1) ** X	(2) 0	(3) 0	(4) 0
(5) X	(6) 0	(7) 0	(8) 0
(9) X	(10) 0	(11) 0	(12) 0
(13) X	(14) X	(15) X	(16) 0

* Note: Samples consisted of 12 grams of starter composition loaded in a Mk 6 - 3 Marine Marker phenolic cup fitted with the usual nitrocellulose cup and powder fuze.

X indicates reproducible ignition failures.

** Refer to Table I for composition of each sample number.

TABLE XV

PRESSURE - TIME CURVE DATA ON PRODUCTION BATCHES OF MK 25 MOD 2 STARTER COMPOSITION (16 OCT - 26 NOV 1963)

BATCH NO.	θ	P_{max}	tP_{max}
# 390	57°	6.75 psi	7.5 secs
391	59.5	6.88	6.4
392	58	7.13	6.6
393	67	7.75	6.6
408	46	6.56	7.6
409	60	7.00	7.1
410	62	7.50	6.6
411	60	6.86	7.1
412	68	8.63	7.1
413	65	8.76	7.3
414	63.5	8.13	7.6
415	63	9.25	7.3
416	61	9.00	7.6
417	63	9.00	7.4
418	63	9.63	7.0
419	62	9.31	7.3
420	68.5	9.13	7.0
421	65	8.88	7.4
422	56	7.25	7.0
423	56	7.31	7.0
424	62	7.88	7.0
425	41	6.88	7.4
426	58	7.75	7.3
427	52	7.50	7.6
428	58	7.75	7.0
429	55	7.63	7.6
430	64	7.30	7.3
431	60	7.38	7.2
432	59	7.63	7.9
433	59	7.63	7.5
434	60	7.00	6.5
435	63	7.10	6.6
436	65	7.00	6.9
437	59	7.00	7.4
438	60	7.25	6.9
439	56	7.00	7.0
440	61	7.38	7.1
441	66	7.25	7.0

TABLE XV (CONTINUED)

BATCH NO.	θ	P_{max}	tP_{max}
# 456	61°	7.10 psi	7.4 secs
457	57	6.88	7.6
458	63	8.13	7.9
459	63	7.49	7.1
460	61	8.06	7.6
461	65	8.06	7.5
462	65	8.25	8.0
1	66	8.31	7.6
2	67	8.31	7.3
3	64	8.19	8.0

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