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U. S. NAVAL AMMUNITION DEPOT

CRANE, INDIANA

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U. S. NAVAL AMMUNITION DEPOT
Crane, Indiana

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A PRELIMINARY INVESTIGATION OF THE REACTIVITY OF LEAD DIOXIDE

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TABLE OF CONTENTS

Page

Foreword - vi

Acknowledgements - vii

Abstract - viii

I. Introduction - 1

II. Background - 4

III. Objectives - 8

IV. Experimental Results - 9
1. Determination of the reactivity of lead dioxide
2. Particle size
3. Burning characteristics exhibited by pressure-time curves
4. Burning rate of delay bodies
5. Thermal analysis
6. Calorimetry
7. Chemical analysis
8. Density
9. X-ray diffraction patterns
10. X-ray effluorescent spectroscopy

V. Conclusion 27

VI. Future Work - 34

Literature Cited - 35

Appendix I - 36

Figure 1. Rate Calorimetry Apparatus for the Determination of the Reactivity of Lead Dioxide

Figure 2. Reactivity Curve of Lead Dioxide from Manufacturer L Lead Dioxide vs. Oxalic Acid-Hydrochloric Acid-Ethanol Reagent

Figure 3. Reactivity Curve of Lead Dioxide from Manufacturer M Lead Dioxide vs. Oxalic Acid-Hydrochloric Acid-Ethanol Reagent

Figure 4. Reactivity Curve of Lead Dioxide from Manufacturer N Lead Dioxide vs. Oxalic Acid-Hydrochloric Acid-Ethanol Reagent

Figure 5. Reactivity Curve of Lead Dioxide from Manufacturer O, Lead Dioxide vs. Oxalic Acid - Hydrochloric Acid - Ethanol Reagent

Figure 6. Reactivity Curve of Lead Dioxide from Manufacturer P, Lead Dioxide vs. Oxalic Acid - Hydrochloric Acid - Ethanol Reagent

Figure 7. Reactivity Curves for Lead Dioxide Samples from Five Domestic Manufacturers

Figure 8. Reactivity Curve of Lead Dioxide from Manufacturer O (1.2μ Fraction) Lead Dioxide vs. Oxalic Acid - Hydrochloric Acid - Ethanol Reagent

Figure 9. Reactivity Curve of Lead Dioxide from Manufacturer O (1.55μ Fraction) Lead Dioxide vs. Oxalic Acid - Hydrochloric Acid - Ethanol Reagent

Figure 10. Reactivity Curve of Lead Dioxide from Manufacturer O (1.76μ Fractional) Lead Dioxide vs. Oxalic Acid - Hydrochloric Acid - Ethanol Reagent

Figure 11. Plot of Inflection Point of Temperature-Time Curves Versus Reciprocal Particle Size for Lead Dioxide Samples from Five Domestic Manufacturers

Figure 12. Plot of Inflection Point of Temperature-Time Curves Versus Reciprocal Particle Size Multiplied by Absolute Density for Lead Dioxide Samples from Five Domestic Manufacturers

Figure 13. Huminco-Orr Pore Volume-Surface Area Analyzer for the Determination of Specific Surface Area

Figure 14. A Pressure-Time Curve of a Typical Mk 25 Mod 2 Starter Composition

Figure 15. Pressure-Time Curve of 2-3-5 Starter Composition Made with Lead Dioxide from Sample L-1 from Manufacturer L

Figure 16. Pressure-Time Curve of 2-3-5 Starter Composition Made with Lead Dioxide Sample L-2 from Manufacturer L

Figure 17. Pressure-Time Curve of 2-3-5 Starter Composition Made with Lead-Dioxide Sample M-1 from Manufacturer M

Figure 18. Pressure-Time Curve of 2-3-5 Starter Composition Made with Lead Dioxide Sample M-2 from Manufacturer M

Figure 19. Pressure-Time Curve of 2-3-5 Starter Composition Made with Lead Dioxide Sample N-1 from Manufacturer L

Figure 20. Pressure-Time Curve of 2-3-5 Starter Composition Made with Lead Dioxide Sample N-2 from Manufacturer N

Figure 21. Pressure-Time Curve of 2-3-5 Starter Composition Made with Lead Dioxide Sample N-3 from Manufacturer N

Figure 22. Pressure-Time Curve of 2-3-5 Starter Composition Made with Lead Dioxide Sample N-4 from Manufacturer N

Figure 23. Pressure-Time Curve of 2-3-5 Starter Composition Made with Lead Dioxide Sample O-1 from Manufacturer O

Figure 24. Pressure-Time Curve of 2-3-5 Starter Composition Made with Lead Dioxide Sample P-1 from Manufacturer P

Figure 25. Pressure-Time Curve Slope of 2L-3C-5S Starter Composition Versus the Reciprocal Particle Size for 13 Lead Dioxide Samples from Six Domestic Manufacturers

Figure 26. Plot of Boron - Lead Dioxide Delay Burning Rate Versus Reciprocal Particle Size Multiplied by Absolute Density for Five Lead Dioxide Sources

Figure 27. Plot of Boron - Lead Dioxide Delay Burning Rate Versus Reciprocal Particle Size Multiplied by Absolute Density for Five Lead Dioxide Sources

Figure 28. Plot of Boron - Lead Dioxide Delay Burning Rate Versus Reciprocal Particle Size Multiplied by Absolute Density and Apparent Density for Five Lead Dioxide Sources

Figure 29. Typical DTA Thermogram of Lead Dioxide from Manufacturer L

Figure 30. Typical DTA Thermogram of Lead Dioxide from Manufacturer M

Figure 31. Typical DTA Thermogram of Lead Dioxide from Manufacturer N

Figure 32. Typical DTA Thermogram of Lead Dioxide from Manufacturer O

Figure 33. Typical DTA Thermogram of Lead Dioxide from Manufacturer P

Figure 34. Typical DTA Thermogram of Lead Dioxide from Manufacturer Q

Figure 35. Typical DTA Thermogram of a 2:1 PbO_2:S Composition Using Lead Dioxide from Manufacturer L

Figure 36. Typical DTA Thermograms of 2:1 PbO_2:S Composition Using Lead Dioxide from Manufacturer M

Figure 37. Typical DTA Thermograms at 2:1 PbO_2:S Composition Using Lead Dioxide from Manufacturer N

Figure 38. Typical DTA Thermogram of 2:1 PbO_2:S Composition Using Lead Dioxide from Manufacturer O

Figure 39. Typical DTA Thermograms of 2:1 PbO_2:S Composition Using Lead Dioxide from Manufacturer P

Figure 40. Typical DTA Thermogram of 2:1 PbO_2:S Composition Using Lead Dioxide from Manufacturer Q

Figure 41. Plot of Enthalpy vs. Percent of Silicon Fuel for Lead Dioxide Samples from Five Manufacturers

Figure 42. Plot of Reaction Rate Constant, K, Versus Surface Area for Lead Dioxide Samples from Five Producers

Table I. Reactivity Data on Lead Dioxide Samples from Five Domestic Manufacturers

Table II. Values for the Reaction Rate Constant K in the Equation $\left.\frac{\Delta T}{\Delta t}\right|_{t=ti} = K/d$

Table III. Comparison of Reactivity and Various Property Values for 13 Lead Dioxide Samples from Six Domestic Manufacturers

Table IV. The Relationship Between the Average Particle Diameter, The Surface Area and the Reactivity of Lead Dioxide from Five Domestic Manufacturers

Table V. Burning Characteristics of Boron-Lead Dioxide Delay Bodies

Table VI. Differential Thermal Analysis Peaks for Lead Dioxide Samples from Six Domestic Manufacturers

Table VII. Differential Therman Analysis Peaks for 2:1 Lead Dioxide-Sulfur Mixture Utilizing Lead Dioxide Samples from Six Domestic Manufacturers

Table VIII. Calorific Values for the Heats of Reaction of Different Ratios of Lead Dioxide and Silicon

Table IX. Chemical Analysis of Twelve Lead Dioxide Samples from Six Domestic Manufacturers

Table X. d - Spacings Obtained from X-ray Diffraction Patterns of Lead Dioxide Samples from Five Domestic Manufacturers

Table XI. ASTM Powder Diffraction Data Cards for Lead Dioxide

Appendix II. Key Words

FOREWORD

The effort described in this report was authorized under AIRTASK A35-532-022/323-1/F008-17-02, Air Launched Pyrotechnic Development, Chemical Standards (Pyrotechnic Properties), Work Unit No. 6, and was performed at NAD Crane between June 1967 and May 1968. The investigation of the reactivity of lead dioxide was carried out at the same time as the similar work on red phosphorus reactivity, which has already been reported in NADC RDTR No. 110. Again it should be said that this report is written at a time in the investigation when the basic objectives have been reached, although many questions remain to be answered. Consequently, this is not necessarily a final report.

ACKNOWLEDGEMENT

A report such as this one is founded upon the efforts of a great many people - chemists, physicists, metallurgists, mathematicians, statisticians, laboratory technicians, data processors, photographers, proof-readers and typists. While it is not practical to list all of these people by name, the authors nevertheless wish to recognize their efforts. In particular the authors wish to express their appreciation to Mr. Duane Johnson for his many valuable insights and suggestions. Also, the contributions of the staff of the Quality Evaluation Laboratory are gratefully acknowledged. The efforts of Mrs. Harriet Mitchell in putting this report together in its final form have been invaluable.

ABSTRACT

A study is made of the performance characteristics of lead dioxide specimens from five U. S. manufacturers. Reactivity data is obtained using temperature-time curves, pressure-time curves, and burning rate of delay bodies. The relationship of chemical and physical properties of lead dioxide to its performance in the various tests, and the relationship of the various performance tests to each other, are considered.

A PRELIMINARY INVESTIGATION OF THE REACTIVITY OF LEAD DIOXIDE

INTRODUCTION

1. Although chemicals used in pyrotechnic compositions are purchased under appropriate military specifications, which are supposed to control the chemical and physical properties so that a degree of consistency can be expected in the performance of the composition. many practical pyrotechnicians are convinced from experience that unpredictable variations occassionally appear in the performance characteristics of these chemical components. These variations are difficult to document for several reasons. For one thing, military specifications do not usually require a performance test to determine the reactivity of the components, but instead assume that if the chemical and particle size requirements are met, then the reaction characteristics will be acceptable. Secondly, variations are often subtle and may only occassionally become pronounced enough to cause serious performance changes. Since there are usually no laboratory control tests available to measure reactivity, except the quality control tests that are run on the finished units, it is difficult to determine whether the process, the chemical components, or the hardware is the source of the failure. If the chemical components are suspected, chemical analysis and particle size determination may be rerun on each component. However, the materials may very well pass the tests, although one of the materials is actually the source of trouble, since the specifications tests do not necessarily reveal reactivity variations.

2. Military specifications for chemical components used in pyrotechnic compositions are necessarily compromises between a set of ideal properties and the practical limitations of commercial manufacturing processes. Certainly, the more rigorous the requirements the more expensive is the process needed to meet them. Furthermore, the "ideal properties" of a material depend upon its use and indeed may not always be understood. The April 1968 edition of Metal Progress was devoted to a special report entitled: "Characterization - Industry's Most Urgent Materials Problem ....." It is the thesis of this special report that most materials are so poorly characterized that consumers cannot tell manufacturers precisely what properties they require. What are the ideal properties of lead dioxide when it is used as a component in one of the starter compositions? They are not really known. Consequently, certain "reasonable" or minimum requirements are established for purity, contaminants, and particle size that are a compromise between what the pyrotechnician thinks he needs to make a composition with predictable performance and what the manufacturer can make at an acceptable price. There is, of course, a good deal of looseness in this arrangement. Variations in the chemical components inevitably appear and, consequently, so do variations in the performance of the final pyrotechnic item. The variations in the components may at times be so gross that the component fails to meet the specification requirements. On the other hand the component may meet the specification requirement and still introduce an

undesirable variation in the performance of the composition. At best, formula changes must be made to compensate for the variation; at worse, the material may be unusable.

3. One way out of this situation is to prescribe additional requirements for the material over and above the general specification requirements. Besides increasing the cost of the material, or running into procurement problems at any cost, the "additional requirements" needed again may not be known.

4. Another approach could be the development of a performance test for the material. In such a test the reactivity of the material would be evaluated. Since the reactivity of the material - that is, the ease and rapidity with which the material interacts with other materials - depends upon the totality of all physical and chemical properties, the effect of variations in the material could be seen even if the causes were not known.

5. This is the approach that has been used in the study of various chemical materials which are used in current pyrotechnic compositions. Variations in the behavior of lead dioxide, which is a basic component of an important starter composition, have been suspected from time to time, but no hard data are available to support this suspicion. Consequently, an investigation of the reactivity, as well as some of the chemical and physical properties, of lead dioxide has been undertaken.

BACKGROUND

1. One of the traditional starter compositions used in conjunction with red phosphorus flare compositions is based on the reaction between crystalline silicon, lead dioxide, and cupric oxide. Various proportions of these three components have been used in different applications; and, on occassion, changes in the formula have resulted from unexpected changes in burning characteristics that have contributed to malfunctions.

2. Formerly the Mk 25 Mod 2 Marine Location Marker employed a starter composition consisting of 5 parts by weight of lead dioxide, 6 parts of cupric oxide, and 7 parts of silicon which we will designate 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 cupric oxide and 5 parts silicon, or 2L-3C-5S. In March 1962, the Quality Evaluation Laboratory conducted a statistically designed experiment on the Mk 25 Marine Location Marker. The first experiment investigated eight factors at three levels involving the performance of 505 specially prepared units. 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 signal units were prepared and tested. One of the conclusions of these two statistically designed 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. However, it was not explained why the 5L-6C-7S formula that had once functioned satisfactorily had lately begun to burn too energetically. On the basis of these difficulties an investigation was begun by W. Ripley in April 1963 to elucidate the factors that determined the behavioral characteristics of this family of starter compositions. The results of this investigation were subsequently published in March 1964 as RDTR No. 41 (1). During this investigation a performance test was used which utilized the pressure-time curve obtained when the starter composition burned in a closed vessel equipped with a transducer and a recorder. This test led to the discovery of an unusually reactive silicon specimen that otherwise met the specification requirement and resembled normally reactive silicon specimens in all other properties studied except one - effluorescent spectroscopy revealed the existence of traces of manganese and chromium in the energetic silicon. Since this investigation was done, more burning rate problems have been encountered with the 2L-3C-5S starter composition formula. This time suspicion has fallen upon all of the chemical components, and particularly upon the lead dioxide.

3. Lead dioxide was first prepared by Scheele in 1774 by

treating red lead with chlorine, and soon afterwards by Priestly who treated red lead with nitric acid (2). Lead dioxide also exists in the natural state as the mineral plattnerite. It is manufactured industrially by various methods (3). It may be prepared by dissolving lead monoxide from red lead (Pb_3O_4) with dilute nitric acid. It may be obtained from divalent lead salts such as lead acetate by oxidation with calcium hypochlorite. Or it can be prepared by electrolyzing a sodium chloride solution in which lead monoxide is suspended. From the variations reported in such properties as the density and the decomposition temperature, it is reasonable to assume that the characteristics of the product are influenced by the nature of the starting material and by the nature of the manufacturing process.

4. Native lead dioxide occurs in Idaho and Scotland as a fine crystal with a gray-black color and a brown streak. Manufactured lead dioxide varies in color depending to some extent on the particle size. Finer particle material appears more reddish. Densities reported in the literature vary from 7.0 to 9.4 g/cc. (2) Remy reports the X-ray density to be 9.42 g/cc. (3) The crystal structure is said to be the same as that of tin dioxide which is usually tetragonal but may also exist in the rhombic and hexagonal forms. (2) Native crystals of lead dioxide are tetragonal with a reported axial ratio of a:c being 1:0.6764. (2) On the other hand, samples of lead dioxide prepared in the laboratory by Ferari were tetragonal with a being 4.984°, c being 3.40A° and the axial ratio a:c being 1:0.682. (2)

Copies of ASTM powder diffraction data cards for lead dioxide are shown in Table XI.

5. According to J. Heyes, the structure of lead dioxide is represented with divalent lead and oxygen attached to a quadrivalent oxygen atom: (2)

$$Pb = O = O$$

But A. Colsen showed that the lead is quadrivalent and suggested the structure:

$$O = Pb = O$$

L. Marino argued that the lead is quadrivalent, and that one or both of the oxygen atoms are also quadrivalent. The unsymmetrical formula for the oxide, shown below on the left, is preferred because the lead sulfite obtained by reducing the oxide with sulfur dioxide is unsymmetrical: (2)

Marino also assumed that lead dioxide can exist in both single and double molecules: (2)

It was formerly believed that there is a pseudo-cubic phase of lead dioxide represented as $PbO_{1.87}$. However, Katz has shown that this new phase is characterized by the composition $PbO_2 \cdot x\ PbO$ in which x varies from 0.75 to 2. (2) This composition is not to be understood as a mechanical mixture, but as a solid

solution of PbO_2 and PbO_1.

6. According to Mellor lead dioxide is decomposed when exposed to light, forming red lead and oxygen: (2)

$$3\ PbO_2 \longrightarrow Pb_3O_4 + O_2 \uparrow \qquad \text{Equation 1}$$

Moderate heat is said to decompose lead dioxide to red lead and strong heat to decompose it to red lead and oxygen. (2) The existence of lead sequioxide, Pb_2O_3, is supported by some and discounted by others. According to Remy Pb_2O_3 is not formed during the thermal degradation of PbO_2. However, the existence of other oxide intermediates between PbO_2 and PbO is accepted, although they have not yet been characterized. (3)

7. Lead dioxide is a powerful oxidizer. It inflames if triturated with sulfur or red phosphorus. (3) When warmed with concentrated sulfuric acid, it evolves oxygen; with concentrated hydrochloric acid it evolves chlorine. As already noted above, it is unstable to light and heat. In pyrotechnics it is used with such fuels as silicon and boron, and even zirconium metal. The obscurity of its structure and composition, the variations in its physical and chemical properties, and the lack of information on the correlation between structure, composition, and properties, indicate that further characterization of the material and its behavior are required.

OBJECTIVES

1. The present investigation has had six principal objectives:

   a. To find laboratory methods of measuring the reactivity, or the reaction rate, of lead dioxide, and ultimately

of other pyrotechnic chemicals.

b. To compare and correlate when possible reactivity results obtained from different methods of determining reactivity.

c. To investigate a quantitative relationship between the average particle size, the surface area, and the reactivity of lead dioxide.

d. To determine which method of measuring the particle size is more valid in predicting the reactivity of lead dioxide.

e. To determine if other factors besides the average particle size or surface area affect the reactivity of lead dioxide.

f. To determine the variations in reactivity that exist in lead dioxide currently used in production, and in lead dioxide from different sources.

EXPERIMENTAL RESULTS

1. Determination of the reactivity of lead dioxide

a. A laboratory test method for determining the reactivity, or the reaction rate, of a solid material like lead dioxide must necessarily be a destructive test. The lead dioxide is attacked by some chemical agent, and in the process of the ensuing reaction the lead dioxide is destroyed. The rate at which the lead dioxide is destroyed is somehow measured and recorded, and this rate is assumed to be related to the reactivity of the lead dioxide.

b. Since the lead dioxide must react with another substance, three general modes of reaction are possible: the

lead dioxide can react with a gas, with a liquid, or with a solid. While all three of these modes are currently under study, this report is mainly concerned with a study of the reaction of solid lead dioxide with a liquid reactant, and with the burning characteristics of certain solid-solid systems.

c. Lead dioxide is dissolved by many liquid chemical reagents. If we obtain a temperature-time curve of the reaction between lead dioxide and some liquid reactant under isothermal conditions, two requirements must be satisfied in choosing a reactant: sufficient heat must be generated and the reaction must not proceed either too rapidly or too slowly. Reactions with hydrogen peroxide and hydrochloric acid proved to be too rapid, while the reaction with oxalic acid was slow and developed little heat. A reagent was finally developed, based on an alcoholic solution of oxalic and hydrochloric acids, which gave a satisfactory time-temperature curve. The oxalic acid solution was prepared fresh each day by adding 120 grams of anydrous oxalic acid and 60 ml of distilled water to a one liter volumetric flask and bringing the solution to the mark with 95% ethyl alcohol. Just before using the reagent, 5 ml of 12N hydrochloric acid was added to 45 ml of alcohol-water solution of oxalic acid. This mixture was at once cooled in an ice bath to 23°C and immediately added to the reaction vessel containing the lead dioxide sample.

d. The apparatus used, which is basically a rate calorimeter, is shown in Figure 1. Essentially, it consists of

a Dewar reaction vessel equipped with a glass stirrer, a funnel for addition of reagent, an inconel-sheathed chromel-constantan thermocouple probe (1/16" O. D.), a cold junction compensator, and a strip chart recorder. The response time of the thermocouple probe was 0.5 seconds over the temperature range of the reaction.

e. In a typical run 4.00 grams of lead dioxide was weighed out on a triple beam balance accurate to 0.01 grams and carefully introduced into the Dewar flask. The temperature of the room was maintained at 23-25°C. 50 ml of the reagent was freshly prepared by mixing 45 ml of alcoholic oxalic acid solution and 5 ml of 12N hydrochloric acid. The reagent was immediately cooled in an ice bath to 23°C and added to the reaction vessel. The stirrer was started at approximately 6 revolutions per second. Different chart speeds and millivolt ranges were required for different lead dioxide samples. More reactive specimens were run at 2.5 mv and 4 in./min. and less reactive specimens were run at 1.25mv and 1/3 in./min.

f. The reaction mechenism of this system is somewhat complex and is probably represented by the following equations:

$$PbO_2 + H_2C_2O_4 \longrightarrow PbO + H_2O + 2CO_2\uparrow + \Delta H \qquad \text{Equation 2}$$

$$PbO + 2HCl \longrightarrow PbCl_2\downarrow + H_2O + \Delta H$$

$$PbO_2 + 4\,HCl \longrightarrow PbCl_2 + 2\,H_2O + Cl_2\uparrow + \Delta H \qquad \text{Equation 3}$$

g. Commercial lead dioxide specimens were obtained from five different manufacturers. In order to study the relationship

between the particle size and the reactivity, the five specimens were fractionated by sedimentation and liquid elutriation. Separation using distilled water was relatively easy on the large particle specimens, but on the small particle specimens separation was difficult at best. This difficulty in obtaining relatively coarse and fine fractions indicates a limited particle size distribution as well as the limits of the fractionating technique itself.

h. Figures 2 - 6 show reaction rate curves for the five parent samples of lead dioxide. In these curves temperature is indicated on the Y coordinate and time on the X coordinate. Figure 7 shows the reaction rate curves plotted on the same scale. Figures 8 - 10 show reaction rate curves of three fractions obtained from Manufacturer O. All of these curves reveal the rate at which heat is generated when lead dioxide reacts with an excess of alcoholic oxalic acid-hydrochloric acid reagent. Table I shows the dimensions and properties of the reaction rate curves for all the parent samples as well as the fractions obtained from them. Figure 11 shows the reciprocal of the average particle diameter plotted as a function of the tangent of the inflection point of the individual reaction rate curves. Figure 12 shows the reciprocal of the average particle diameter multiplied by the reciprocal of the absolute density plotted as a function of the tangent of the inflection point of the individual reaction rate curves.

i The temperature-time curves obtained from exothermic reaction of lead dioxide with alcoholic oxalic acid-hydrochloric acid solution are sigmoid type curves. This type curve is characteristic of autocatalytic reactions, although it has not been definitely demonstrated that the reaction is in fact autocatalytic. The inflection point of each curve has been chosen to characterize the reaction rate of the individual sample, since at this point the rates of the two competing processes - autocatalysis which increases the rate process versus depletion of lead dioxide which slows the rate process - are at equilibrium. The rate of reaction at the inflection point is expressed as the value of the slope at that point. When the values obtained for the slope at the inflection point are plotted against the reciprocal particle diameter for each of the lead dioxide parent specimens and its fractions, linear relationships are obtained. The individual slopes for each of the five lead dioxide specimens obtained from U. S. Manufacturers are shown in Figure 11. The wide range of values for the different slopes is an indication of the variations in the reactivity of the different lead dioxide specimens. For example, lead dioxide samples furnished by Manufacturer L and Manufacturer P have comparable particle sizes and yet they stand at the opposite extremes in terms of reactivity. The reaction rate of the specimen from Manufacturer P is in the range of 19 times as fast as that of Manufacturer L. Moreover, the heat energy released from the different specimens is not

the same. The temperature rise shown by the peak height of the curve is about 50% greater for specimens M, N, and P than for specimens L and O, necessitating that they be recorded on a higher millivolt range and at a faster chart speed. A higher heat of reaction indicates a different internal energy and therefore a different composition or structure. The linear plots shown for each of the lead dioxide specimens in Figure 11 can be represented by the equation:

$$\left.\frac{dT}{dt}\right|_{t = t_i} = \frac{K}{d} \qquad \text{Equation 4}$$

Where t_i equals the lapsed time at the point of inflection, $\frac{dT}{dt}$ equals the rate of temperature increase, d equals the average particle diameter, and K equals a proportionality constant. Values for K are shown in Table II.

2. Particle size

a. The average particle size of the five parent lead dioxide samples was determined by the air permeability method using the Fisher Sub Sieve Sizer. The density obtained experimentally by the pyconometer was used instead of the value of 9.38 g/cc given in most reference books. (A) Values are shown in Table III.

b. The surface area of the phosphorus samples was studied by the nitrogen adsorption method. A Numinco-Orr

Surface Area - Pore Volume Analyzer, Model MIC-103, shown in Figure 13, was used. A quantity of sample was weighed out approximately and placed in the sample tube to give a total surface area between 1 and $10m^2$. The sample tube containing the sample was then attached to the instrument and degassed for 15 hours at 100°C and under a vacuum of 1 micron of mercury. Dry helium gas under liquid nitrogen was used to measure the dead space volume before the adsorption measurement. Nitrogen gas under liquid nitrogen was used as the adsorbate during the actual tests. Several pressure readings, which were indicative of the amount of nitrogen adsorbed, were taken in each test. The sample was then reweighed to an accuracy of 0.001g. Calculations were based on the area occupied by a single nitrogen molecule, which is $15.8A°^2$. Points were calculated from the pressure readings and plotted on graph paper. From the slope and intercept of the best straight line through the data points, the specific surface area, Sg, was found.

c. A comparison of the specific surface area, Sg, and the average particle diameter for five parent samples of lead dioxide and four fractions of one of the parent samples (Sample O) is shown in Table IV. Inconsistencies between values for the APS and values for the surface area are evident: e.g., the APS of Sample L is 2.15 u with a surface area of .59 m^2/g, while the APS of Sample P is 2.10u and the surface area is 3.72 m^2/g.

Also it can be seen in Figure 7 that the two groups of lead dioxide samples are determined by their surface areas and not their average particle diameters. Obviously, this is an instance in which the average particle diameter is not a function of surface area and where the surface area is the true property that relates to the reactivity.

3. Burning characteristics exhibited by pressure-time curves

a. Since late 1963 the performance of the 2L-3C-5S starter composition used in the Mk 25 and Mk 58 Marine Location Markers has been evaluated on the basis of its pressure-time curve. This pressure-time curve is obtained by combusting 12 grams of the starter composition in a closed vessel which is equipped with a transducer and a recorder. The apparatus and the procedure have been described in RDTR No. 41. Based on this study an acceptable range of burning characteristics for the Mk 25 Mod 2 starter composition was determined. Figure 14 shows the pressure-time curve for a typical starter composition obtained during that study. Three properties of the curve were used to characterize the burning performance of the composition. The burning rate, θ, is obtained by finding the angle of the slope of the curve at $t_{\frac{1}{2}P_{max}}$, that is, the time at which one-half of the maximum pressure is attained. The accepted range for the angle θ was chosen on the basis of experience to be 55° to 68°. The maximum pressure, P_{max}, was assigned a value of 6.75-9.65 psi. The time required for the pressure to reach its

maximum value, t P_{max}, was assigned a range of 6.1-7.9 seconds. Again, there was no inner necessity about these performance requirements. They were selected as reasonable values based on the performance of a great number of production batches tested over several months. While this method was useful in evaluating the burning characteristics of the starter composition, no rigorous analysis of the significance of the pressure-time curve was performed at that time, or has been performed since. And although various factors which affect the pressure-time curve--composition, particle size, moisture, contaminants, crystalline modifications--were investigated, undesirable variations that eluded explanation have to appear from time to time.

b. Although the problem of a standard oxidizer and a standard fuel has not yet been solved to the satisfaction of everyone, some reproducible variations can be found among starter compositions made with the same silicon and cupric oxide but with different specimens of lead dioxide. Figures 15-24 show pressure-time curves of 2L-3C-5S starter composition made from ten different lead dioxide specimens obtained from six U. S. manufacturers. Table III shows the values for the burning characteristics of a total of 13 specimens from these six manufacturers--the ten of which pressure time curves are shown are included--along with other physical and chemical characteristics.

c. Altogether, this data presents a baffling picture of contradictions and inconsistencies. While the pressure-time curves obtained on a single specimen are fairly reproducible, there are still some individual runs that are far beyond the norm, indicating that variations do exist in the procedure itself. However, any attempt to relate the physical and chemical properties of lead dioxide that were investigated during the course of this work to the burning characteristics shown by the pressure-time curves appears to be futile. Take particle size, for example: there is no discernible correlation between the tangent of θ and the reciprocal of the average particle diameter. Inspection of Table III will show that specimens with small average particle diameters are sometimes relatively fast burning and sometimes relatively slow burning. The smallest specimen with an APS of 0.32u is comparable in burning rate with specimens having APS values of 0.51u and 1.65u. This lack of pattern or trend is all too clearly shown by the scatter of points in Figure 25, where tan θ is plotted versus the reciprocal of the average particle diameter. Nor is there any discernable correlation between the absolute density or the apparent density and the burning rate. Specimen L-1 with the highest absolute density has the high value for the angle θ of 61°; but specimen Q with the second highest absolute density has one of the lowest values for the angle θ, 42°. This same lack of correlation also exists between the apparent density and the burning rate. Nor is their any

obvious relationship between the purity and the burning rate. Sample N-2 assayed 79.5% PbO_2, which is about 15% below the minimum specification requirement of 95%. Yet it burns relatively fast - θ is 64° and the maximum pressure is 8.6 psi - while the two slowest burning samples have purities above 96%. All this indicates that some other factor or group of factors outside those considered in this investigation determine the burning rate. This data also suggests that the military specification requirements of lead dioxide have little or no correlation with the burning characteristics of the starter composition of which the lead dioxide is an important component.

4. Burning rate of delay bodies

a. The inconclusiveness of the pressure-time curve study made it desirable to investigate further the burning rate of solid-solid lead dioxide compositions. Consequently, it was decided that the burning time of delay bodies which normally utilize a lead dioxide composition should be investigated. This composition is prepared by screening together 85.1% lead dioxide and 10.6% boron. After the mixture has been screened three times, it is combined with 4.3% viton which has been dissolved in acetone so that the resulting solution is 16% viton. The mixture is worked until it is almost dry and then it is screened through a No. 16 U. S. Standard Sieve and finally through a No. 30 U. S. Standard Sieve. It is then pressed in 500 mg increments into a 1" x 1/4" I. D. aluminum delay body under a dead load of

1000 lbs.

b. The burning rate in grams per second of ten lead dioxide specimens from five U. S. manufacturers is shown in Table V. Also the weight of composition that could be pressed into the 1" x 1/4" I. D. aluminum delay body is shown, as well as the burning time per inch. It can be seen that the burning rate varies from 2.97 g/sec for specimen P to 5.19 g/sec for specimen N-4. It is of passing interest to note that this specimen with the fastest burning rate in a delay composition exhibited the slowest burning rate on the pressure-time curve. Furthermore, it can be seen that the weight of the delay composition which could be pressed into the body varies from 3.850 grams for Specimen L to 3.000 grams for specimen N-1. Thus it would appear that there is a correlation between the average particle diameter, the apparent density, and the absolute density of the lead dioxide specimens, and the loaded density of the composition.

c. Figure 26 shows the plot of the burning rate in g/sec versus the reciprocal of the product of the absolute density and the average particle diameter. Figure 27 shows the plot of the burning rate in g/sec versus the reciprocal of the product of the apparent density and the average particle diameter. Figure 28 shows the plot of the burning rate in g/sec versus the reciprocal of the average particle diameter multiplied by the sum of the reciprocals of the apparent density and the absolute density. The fact that the wide differences shown in

Figure 26 become much less pronounced in Figure 28 indicates that the difference in burning rates of the various lead dioxide-boron delay compositions depends almost entirely upon the average particle diameter, the apparent density, and the absolute density of the lead dioxide specimen used in the delay composition.

5. Thermal Analysis

a. Differential thermal analysis was performed on samples of lead dioxide obtained from six domestic manufacturers. Values for the endothermic peaks are shown in Table VI and typical thermograms of lead dioxide samples from the different manufacturers are shown in Figures 29 to 34. From this data it can be seen that the decomposition mechanism varies for the different samples. For Sample L decomposition begins at about 400°C and peaks at 465°, 512°, and 645°C. This thermogram shows a characteristic curve which is not quite like the curves of any of the other lead dioxide samples. For Sample M decomposition begins at about 350°C and peaks at 417°, 458°, and 640°C. Again the material has a characteristic curve. Decomposition of Sample N begins at 350° and peaks at 420°, 455°, and 610°C. The curve of the material has the same pattern as that of Sample M. Decomposition of Sample O begins at 350°C and peaks at 450°, 458°, and 615°C. The material has a characteristic shape that is unlike curves of the other materials. Decomposition of Sample P begins just above 300°C and peaks at 435°, 480°, and 605°C. This is the first sample to exhibit four distinct and almost

equal endothermic peaks. Again its curve has a characteristic shape. For Sample Q decomposition begins at about 350°C and peaks at 448°, 490°, 535°, and 610°C. Again there are four peaks, indicating that the decomposition mechanism of Sample Q is the same type as Sample P, although it possesses individual characteristics. According to DTA curves of thermal decomposition two general types of decomposition patterns are indicated, with samples showing individual characteristics within these two types. The first type has three distinct peaks, the first two peaks merging while the third peak is distinctly apart. In the second type there are four peaks of about the same height. The four peaks are distinct and separate in Sample P while in Sample Q the first three peaks merge. The temperature at which decomposition begins varies among the different samples from about 300° to 400°C.

b. Differential thermal analysis was also performed on a 2:1 composition of lead dioxide and sulfur. This was to determine any differences in reactivity which might be revealed in a reaction between the various lead dioxide samples from six U. S. manufacturers and a relatively reactive fuel like sulfur. Endothermic and exothermic peaks for the different lead dioxide samples are shown in Table VII. Representative thermograms for lead dioxide from each of the six manufacturers are shown in Figures 35 to 40. Lead dioxide from Manufacturer L shows a sharp exothermic peak at 303°C which indicates ignition

but not explosive ignition. (Figure 35) Sample M showed two kinds of curves (Figure 36), one in which explosive ignition occurred at 125°C and the other in which explosive ignition occurred at 220°C. This same pattern of activity is also shown in Samples N and P. (Figures 37 and 39). Samples O and Q show similar activity pattern (Figures 38 and 40).

c. These thermograms show pre-ignition reactions associated with the melting point of sulfur (110°C). With samples M, N, and P ignition was a result of the reaction that started with the melting of the sulfur. However, this reaction does not always result in ignition even with different runs on the same sample. On the other hand, no runs of samples L, O, and Q ignited at this point, and the general conclusion is that these samples are less reactive. Another pre-ignition reaction is seen beginning at about 200°C in those samples that did not ignite after the sulfur had melted. This temperature is not associated with any particular changes that appear in the DTA thermograms of either sulfur or lead dioxide. However, a major exothermic reaction begins at about this temperature and culminates in a peak at 303°C for sample L-1, at 310°C for sample P, and at 295°C for sample Q. This same PIR culminates in ignition for sample M-2 at 220°C, and in ignition for sample O at 310°C. From these results it can be said that samples L and Q are definitely less reactive than the other samples under these test

conditions since they are the only samples that did not undergo rapid propagative ignition. Otherwise, in general, the results of these tests do not indicate clear and consistent differences in the behavior of the various lead dioxide samples.

6. Calorimetry

a. Calorific values for the heats of reaction of 2L-3C-5S starter compositions made from the various lead dioxide samples obtained from the six domestic manufacturers are shown in Table III. It can be seen that values range from 372.44 cal/g for sample O to 353.34 cal/g for sample N-2. It can be seen from the results given in Table III that large variations in the purity of the lead dioxide used in the starter compositions do not show correspondingly large variations in the caloric value of the compositions. Sample N-2 assays at 79.5% PbO_2 - 15.5% below the minimum specification requirement - and yet it shows barely a 2% decrease in calorific output from other samples (N-4 and P-1) that assay about 96% PbO_2. Moreover, this low purity does not particularly affect the other performance tests in an adverse way: the pressure-time curve is fast and the delay burning rate average. Thus the relation between the performance and the purity is anything bur clear. Indications are that factors more important than the PbO_2 assay dominate the performance of the compositions.

b. Calorific values for the heats of reaction of different ratios of lead dioxide and silicon are shown in Table VIII.

From this table Figure 41 was obtained in which the enthalpy is plotted as a function of the percent of the silicon fuel. The enthalpy, q, is equal to the heat per mole of available oxidizer; or

$$g = \frac{\Delta H \times \text{molecular weight of oxidizer}}{\text{weight of composition} \times \text{percent of oxidizer}}$$

where ΔH is the calorific value of the fuel-oxidizer combinations shown in Table VIII. Figure 41 indicates still another way of demonstrating inherent differences in the lead dioxide samples. At the stoichiometric point of about 18% silicon, the enthalpy varies from approximately 13.5 K-cal/mol for sample N to 15.0 K-cal/mol for sample P, a variation of almost 10%.

7. Chemical Analysis

a. Chemical analysis was performed upon 13 lead dioxide samples from six domestic manufacturers. The results of the chemical analysis is shown in Table IX. The purity as % PbO_2 was obtained according to the method described in MIL-L-376B for lead dioxide, technical. This method is based on the assumption that only PbO_2 in the sample will decompose hydrogen peroxide in dilute nitric acid, whereas in fact various contaminants might also decompose hydrogen peroxide. The samples analyzed exhibited a wide range of values for purity, from 79.5% for sample N-2 to 98.1% for sample Q. More than half of the samples, however, would not have passed the minimum requirement of 95% imposed by the specification. The percent of lead was determined gravimetrically as lead chromate.

8. Density

a. Densities of lead dioxide samples from 7.0 to 9.4 g/cc have been reported in the literature. Absolute densities of nine lead dioxide samples from six manufacturers are shown in Table III. Values range from a low of 6.82 g/cc for sample N-1 to 9.28 g/cc for sample L-1. The relationship between the density, the structure, and the reactivity is not fully understood. Bur in general higher density is associated with lower reactivity.

b. The apparent density of 13 samples from six manufacturers is also shown in Table III. These values vary from a high of 2.83 g/cc for sample O to a low of 1.36 g/cc for sample N-3. The apparent density is determined by filling a 100 ml graduated cylinder that has been cut off at the 100 ml mark with lead dioxide that is slowly sifted into the cylinder through a powder funnel. The effect of the apparent density of lead dioxide on the packing desnity of a boron-lead dioxide delay, and consequently on its burning rate, has already been discussed in the above section on the burning time of delay bodies.

9. X-ray Diffraction Patterns

a. X-ray diffraction patterns were obtained on lead dioxide samples from five manufacturers using nickel filtered Cu-Kα radiation. While no major differences were found, it does appear - as can be seen from the presence of a small peak at 3.12 ± 0.02A° in Table X - that small amounts of α-PbO_2 are present in samples N, O, and P, which are otherwise pre-

dominately β-PbO_2.

10. X-ray Effluorescence Spectroscopy

a. X-ray effluorescence spectroscopy was performed on lead dioxide samples from five manufacturers revealing only a strong Pb peak.

CONCLUSION

1. The study of materials is ultimately the study of the complex interrelationship between properties, composition, structure, and energy state. These are all merely aspects of a larger whole. A substance has certain properties because of its composition, structure, and energy state.

2. Traditionally, substances have been characterized by their chemical composition (based on a partial rather than an ultimate analysis) and by their physical particulate state. In the course of this work we have adopted an alternate approach to the characterization of substances. Substances have been characterized by their behavior under a given set of conditions. If they behave differently, it has been assumed that they are different; if they are different, then some of their measurable properties must be different.

3. Lead dioxide was among the substances chosen for this study because reports on its structure and properties vary and because its behavior as a pyrotechnic component has more than once come under suspicion. Variations in its density from 7.0 to 9.4 g/cc have been reported in the literature and

similar variations have been found in this study. The color of commercial lead dioxide varies from red-brown to almost black while its particle size varies from approximately 0.3u to approximately 2.4u. The particle size distribution, as evidenced by the difficulties encountered in fractionating the powdered material, also varies from sample to sample, with some materials such as sample O showing a considerable range of particle size, while others such as sample N-3 showing almost no range at all. Based on x-ray diffraction patterns, two types of lead dioxide - α - PbO_2 and β - PbO_2 - have been reported, although all of the samples studied during this investigation were fundamentally β - PbO_2. Differential thermal analysis indicates that there are two distinct types of decomposition mechanism shown by the various lead dioxide samples, one characterized by three endothermic peaks and the other characterized by four endothermic peaks. The heat of reaction of 2-3-5 starter composition made from the various lead dioxide samples varies from 372.4 cal/g to 353.3 cal/g. Chemical analysis utilizing the hydrogen peroxide - lead dioxide reaction indicates that the purity of the samples varies from 79.5% PbO_2 to 95.9% PbO_2. Similarly, the performance and reactivity tests indicate significant differences in the behavior of the various lead dioxide samples.

4. These measurements of properties and performances raise two immediate questions: first, is there any correlation between the various performance tests, e.g., is the same material always the fastest reacting in all of the tests; and secondly,

is there any correlation between the properties of the lead dioxide samples and their performance?

5. Figure 7 shows that the temperature-time curves of the lead dioxide samples fall into two distinct groups. The data on specific surface area in Table IV shows that these two groups depend upon the surface area of the lead dioxide samples. For example, samples L and O which make up the slow reacting group have surface areas of 0.6 m^2/g and 0.96 m^2/g respectively, while samples P, M, and N which make up the fast reacting group have surface areas of 3.72 m^2/g, 4.35 m^2/g, and 4.94 m^2/g respectively. For four of these samples the reaction rate constant is a linear function of the surface area, as shown in Figure 42. However, sample P does not fit into this linear relationship, indicating that its reaction rate constant is influenced by some other factor in addition to the specific surface area. Moreover, the value of the average particle diameter of sample P, 2.38u, is very poorly related to the surface area, 3.72 m^2/g, and to the reaction rate of the sample in a liquid medium. This is an important instance where the apd is entirely misleading as a factor in determing the reactivity, which is in fact related to the surface area. One can only speculate concerning the reason for the large descrepancy between the value given by the Fisher Sub Sieve Sizer and the value given by the Surface Area meter. The particles apparently have a large internal area and may resemble porous balls.

6. If we turn now to the reaction rates of these five specimens in solid-solid reactions - in this case as components in a delay composition - we find little resemblance between the burning rates and the reactivity rates shown in Table III. In the delay burning rates, sample P is the slowest, and samples M, N, and O are the fastest. Not much resemblance to the clear cut division of groups shown in Figure 7. The slopes of the lines in Figure 26 indicate the order of increasing rate of reaction to be N, O, P. L, M with a loose grouping of N and O as the slowest and M, L, and P as the fastest. In Figure 27 where the burning rate in a delay body is plotted against the reciprocal of the average particle size times the apparent density (instead of the absolute density as in Figure 26) the lines draw together somewhat and the groupings change. Now the order of increasing reaction rates are P, L, O, N, and M, with M and N forming one group and O, L, and P another. However, in Figure 28 where the effects of particle size ($\frac{1}{d}$), absolute density ($\frac{1}{\rho_{abs}}$), and apparent density ($\frac{1}{\rho_{apt}}$) are all taken into account, the lines draw even closer together and the slopes of the lines fall once again into two distinct groups, M, P, and N forming the slower group and O and L the faster group. Two things are remarkable about this. The first is that the samples fall into the same groupings that were shown in the liquid reaction in Figure 7: L and O in one group and N, P, and M in the other. In other words, when the effects of the average

particle size, apparent density, and absolute density are normalized - effects that dominate the burning characteristics in a delay - the original groupings based on reactivity in the liquid reagent are restored. The second remarkable thing is that the order of increasing reactivity is almost exactly reversed. Sample L, the slowest in Figure 7, becomes the fastest in Figure 28. In the liquid reaction the order of increasing reaction rates was L, O, N, M, and P; in the delay burning rate the order of decreasing reaction rates is L, O, N, P, and M.

7. If this is indeed true, as it certainly seems to be, it suggests a number of interesting possibilities. It indicates differences of "reactivity" exist over and above differences in purity, particle size, or surface area. It indicates that the reactivity differences may be covered over and obscured because one test is responsive to one set of factors while a second test may be responsive to a second set of factors. And it indicates that differences in reactivity can be seen in different types of tests in which the reaction rate of a series of samples may be reversed.

8. The reactivity results shown in Figure 7, in which powdered lead dioxide reacts with a liquid reagent in which it is suspended, are almost exactly reversed in Figure 28, in which lead dioxide is mixed with boron (and a viton binder) and pressed into a delay composition. And furthermore, the order and magnitude of the reactivities of the five lead dioxide samples undergo changes from Figure 26 to Figure 27 and finally

to Figure 28. We have already suggested an explanation for this second phenomenon. The delay burning rate is largely dependent on properties that affect the packing density--the particle size, the absolute density, and the apparent density. On the other hand, the reaction rate of lead dioxide in acid solution is largely dependent on the surface area and little affected by the packing density. So we see that factors that may heavily affect the rate of reaction in one set of conditions may have little effect on the rate of reaction in another set of conditions. And indeed the properties that cause lead dioxide to react rapidly in solution--that is, the particle size and more directly the surface area--cause it to react more slowly in a delay composition. This is because large particles with a small particle size range do not pack closely in a delay composition, and the increased porosity that results causes the composition to propagate the flame front through it more rapidly.

9. Pressure-time curves are routinely obtained on starter compositions used in the Mk 25 and the Mk 28 Marine Location Markers. The starter composition contains lead dioxide in varying proportions--usually 20% by weight--and the lead dioxide is a key component since it largely controls the ignitability and burning rate of the composition. The effect of formula changes on the pressure-time curves has already been studied in RDTR No. 41. However, continued variations in the same formula have not been satisfactorily explained. In the present study,

it has been shown that lead dioxide specimens from different manufacturers, used in otherwise identical formulas, give a wide range of pressure-time performance curves. This only confirms what was already suspected. The problem will no doubt continue. Moreover, it must be said that the significance of the pressure-time curve is not well understood. This difficulty is compounded by the fact that there appears to be no correlation between the form of the pressure-time curve and the physical and chemical properties of lead dioxide studied in this investigation. Considerable differences in purity and average particle size, upon which the military specification is based, appear to have no directly discernable relationship with the form of the pressure-time curve. This problem is currently under study.

10. Besides the poor correlation between PbO_2 purity and the pressure-time curve--Table III indicates that sample N-2 has a purity of only 79.5% PbO_2 and yet it has a fast pressure-time curve--there is generally also a poor correlation between PbO_2 purity and the heat of reaction of the starter compositions. For example, sample N-3 has a purity of 85.1% PbO_2 and a caorific value of 357.4 cal/g; sample N-4 has a purity of 96.3% PbO_2 and a calorific value of 360.1 cal/g. This would not appear to be consistent and would indicate that the evaluation of the chemical purity has little relation with the actual oxidizing power of the lead dioxide in a pyrotechnic composition.

FUTURE WORK

1. Since the analytical method of determining PbO_2 is not highly specific, and since the relationship between the purity and the heat of reaction and the purity and the pressure-time curve often appears inconsistent, a re-evaluation of the existing analytical technique will be initiated. Other test methods will be explored in an effort to find a procedure that is specific for PbO_2 or that can distinguish between the various oxides of lead.

2. An investigation is already underway to elucidate the form of the pressure-time curve as well as the inter-relationship between the values of θ, P max, and t P max. Furthermore, the properties of lead dioxide that cause samples from different manufacturers to give such different pressure-time curves are being sought.

3. Finally, other performance tests which may be used to predict the burning characteristics of lead dioxide in starter compositions and other pyrotechnic systems will be reviewed. Also consideration will be given to the concept of specifying a constant performance value based on a sliding formula, instead of the present tendency of requiring a rigid formula and a rigid performance, which is based on the mistaken premise that all chemical components that pass current specifications are more or less alike.

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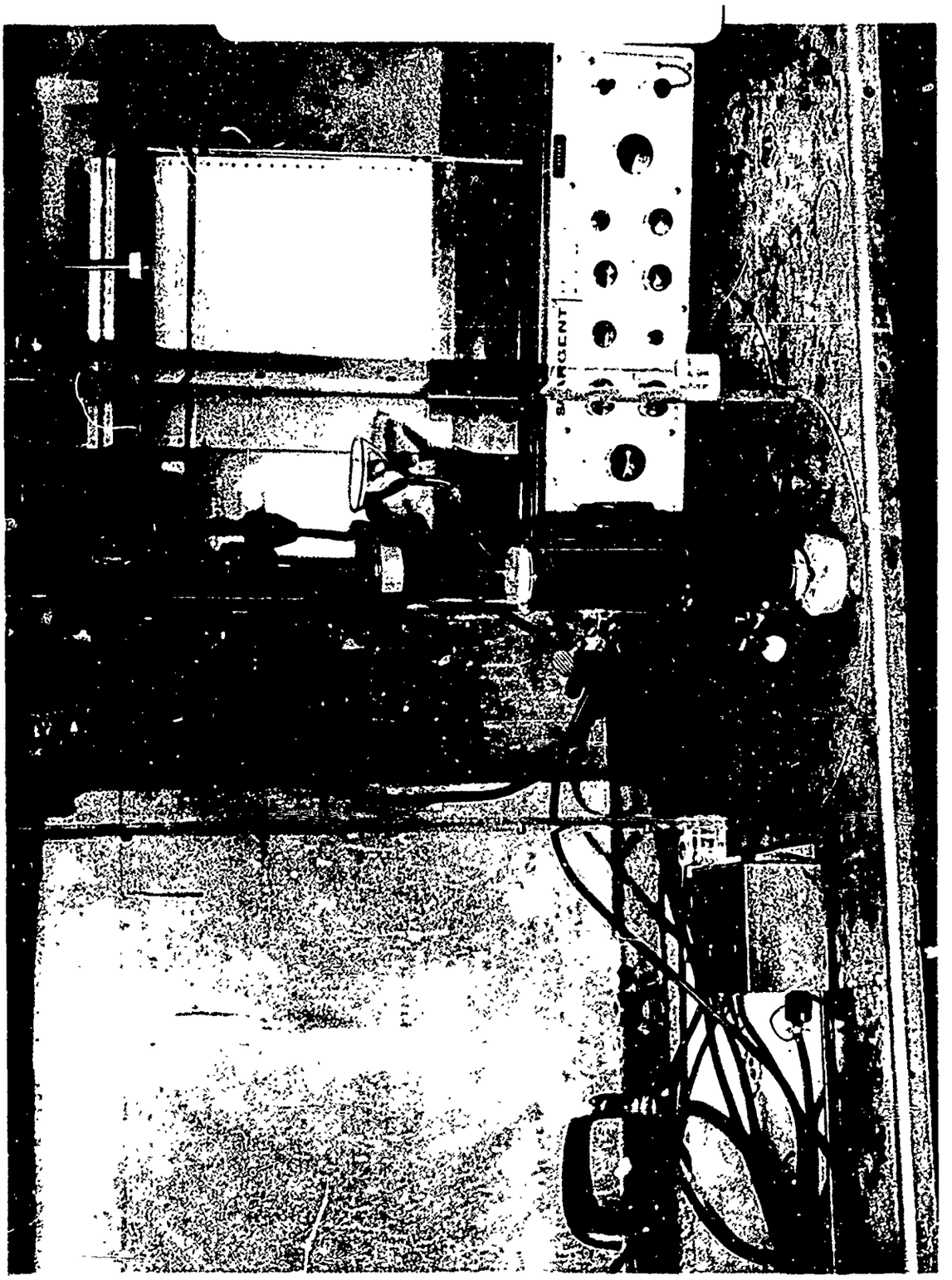
APPENDIX I

FIGURE 1 Rate Calorimetry Apparatus for the Determination of the Reactivity of Lead Dioxide



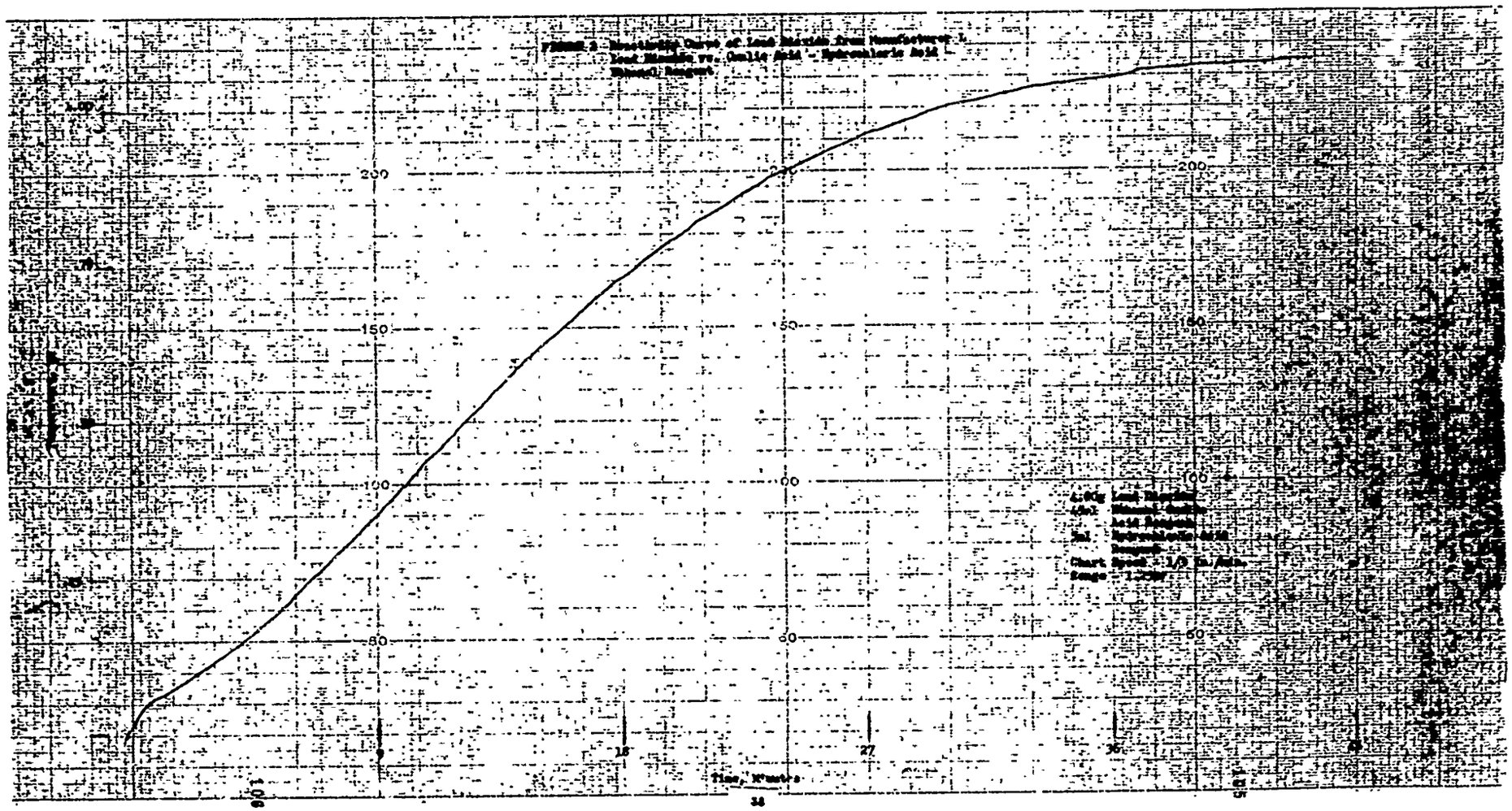
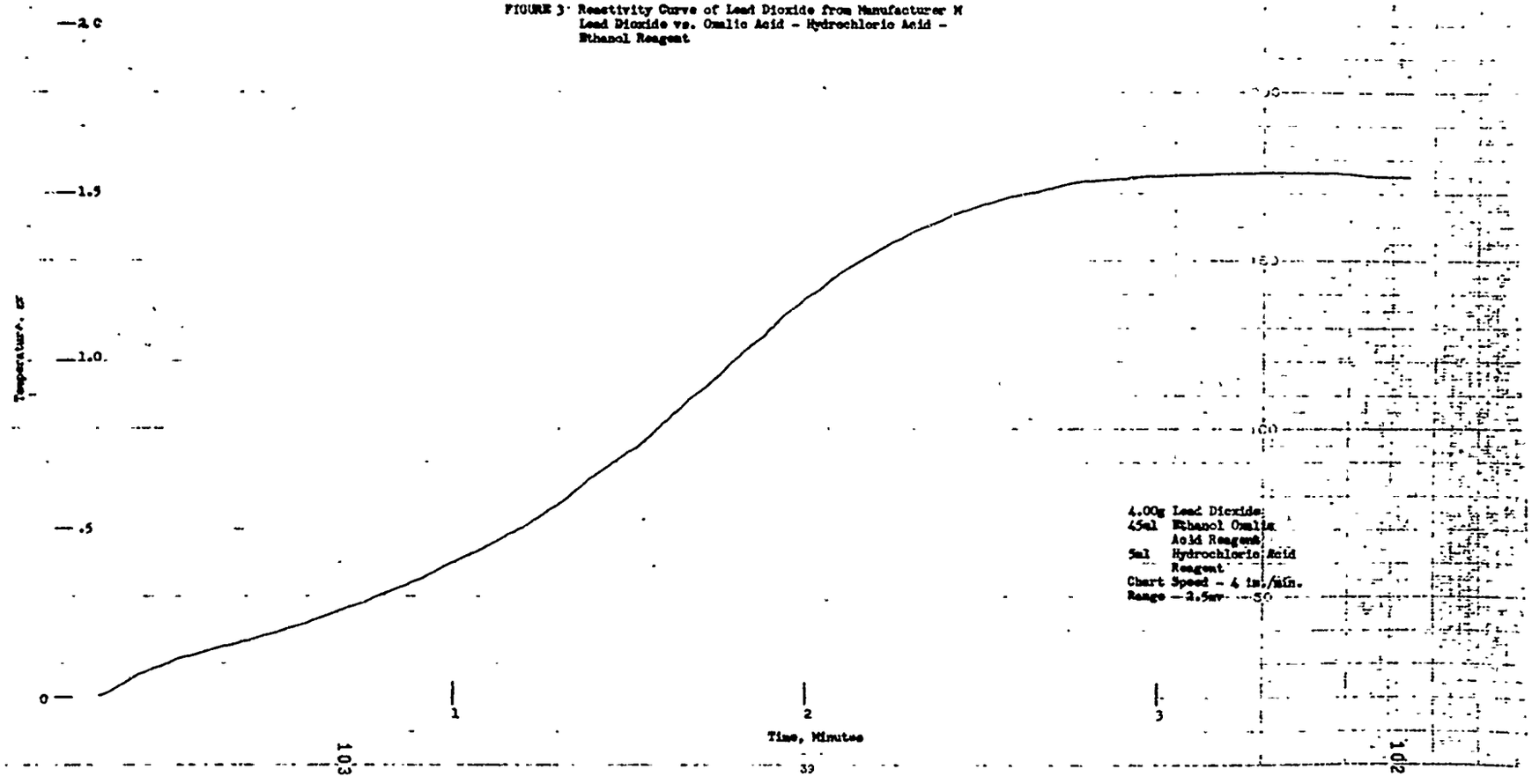

200
150
100
50
18
27
36
Time, Minutes

FIGURE 3: Resistivity Curve of Lead Dioxide from Manufacturer M Lead Dioxide vs. Oxalic Acid - Hydrochloric Acid - Ethanol Reagent



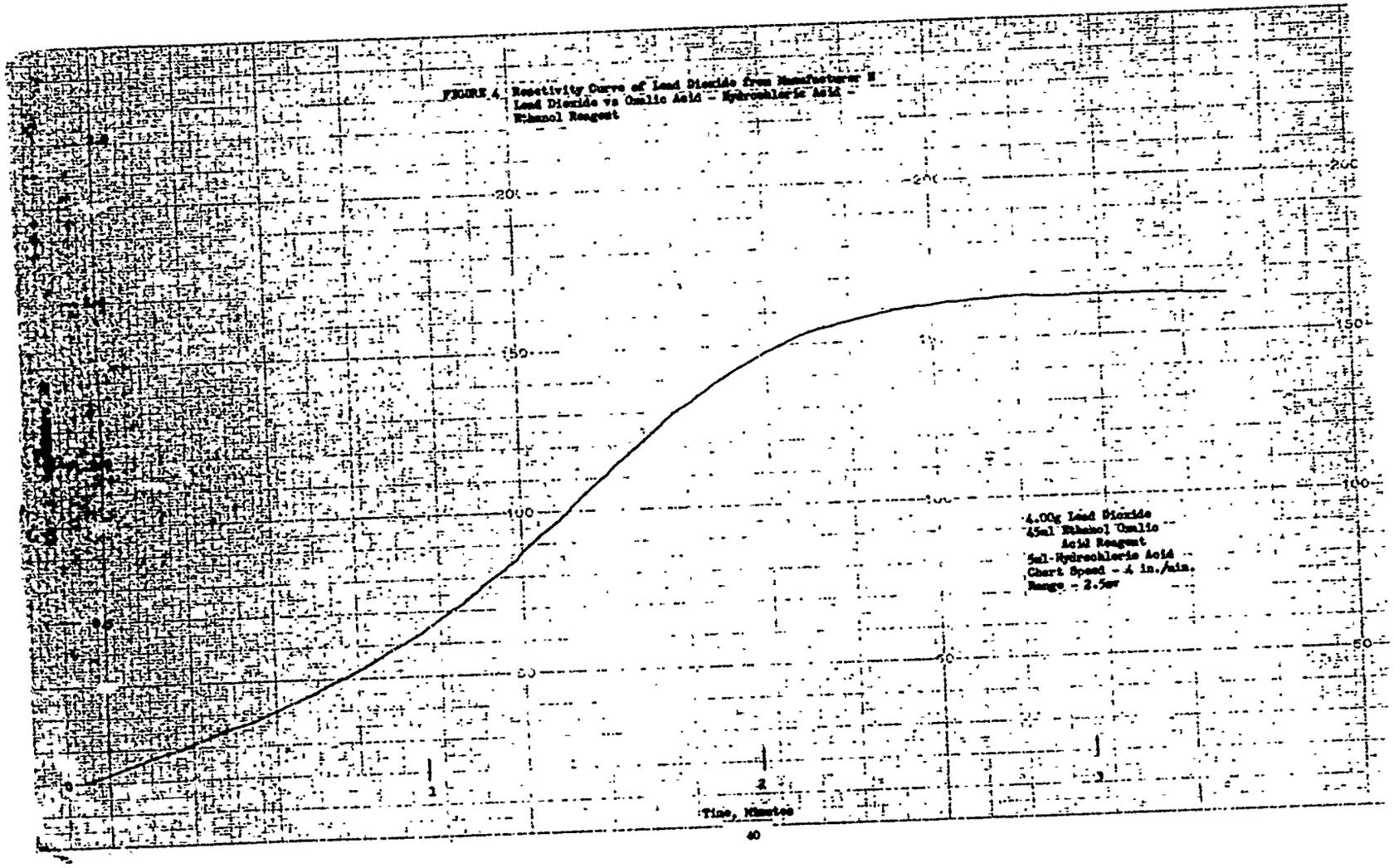


FIGURE 4. Reactivity Curve of Lead Dioxide from Manufacturer B
Lead Dioxide vs Oxalic Acid - Hydrochloric Acid -
Ethanol Reagent

FIGURE 5 Reactivity Curve of Lead Dioxide from Manufacturer O Lead Dioxide vs Oxalic Acid - Hydrochloric Acid - Ethanol Reagent

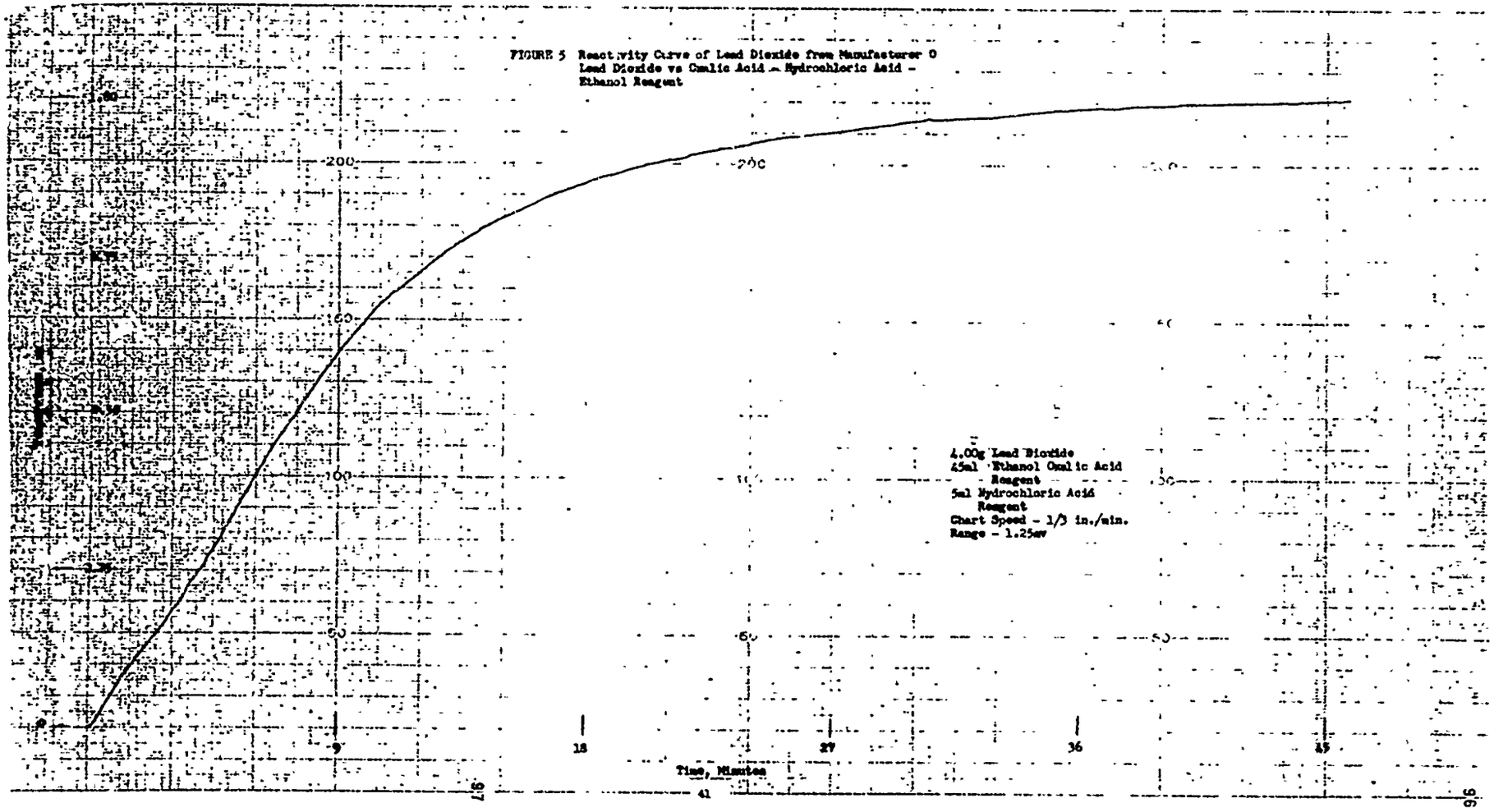
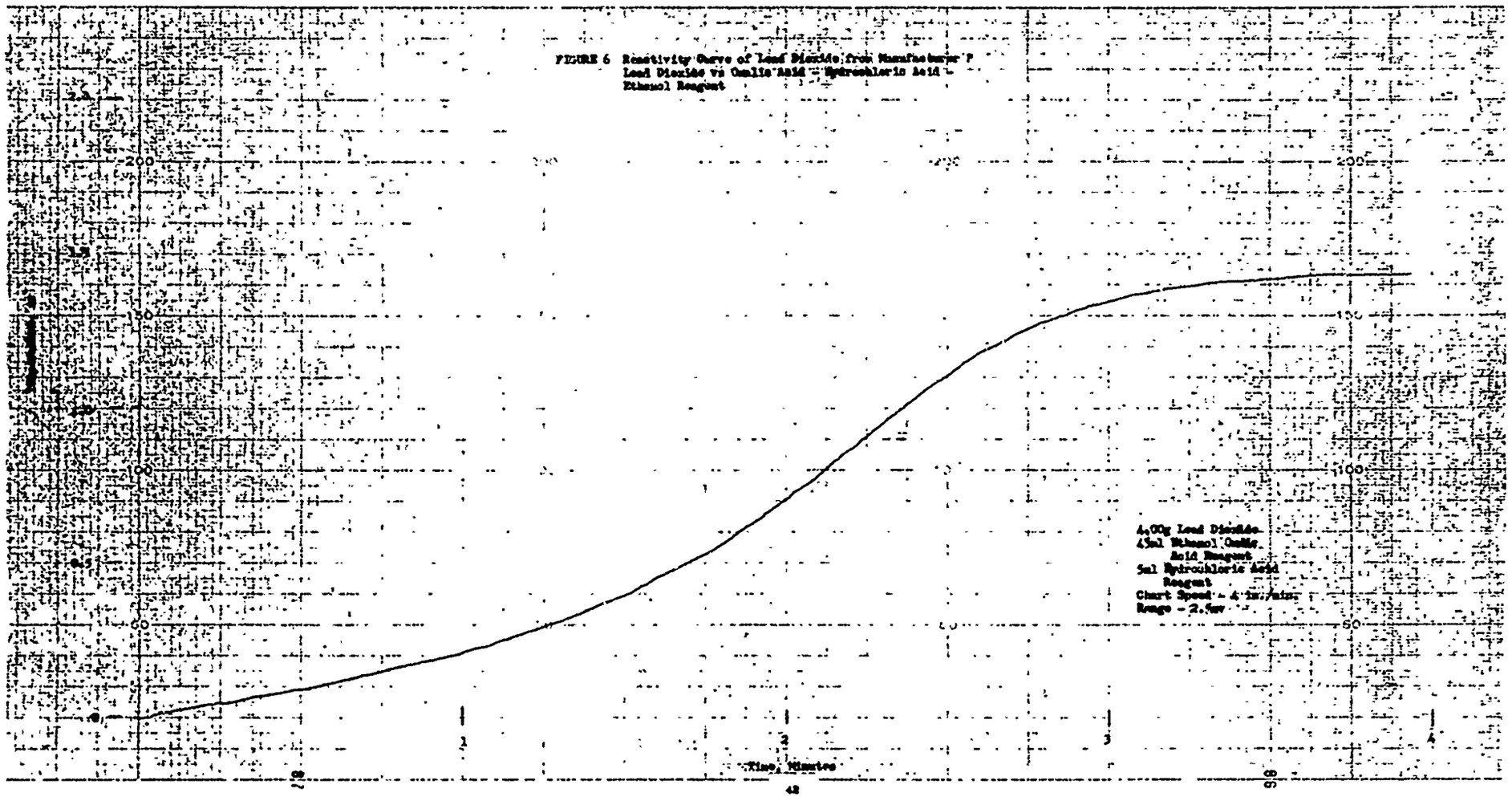


FIGURE 6 Resistivity Curve of Lead Dioxide from Manufacturer P
Lead Dioxide vs Oxalic Acid - Hydrochloric Acid - Ethanol Reagent



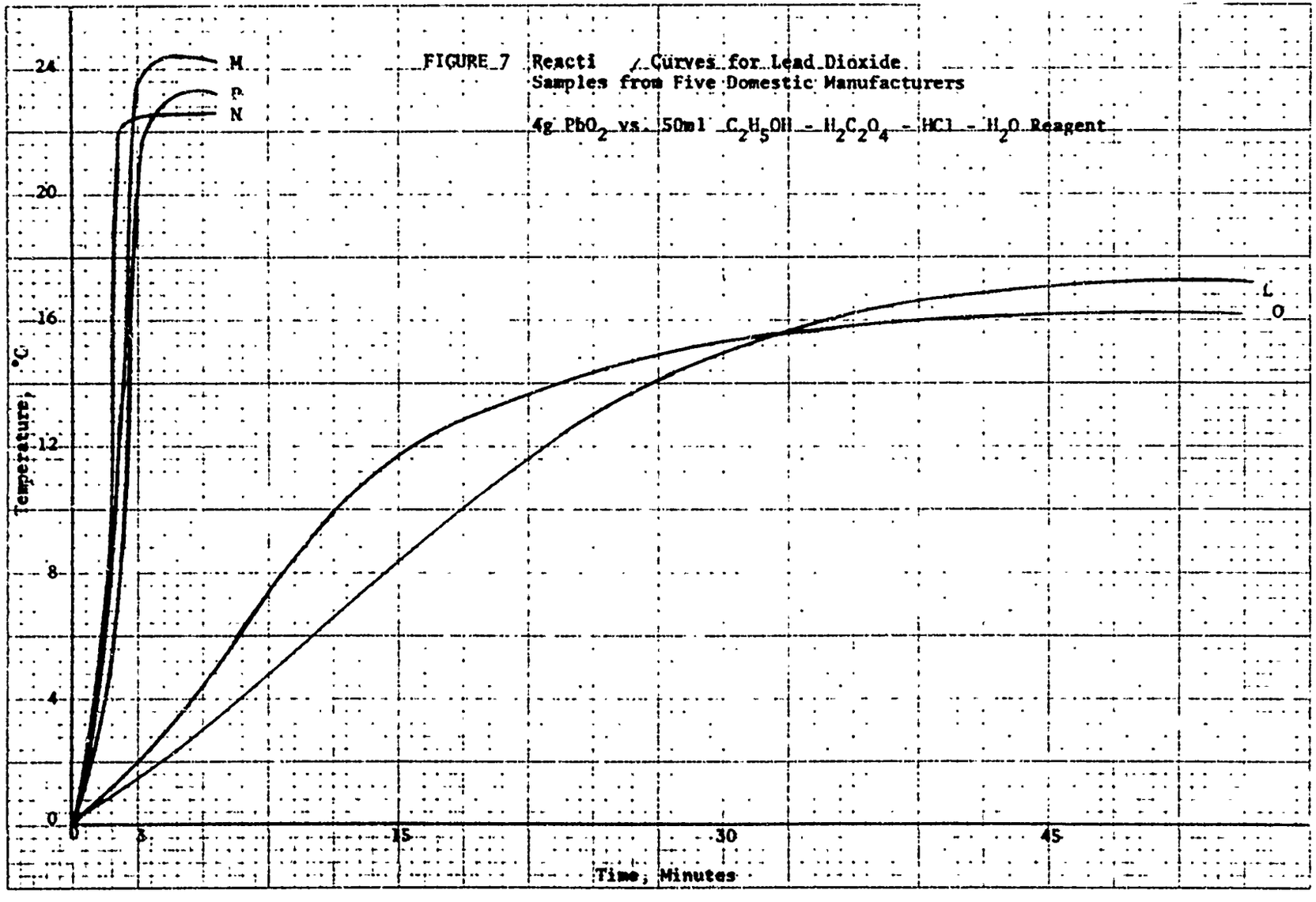
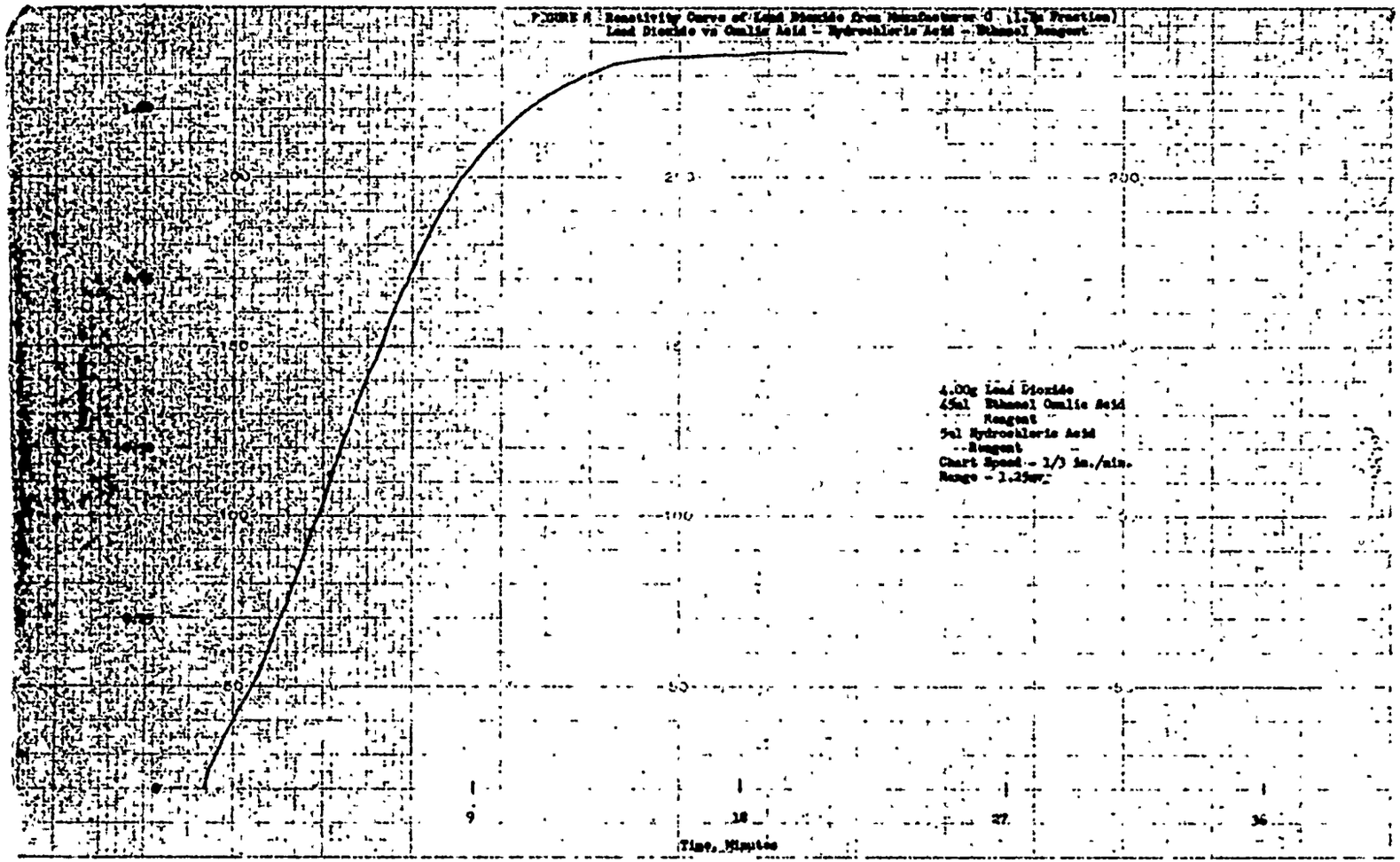


FIGURE 7 Reacti / Curves for Lead Dioxide Samples from Five Domestic Manufacturers

4g PbO_2 vs. 50ml C_2H_5OH - $H_2C_2O_4$ - HCl - H_2O Reagent

FIGURE 8 Sensitivity Curve of Lead Dioxide from Manufacturer (1.5% Fraction)
Lead Dioxide vs Oxalic Acid - Hydrochloric Acid - Ethanol Reagent



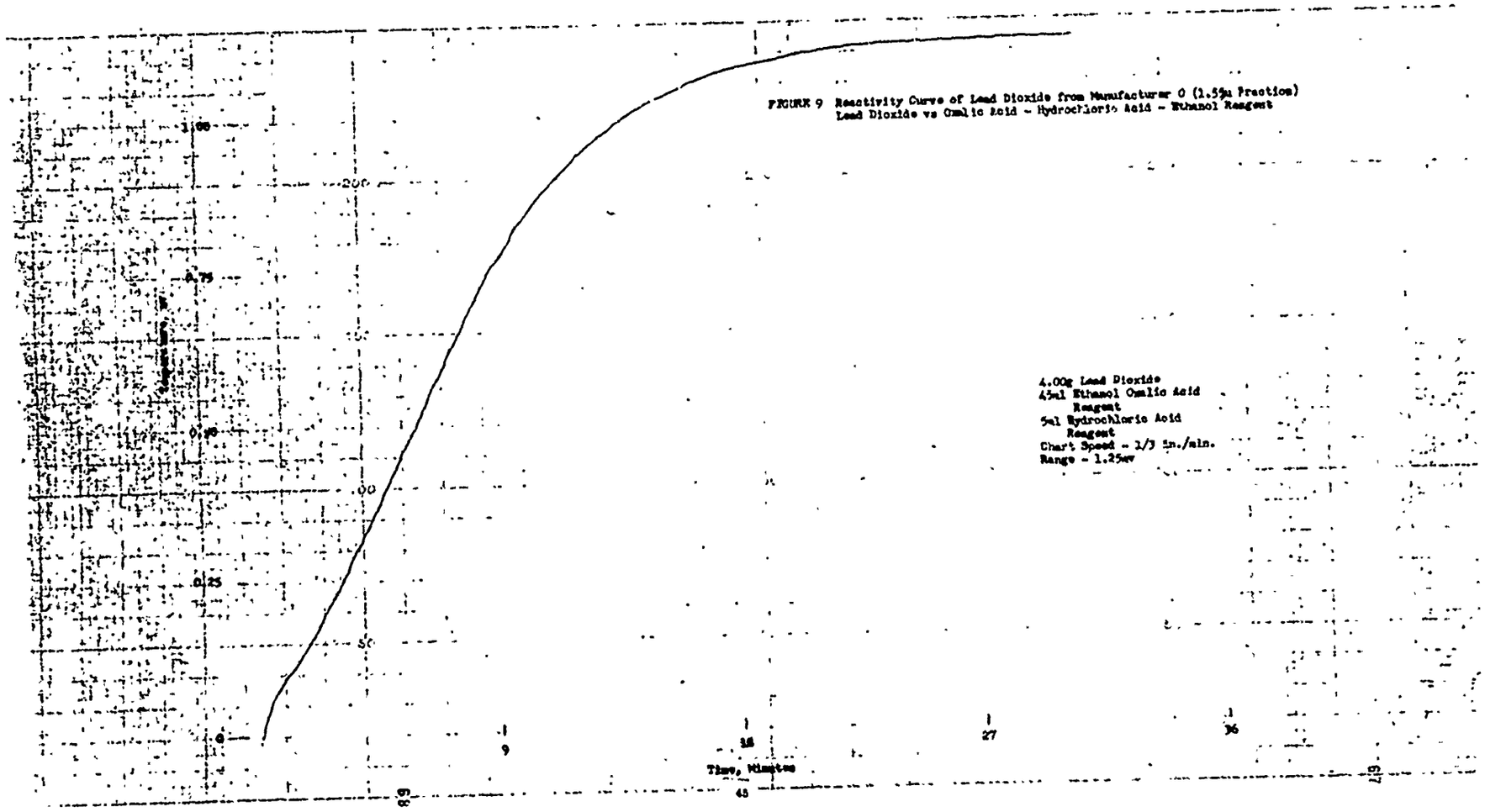


FIGURE 9 Reactivity Curve of Lead Dioxide from Manufacturer O (1.5μ Fraction) Lead Dioxide vs Oxalic Acid - Hydrochloric Acid - Ethanol Reagent

FIGURE 10 Reactivity Curve of Lead Dioxide from Manufacturer O (1.7% Fractional)
Lead Dioxide vs Oxalic Acid -- Hydrochloric Acid -- Ethanol Reagent

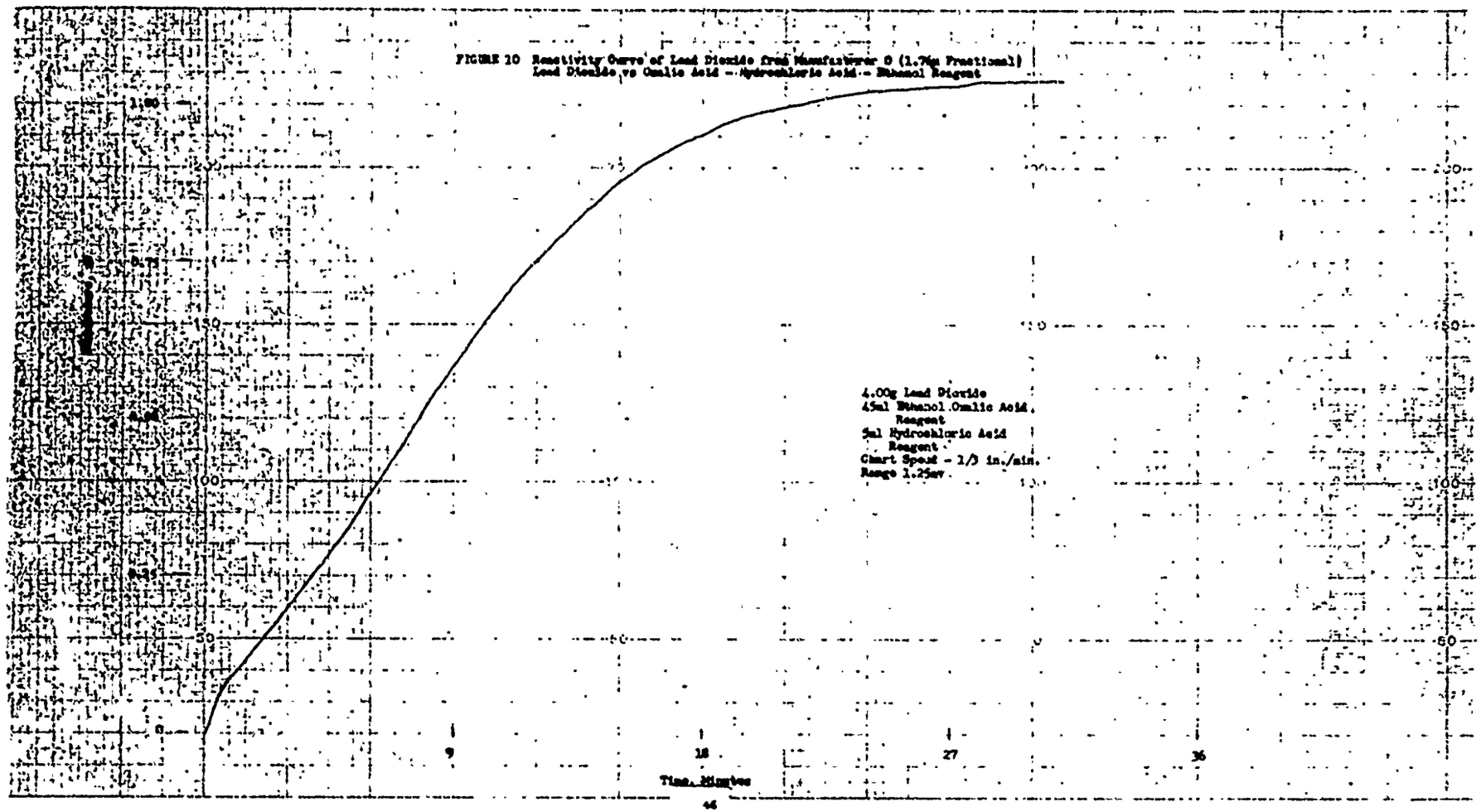


FIGURE 11

Plot of Inflection Point of Temperature-Time Curves Versus Reciprocal Particle Size for Lead Dioxide Samples from Five Domestic Manufacturers

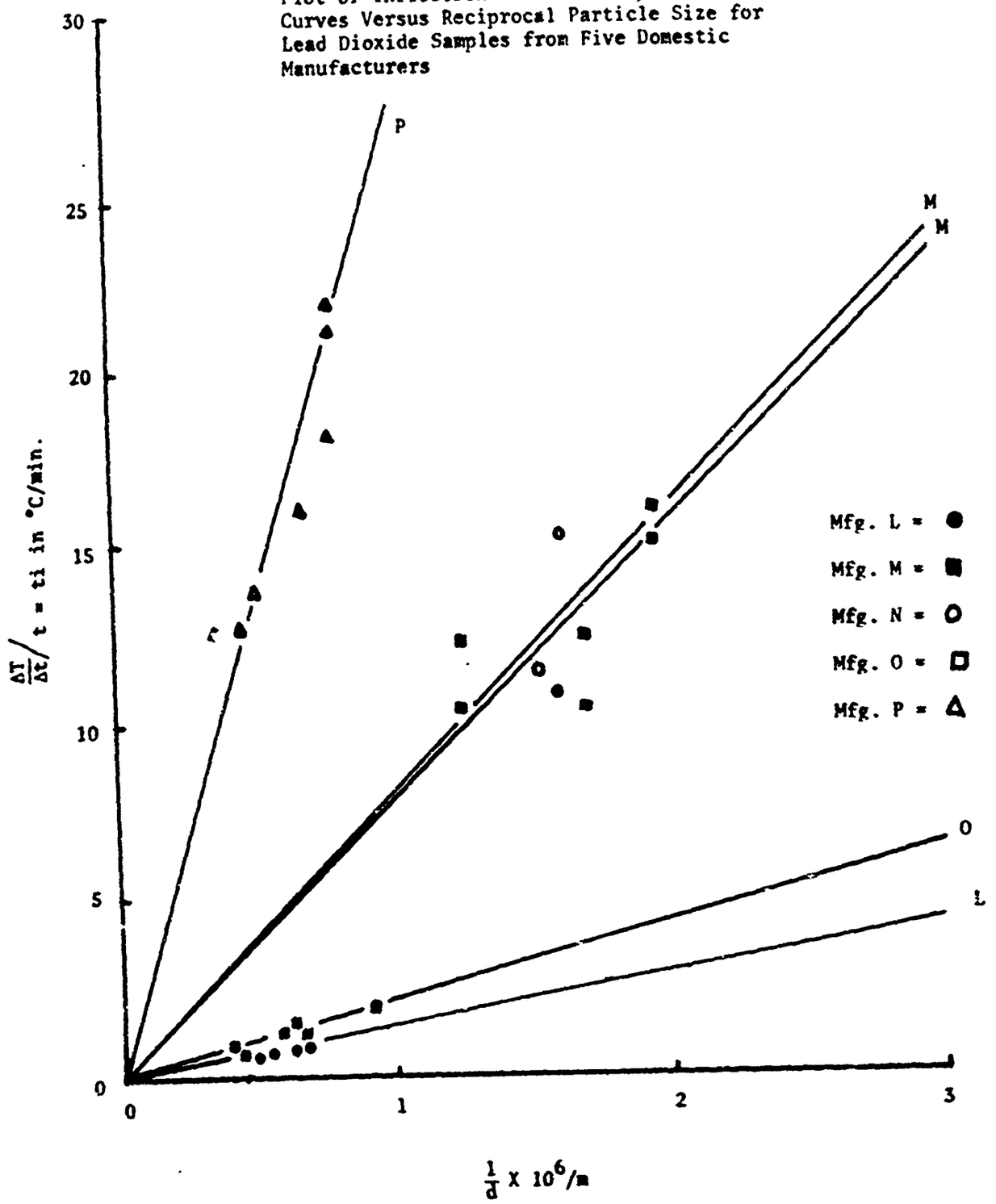
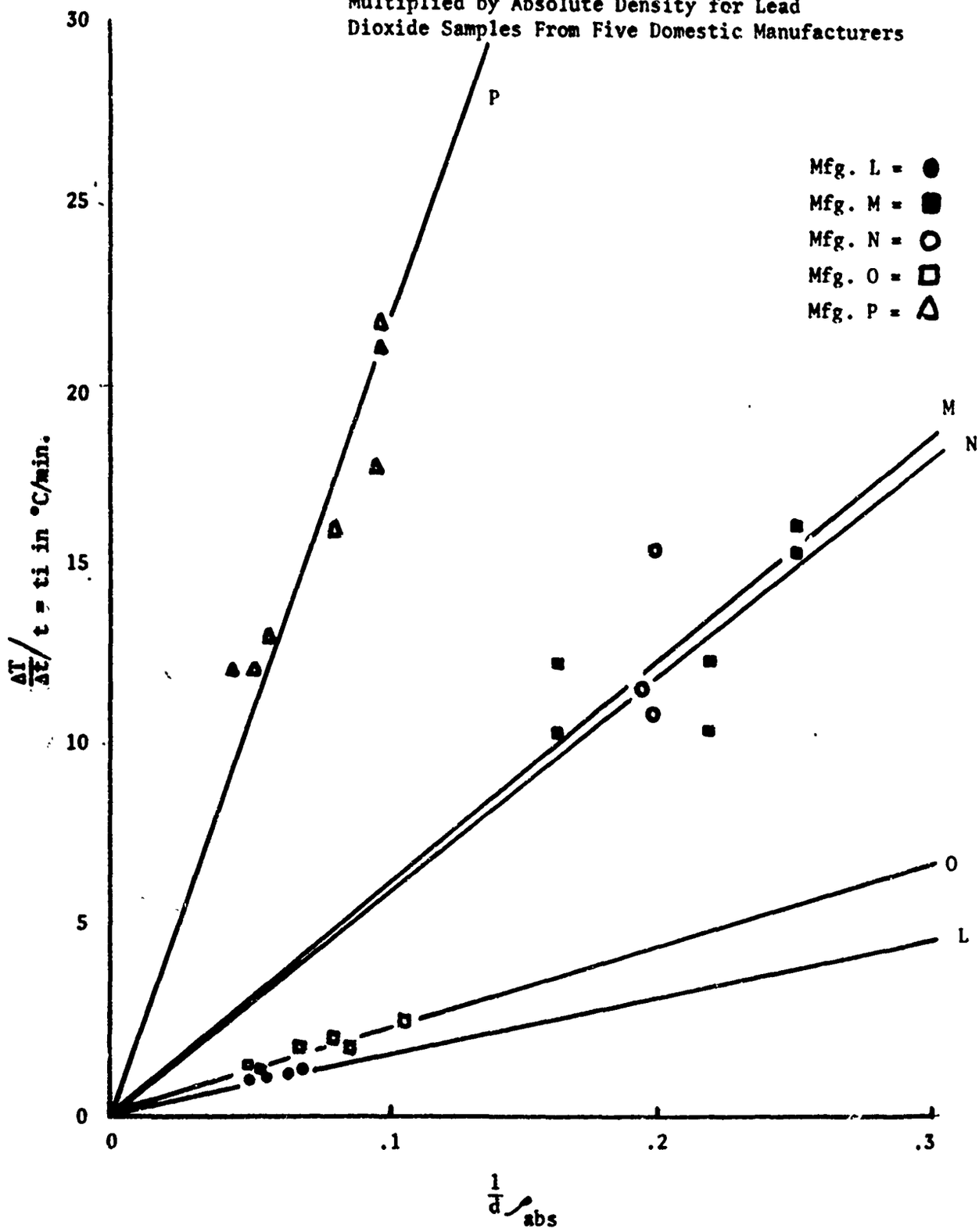


FIGURE 12 Plot of Inflection Point of Temperature-Time Curves Versus Reciprocal Particle Size Multiplied by Absolute Density for Lead Dioxide Samples From Five Domestic Manufacturers



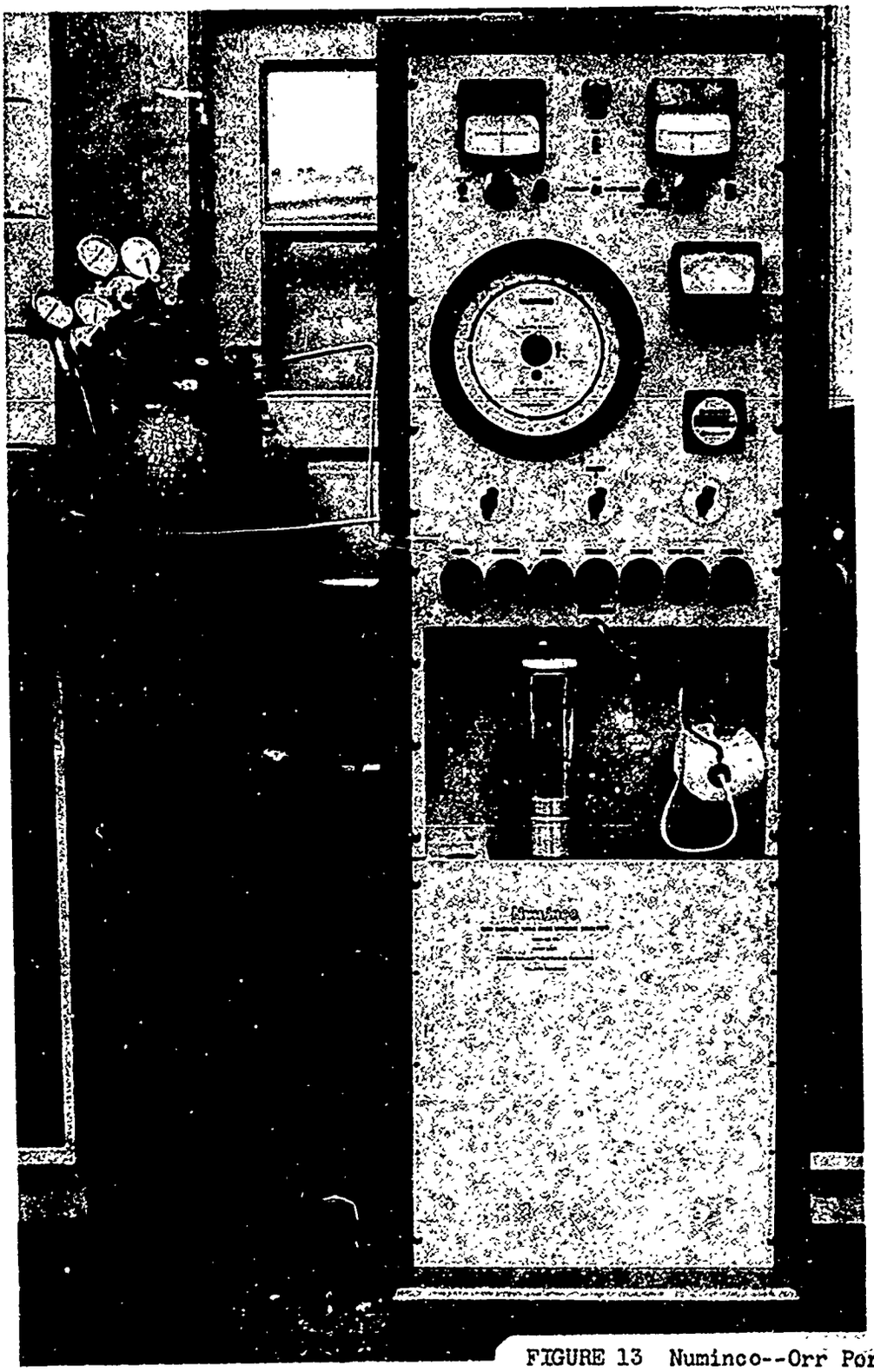
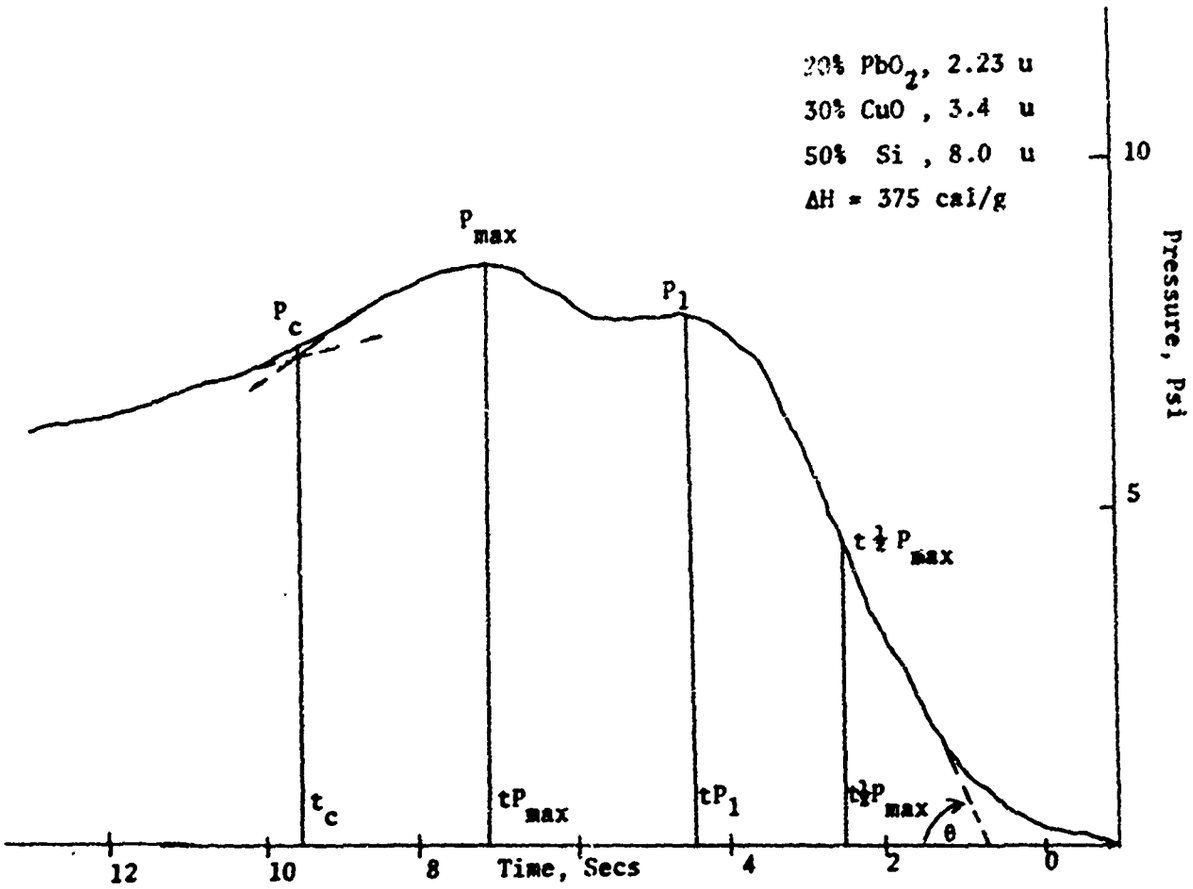


FIGURE 13 Numinco--Orr Pore Volume--Surface Area Analyzer for the Determination of Specific Surface Area

FIGURE 14 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 curve is established.

FIGURE 15 Pressure-Time Curve of 2-3-5 Starter Composition Made With Lead Dioxide from Sample L-1 From Manufacturer L

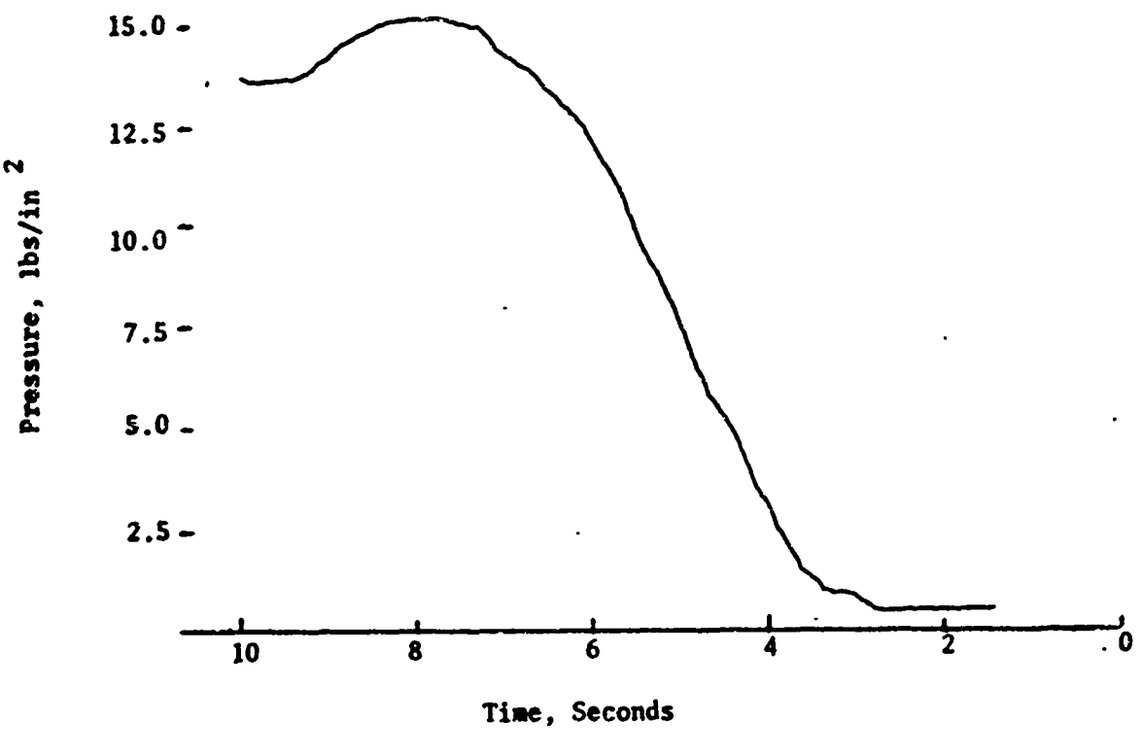


FIGURE 16 Pressure-Time Curve of 2-3-5 Starter Composition Made With Lead Dioxide Sample L-2 From Manufacturer L

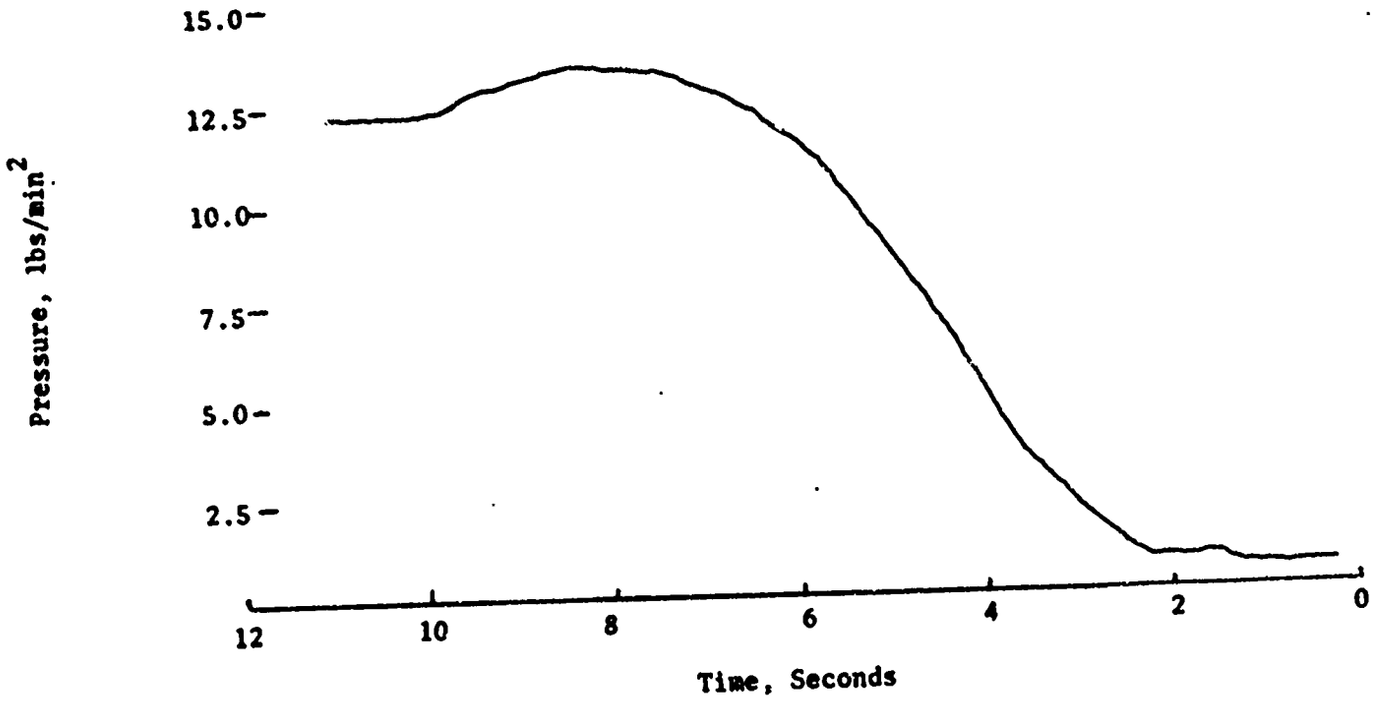


FIGURE 17 Pressure-Time Curve of 2-3-5 Starter Composition Made With Lead-Dioxide Sample M-1 From Manufacturer M

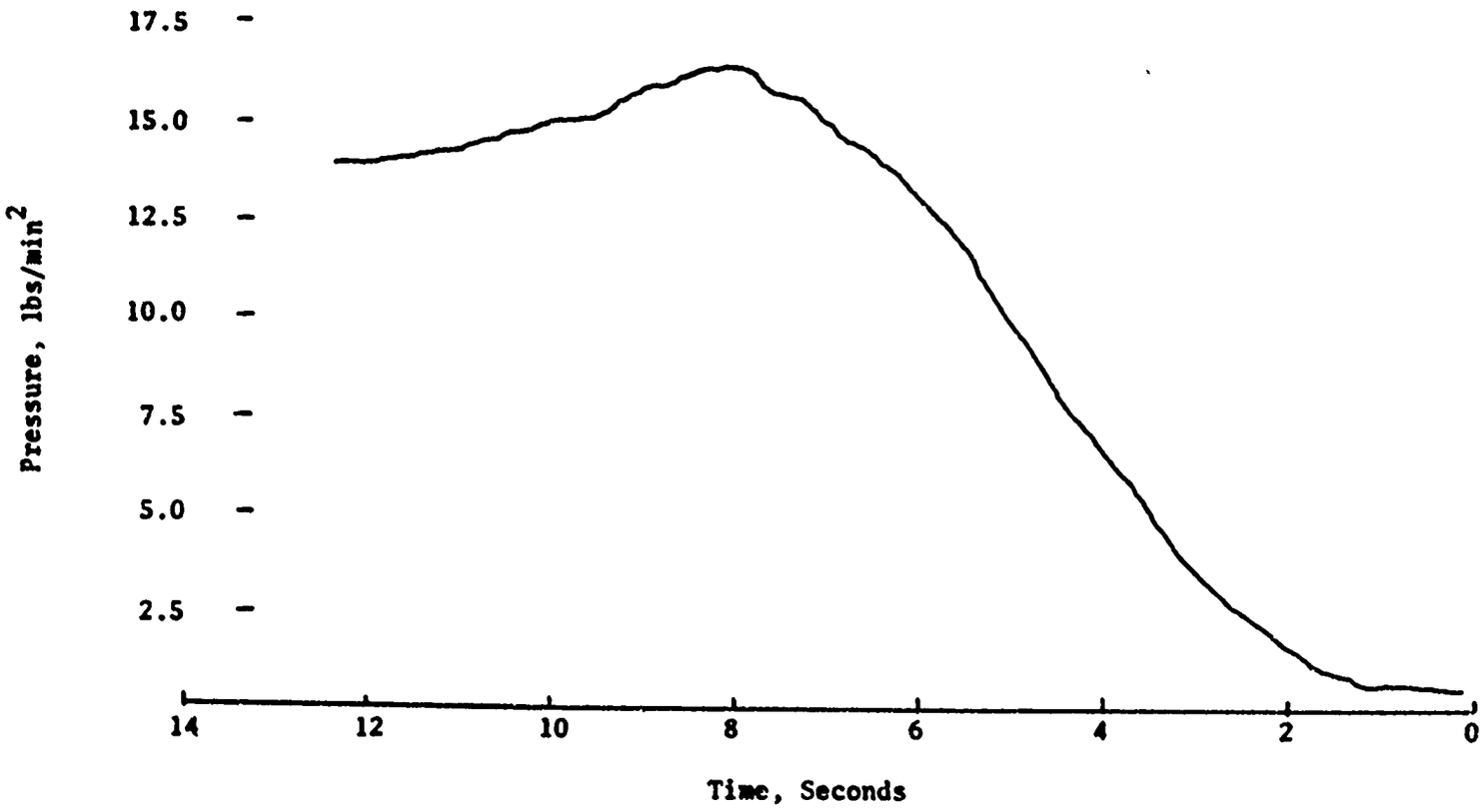


FIGURE 18 Pressure-Time Curve of 2-3-5 Starter Composition Made With Lead Dioxide Sample M-2 From Manufacturer M

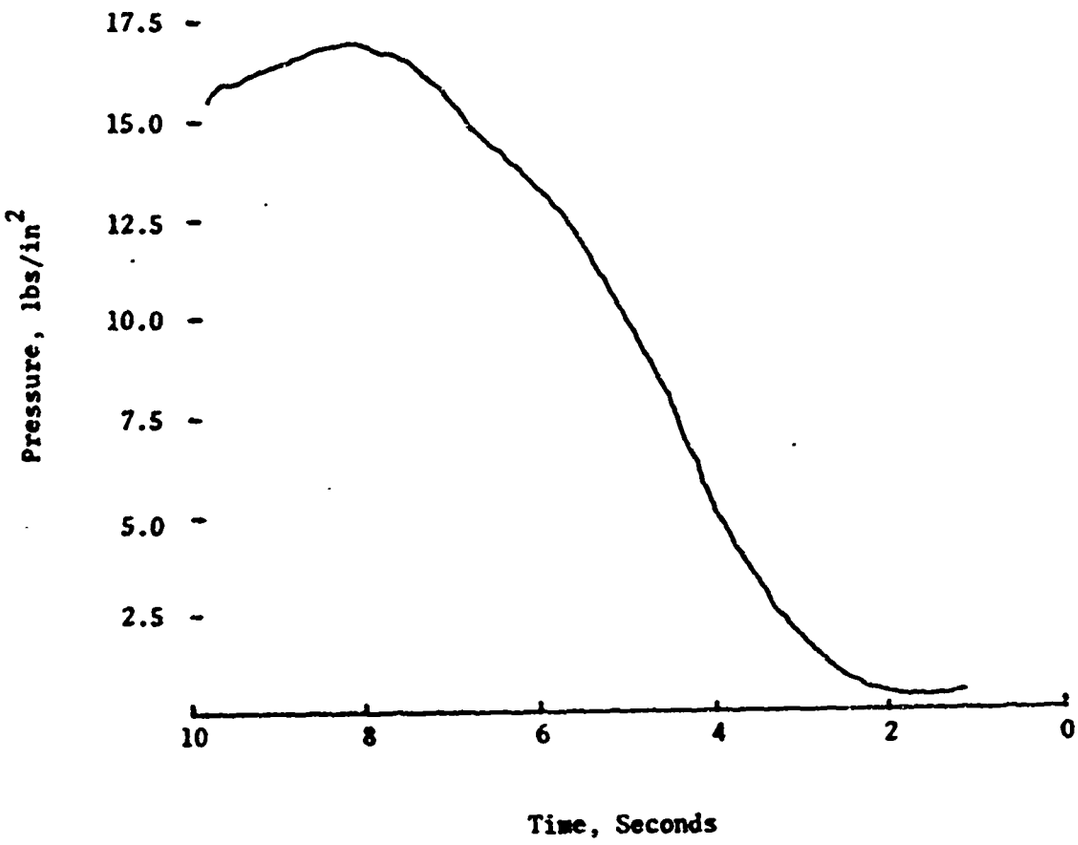


FIGURE 19 Pressure-Time Curve of 2-3-5 Starter Composition Made With Lead Dioxide Sample N-1 From Manufacturer L

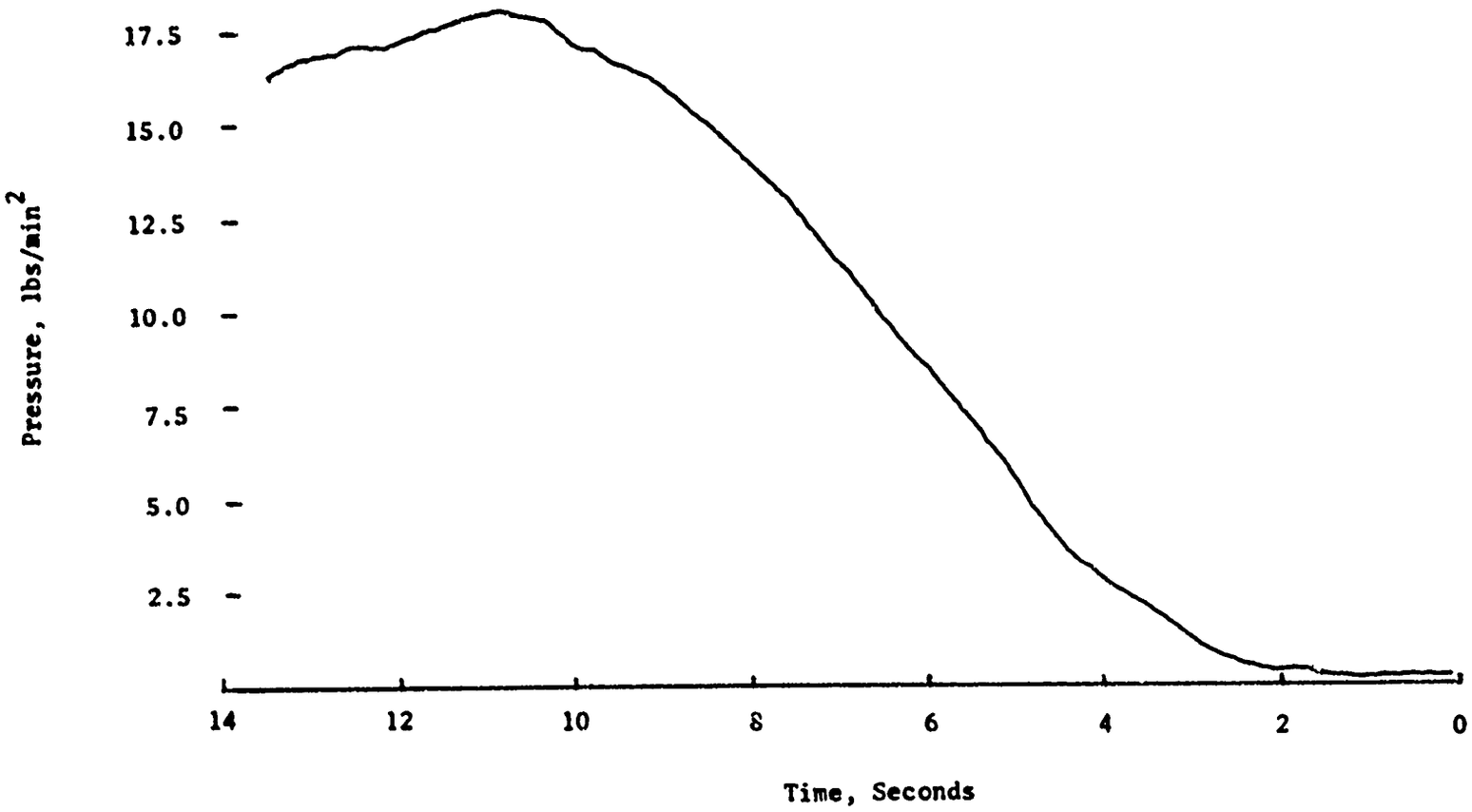


FIGURE 20 Pressure-Time Curve of 2-3-5 Starter Composition Made With Lead Dioxide Sample N-2 From Manufacturer N

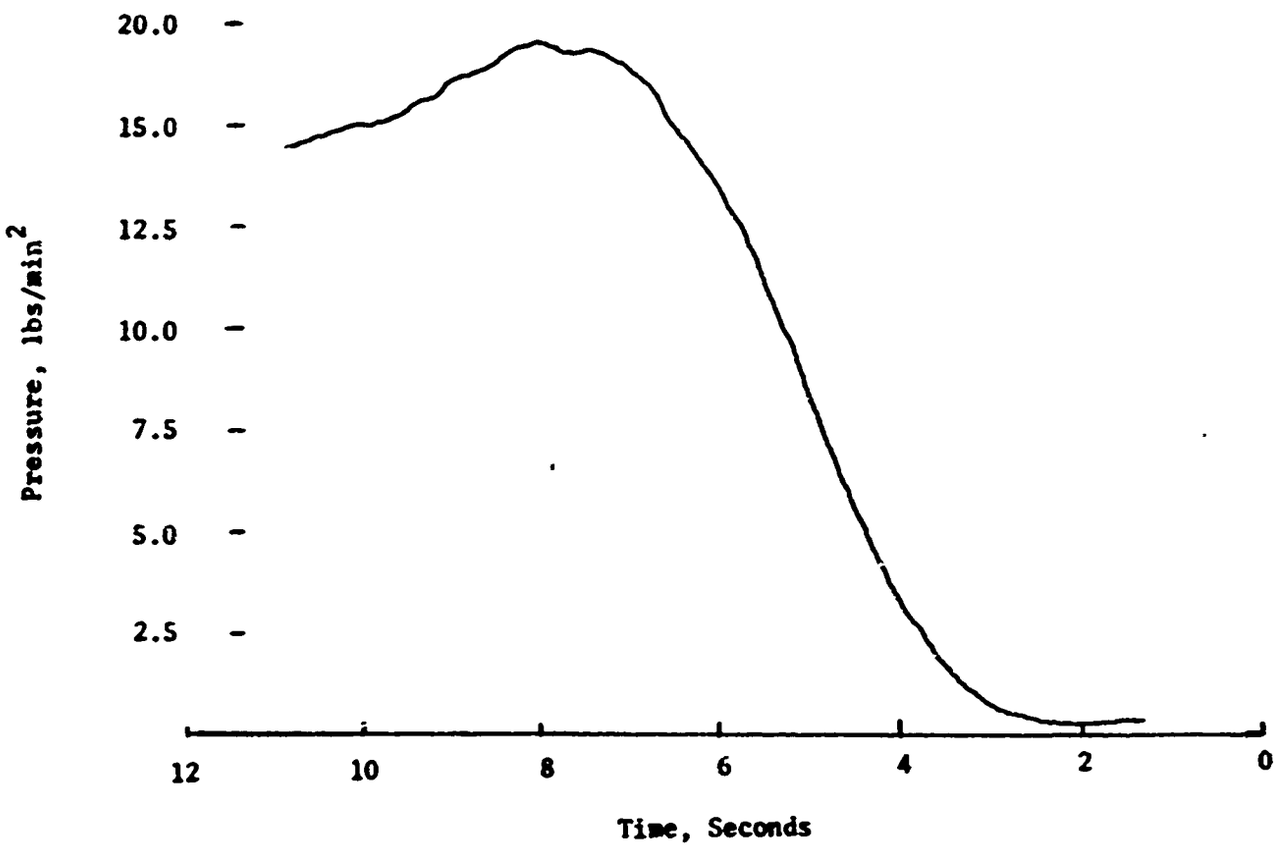


FIGURE 21 Pressure-Time Curve of 2-3-5 Starter Composition Made With Lead Dioxide Sample N-3 From Manufacturer N

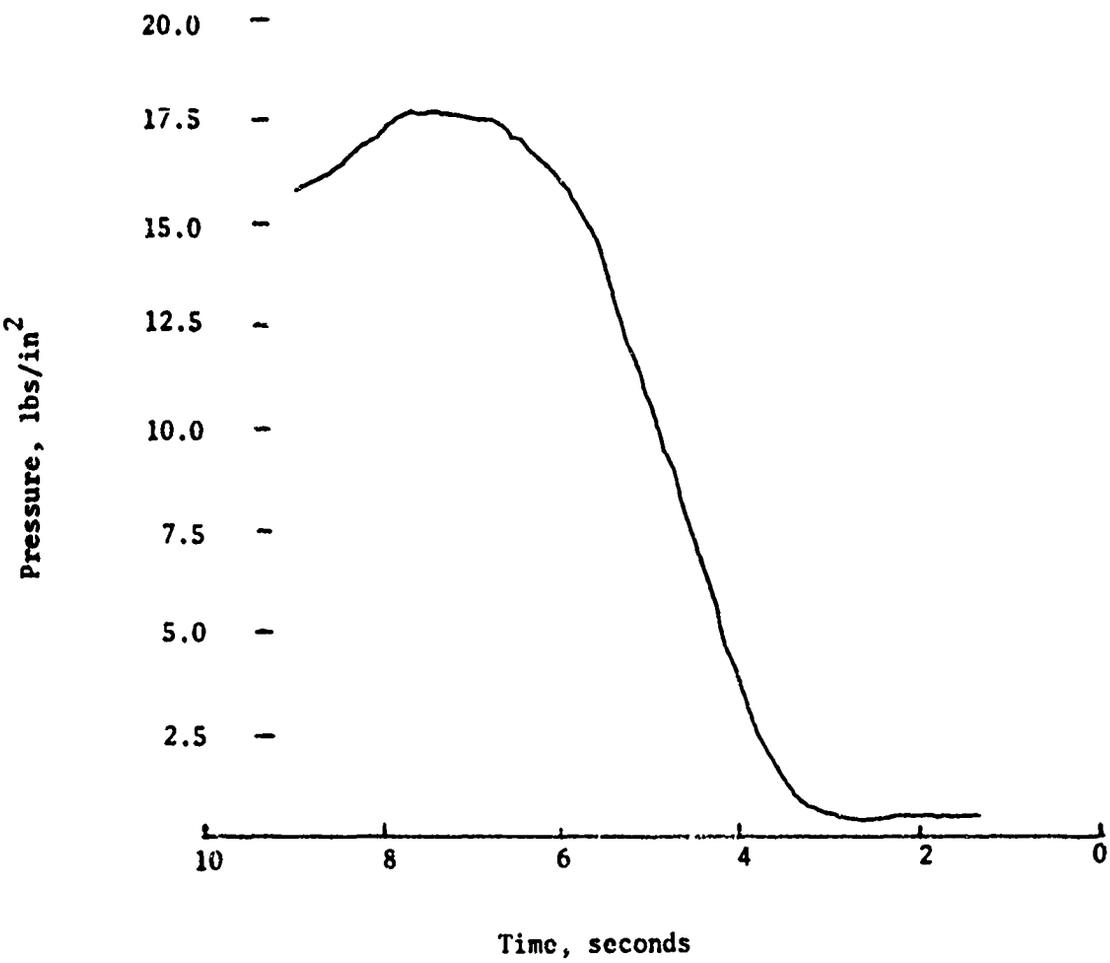


FIGURE 22 Pressure-Time Curve of 2-3-5 Starter Composition Made With Lead Dioxide Sample N-4 From Manufacturer N

FIGURE 23 Pressure-Time Curve of 2-3-5 Starter Composition Made With Lead Dioxide Sample O-1 From Manufacturer O

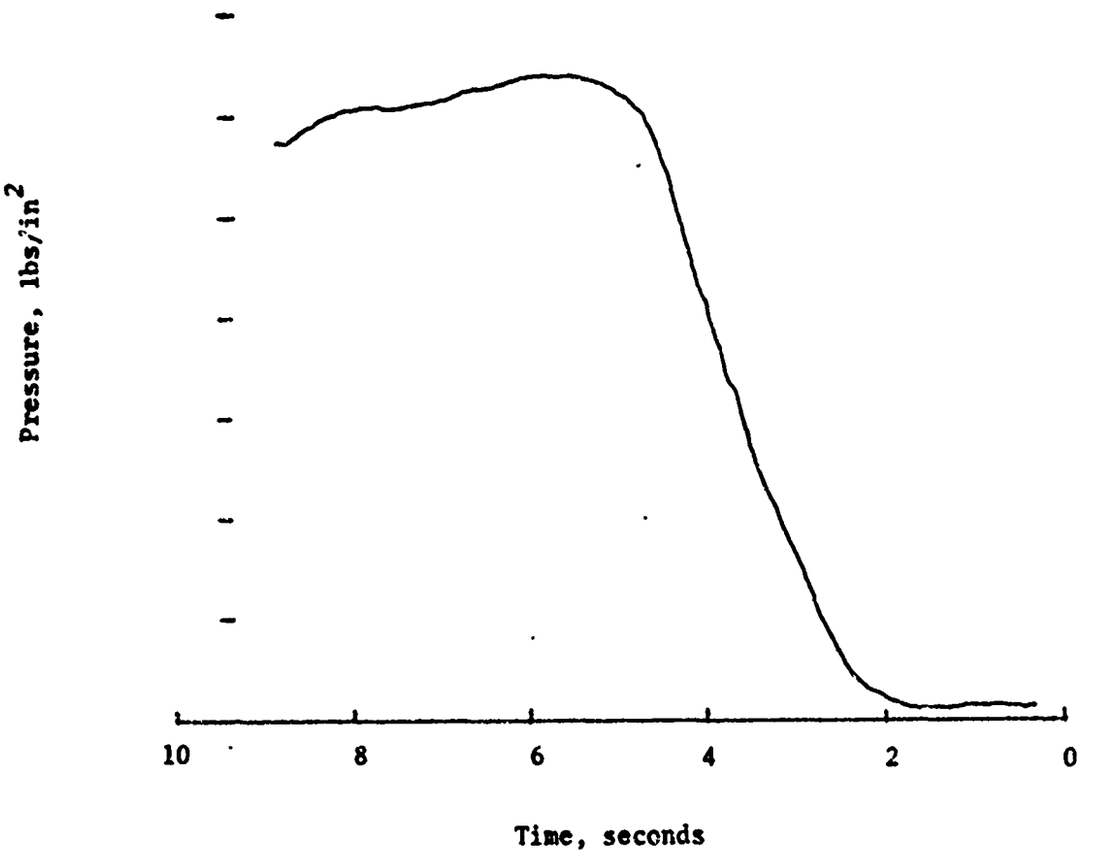


FIGURE 24 Pressure-Time Curve of 2-3-5 Starter Composition Made With Lead Dioxide Sample P-1 From Manufacturer P

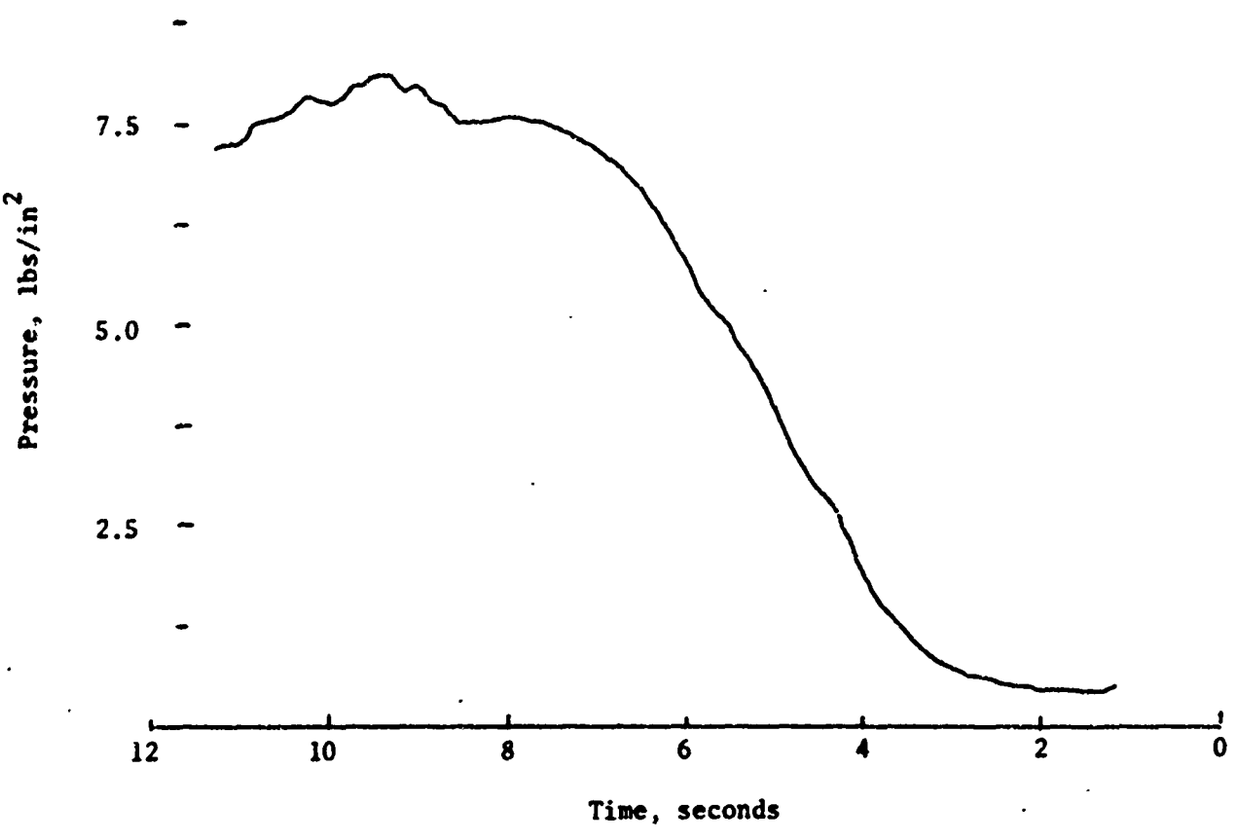


FIGURE 25 Pressure-Time Curve Slope of 2L-3C-5S Starter Composition Versus the Reciprocal Particle Size for 13 Lead Dioxide Samples from Six Domestic Manufacturers

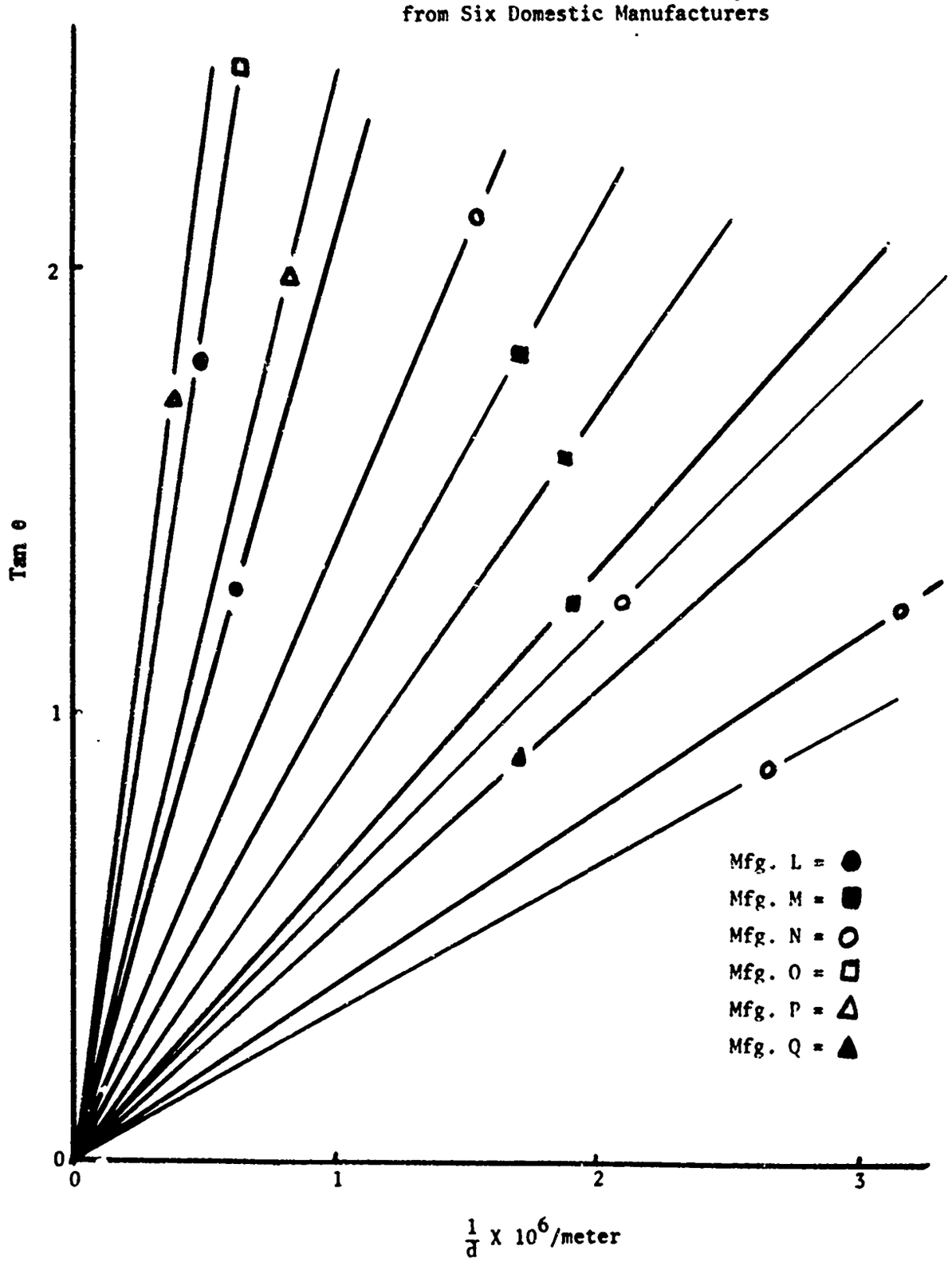


FIGURE 26 Plot of Boron - Lead Dioxide Delay Burning Rate Versus Reciprocal Particle Size Multiplied by Absolute Density for Five Lead Dioxide Sources

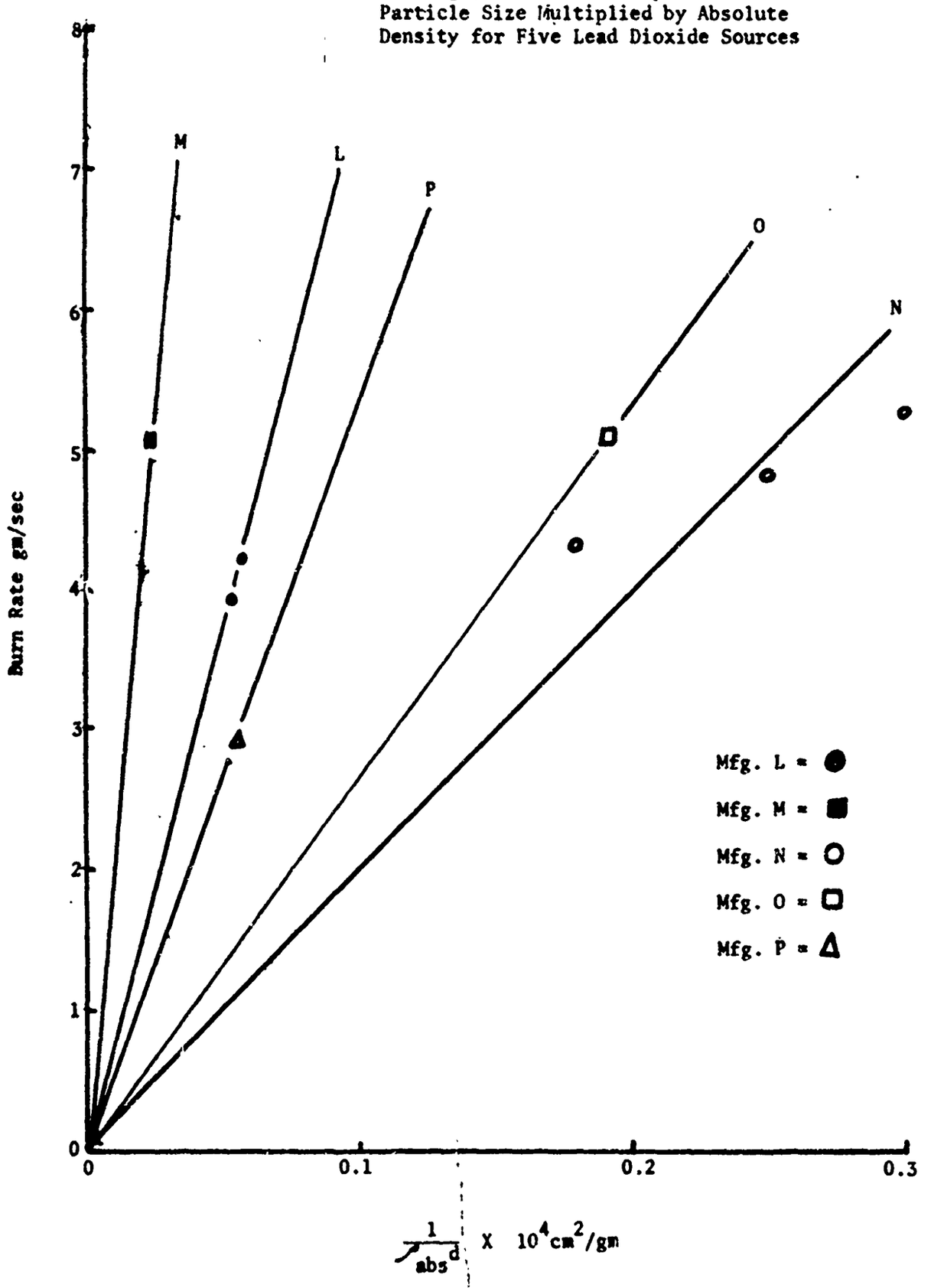


FIGURE 27 Plot of Boron - Lead Dioxide Delay Burning Rate Versus Reciprocal Particle Size Multiplied by Apparent Density for Five Lead Dioxide Sources

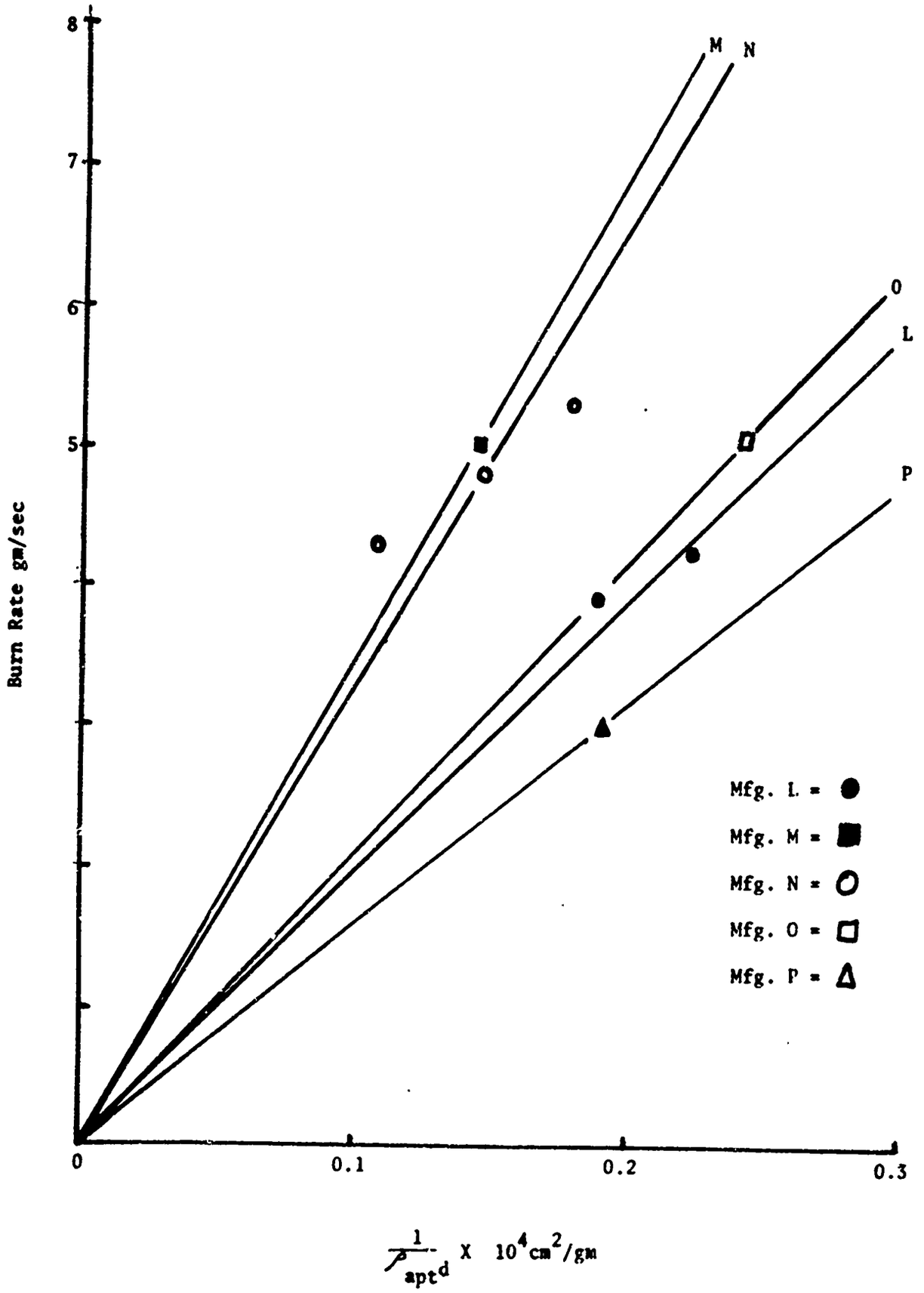


FIGURE 28 Plot of Boron - Lead Dioxide Delay Burning Rate Versus Reciprocal Particle Size Multiplied by Absolute Density and Apparent Density for Five Lead Dioxide Sources

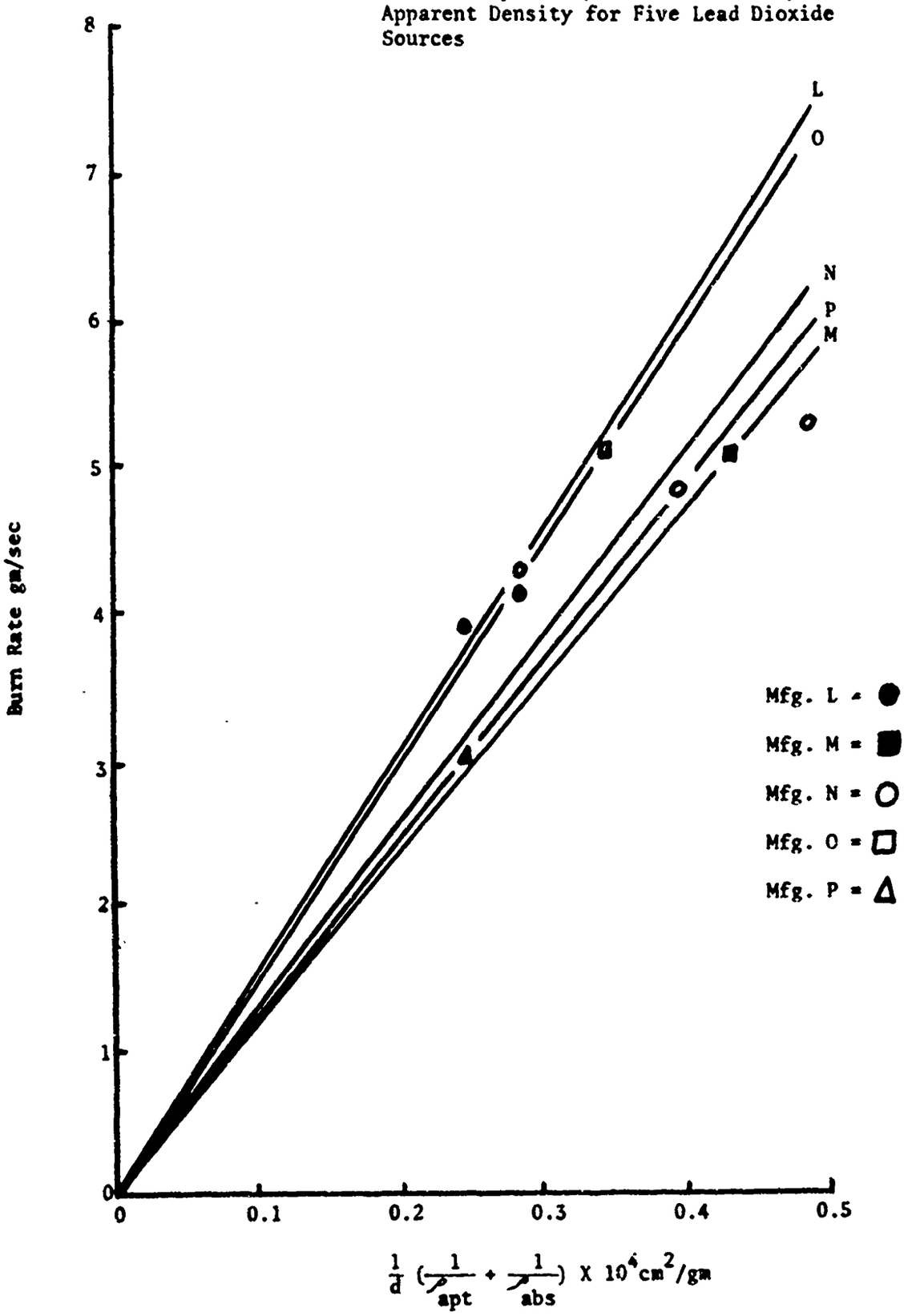


FIGURE 29 Typical DTA Thermogram of Lead Dioxide from Manufacturer L

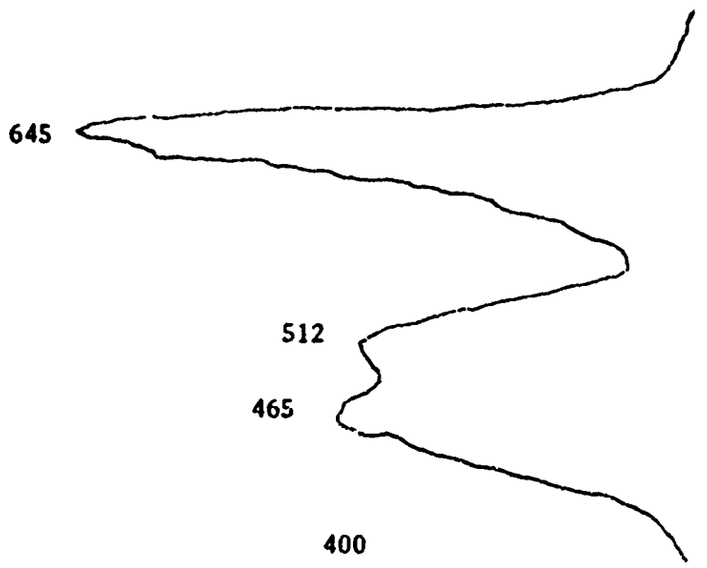


FIGURE 30 Typical DTA Thermogram of Lead Dioxide from Manufacturer M

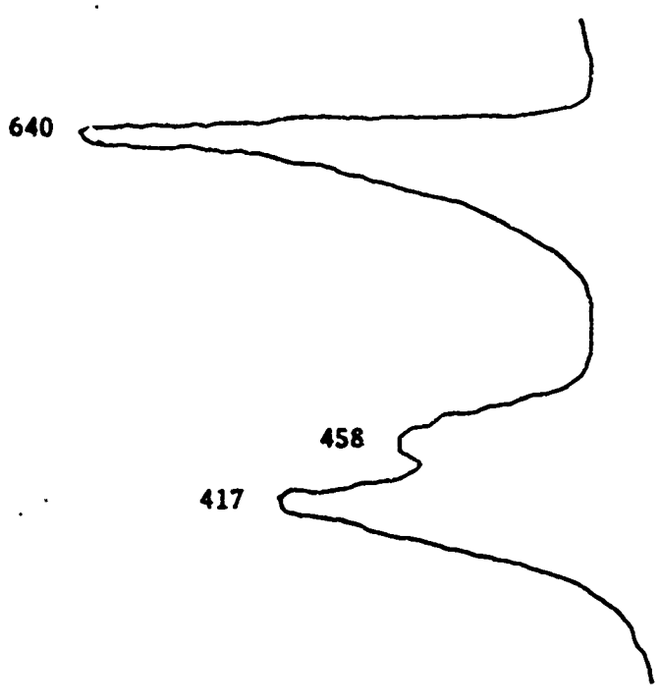


FIGURE 31 Typical DTA Thermogram of Lead Dioxide from Manufacturer N

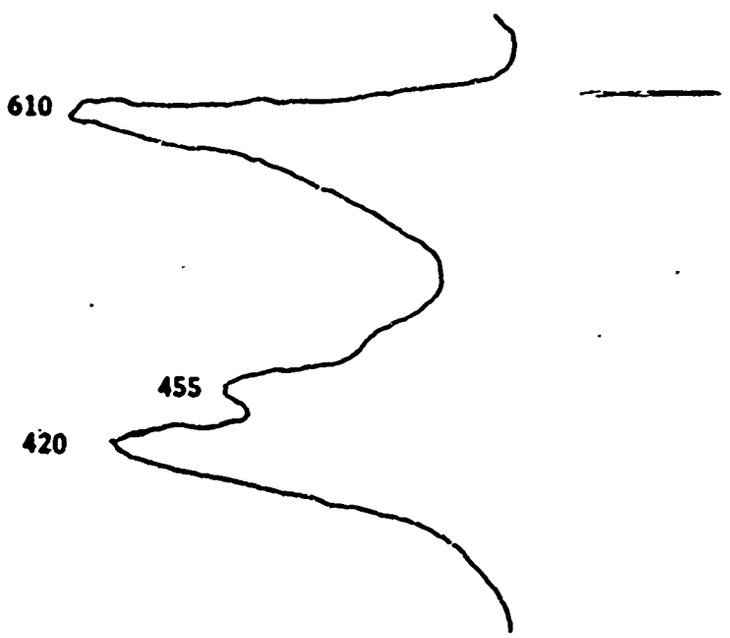


FIGURE 32 Typical DTA Thermogram of Lead Dioxide from Manufacturer O

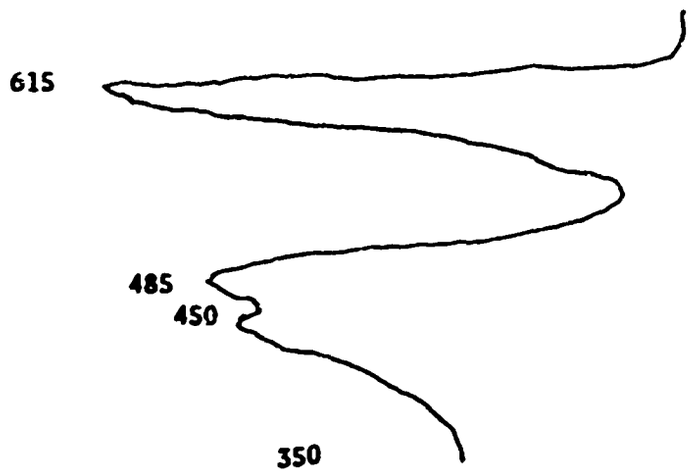


FIGURE 33 Typical DTA Thermogram of Lead Dioxide from Manufacturer P

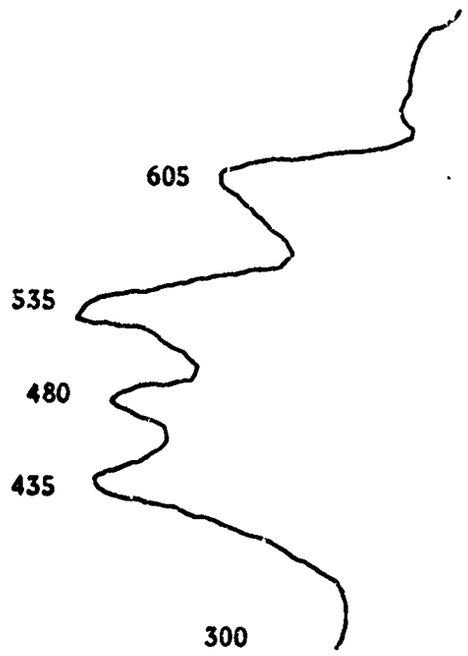
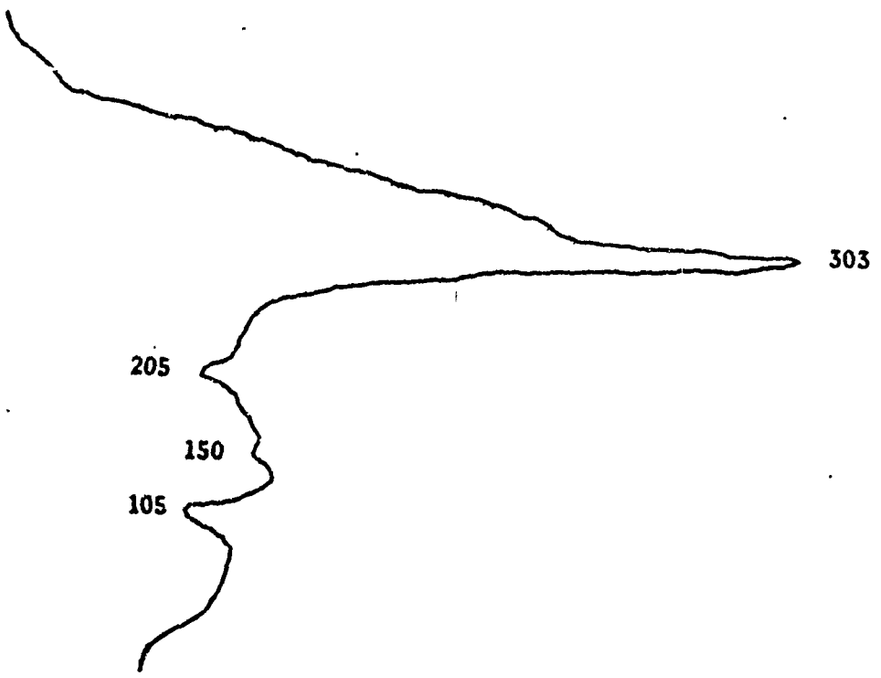


FIGURE 34 Typical DTA Thermogram of Lead Dioxide from Manufacturer Q

FIGURE 35 Typical DTA Thermogram of a 2:1 PbO_2:S Composition Using Lead Dioxide from Manufacturer L



Sample L-2

FIGURE 36 Typical DTA Thermograms of 2:1 PbO_2:S Composition Using Lead Dioxide from Manufacturer M

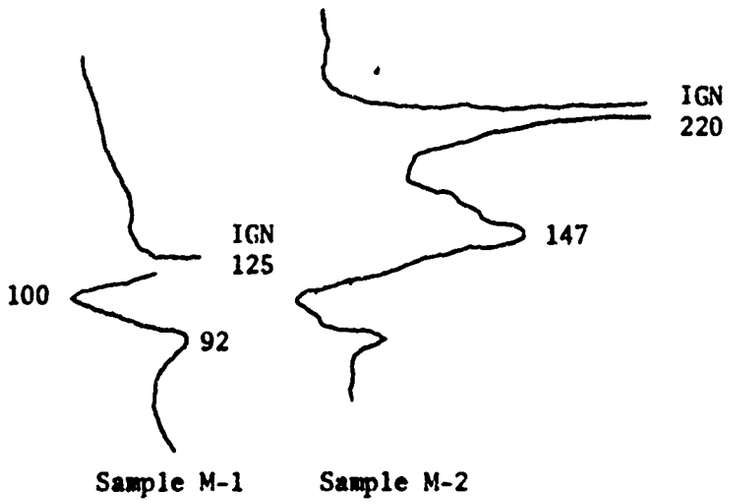


FIGURE 37 Typical DTA Thermograms at 2:1 PbO_2:S Composition Using Lead Dioxide from Manufacturer N

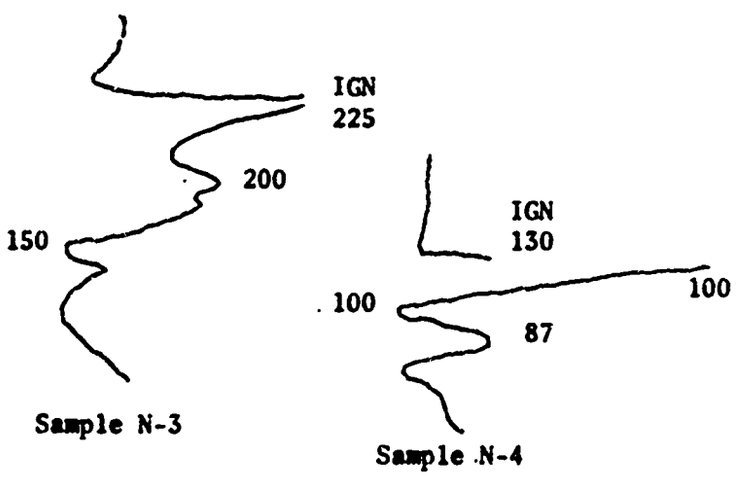
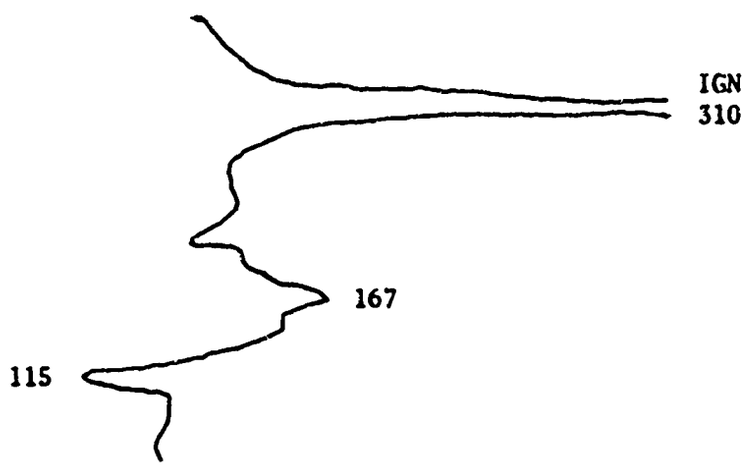


FIGURE 38 Typical DTA Thermogram of 2:1 PbO_2:S Composition Using Lead Dioxide from Manufacturer O



Sample O

FIGURE 39 Typical DTA Thermograms of 2:1 PbO_2:S Composition Using Lead Dioxide from Manufacturer P

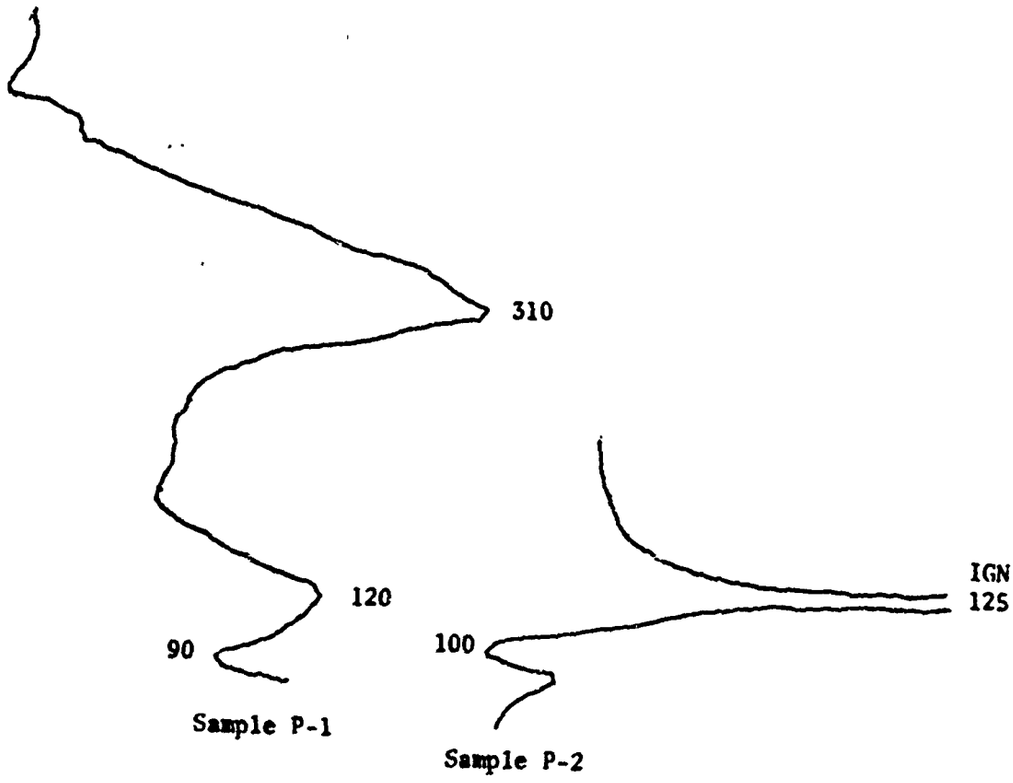
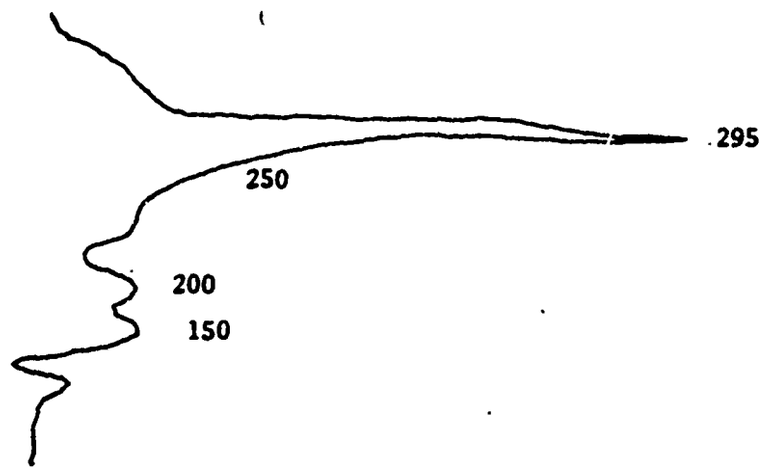
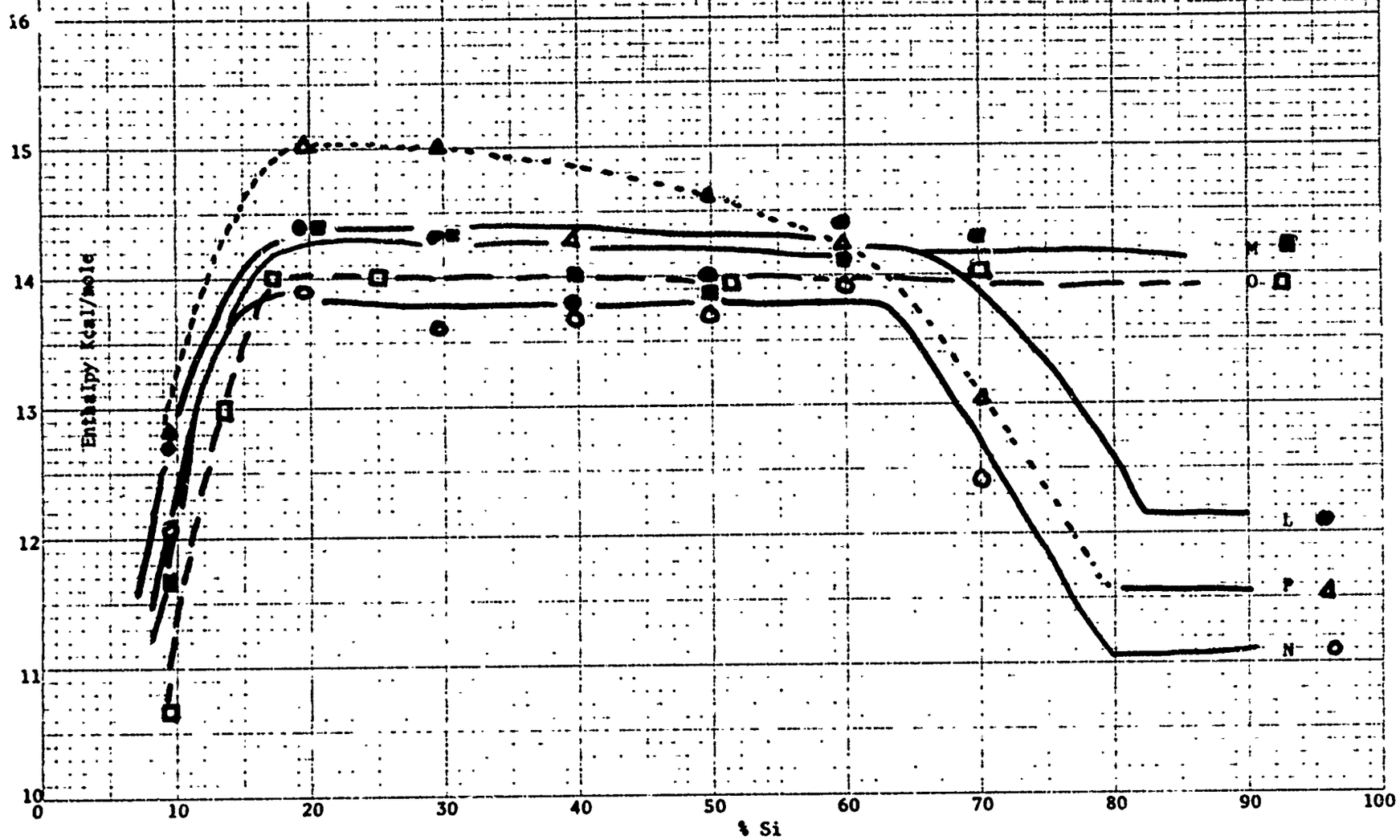


FIGURE 40 Typical DTA Thermogram of 2:1 PbO_2:S Composition Using Lead Dioxide from Manufacturer Q



Sample Q-1

FIGURE 41 - Plot of Enthalpy vs. Percent of Silicon Fuel for Lead Dioxide Samples from Five Manufacturers



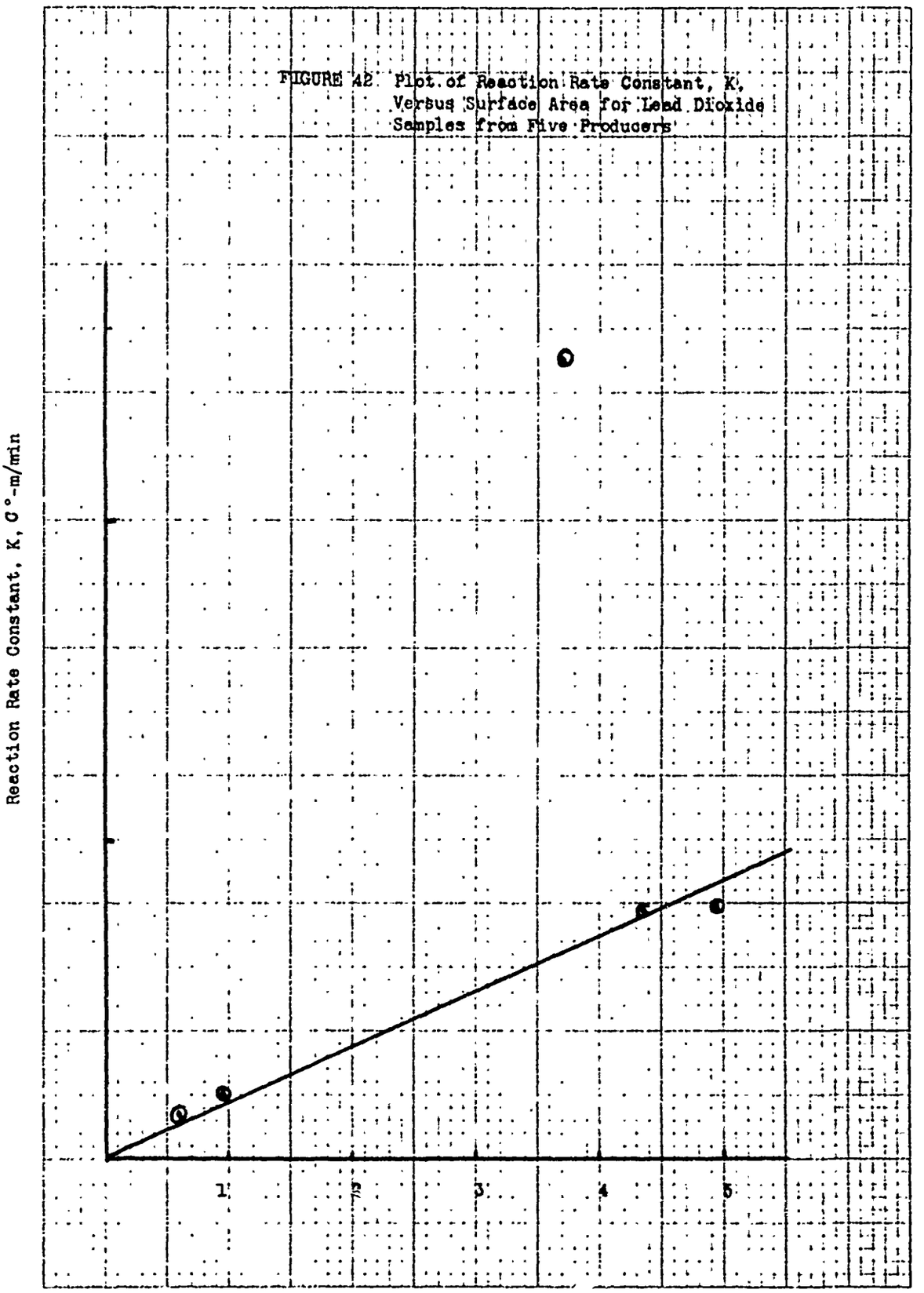


FIGURE 42. Plot of Reaction Rate Constant, K, Versus Surface Area for Lead Dioxide Samples from Five Producers

TABLE I

REACTIVITY DATA ON LEAD DIOXIDE SAMPLES FROM FIVE DOMESTIC MANUFACTURERS

Lead Dioxide Source, Sample, Fraction	Average Particle Size, Microns	h_1 ΔT, °C	Time to Peak, Minutes	Slope at Inflection Point, °C/minute
Manufacturer L				
Sample 1				
Parent	1.73	16.88	39.3	0.69
Fraction 1	1.68	16.52	37.0	0.73
Fraction 2	2.0	16.2	49.0	0.62
Fraction 3	2.23	17.6	60.0	0.61
Manufacturer M				
Sample 1				
Parent	0.5	24.8	3.35	16.0
Fraction 1	0.59	23.04	3.74	10.2
Fraction 2	0.8	22.24	3.77	12.0
Manufacturer N				
Sample 3				
Parent	0.66	22.72	2.8	11.5
Fraction 1	0.64	23.6	3.2	15.3
Fraction 2	0.64	22.96	3.4	14.7
Manufacturer O				
Sample 1				
Parent	1.5	16.08	4.3	1.07
Fraction 1	1.2	17.32	17.0	2.06
Fraction 2	1.76	17.36	33.0	1.71
Fraction 3	1.55	17.92	29.0	2.06
Fraction 4	2.55	16.44	55.5	0.78
Manufacturer P				
Sample 1				
Parent	2.38	24.64	2.27	13.4
Fraction 1	1.85	22.72	3.3	14.0
Fraction 2	2.8	20.96	2.7	13.4

TABLE II

Values for the Reaction Rate Constant K

in the Equation $\left.\frac{\Delta T}{\Delta t}\right|_{t=ti} = K/d$

Manufacturer	K
L	1.40×10^{-6} °C-m/min.
M	7.75×10^{-6} °C-m/min.
N	7.70×10^{-6} °C-m/min.
O	2.10×10^{-6} °C-m/min.
P	26.90×10^{-6} °C-m/min.
Q	0.45×10^{-6} °C-m/min.

TABLE III

Comparison of Reactivity and Various Property Values for 13 Lead Dioxide Samples From Six Domestic Manufacturers

Lead Dioxide Source and Sample	Average Particle Diameter, Microns	Absolute Density, g/cc	Apparent Density, g/cc	Purity	Heat of Reaction, cal/g	Pressure time curve values			Delay Burning rates, g/sec	Reactivity, $K \times 10^{-6}$, °C - m/min.
						θ	P_{max}	tP_{max}		
Manufacturer L										
Sample #1	2.0	9.28	2.63	94.3	369.9	61	7.4	5.5	4.57	1.40
Sample #2	1.65		2.17	94.8	370.1	53	6.36	5.96	3.89	
Manufacturer M										
Sample #1	0.51	7.86	1.38	92.2	358.0	52	7.8	7.4	5.18	7.75
Sample #2	0.52		1.41	89.7	364.4	58	8.2	6.4	5.06	
Sample #3	0.6		1.44			61	8.0	6.0		
Manufacturer N										
Sample #1	0.32	6.82	1.43	89.4	360.1	50	8.7	9.1	4.85	
Sample #2	0.52	7.91	1.38	79.5	353.3	64	8.6	5.36	4.82	
Sample #3	0.66	8.00	1.36	85.1	357.4	66	8.6	4.8	4.27	7.70
Sample #4	0.59	7.70	1.92	96.3	360.4	41	7.3	10.5	5.19	10.3
Manufacturer O										
Sample #1	1.5	7.99	2.83	95.9	372.4	68	7.9	4.0	5.18	2.10
Manufacturer P										
Sample #1	2.38	7.92	2.26	95.9	360.7	59	7.5	6.2	2.97	26.9
Sample #2	1.20		1.68			63	7.1	5.1		
Manufacturer Q										
Sample #1	0.40	8.89	1.72		370.0	49	6.6	7.2	5.13	0.45
Sample #2	0.20					49	6.1	6.9	4.22	

TABLE IV

THE RELATIONSHIP BETWEEN THE AVERAGE PARTICLE DIAMETER, THE SURFACE AREA AND THE REACTIVITY OF LEAD DIOXIDE FROM FIVE DOMESTIC MANUFACTURERS

Sample	Average Particle Diameter, Microns	Specific Surface Area, Sg, m 2/9	Computed Surface Area, $S=\frac{6v}{d}$, m 2/g	Reactivity Constant $K \times 10^{-6}$, °C-m/m
Manufacturer L	2.15	0.59 0.60	.30	1.40
Manufacturer M	0.60	4.94 4.94	1.27	7.75
Manufacturer N-3	0.60	4.38 4.33	1.25	7.70
Manufacturer O				
Parent	1.85	0.96 0.97	.38	2.10
Fraction 1	2.55	0.66 0.67		
Fraction 2	1.76	0.94 1.00		
Fraction 3	1.55	1.14 1.09		
Fraction 4	1.20	1.52 1.49		
Manufacturer P	2.38	3.71 3.73	.32	26.9

TABLE V

Burning Characteristics of Boron-Lead Dioxide Delay Bodies

Lead Dioxide Sample Source	Average Particle Diameter, of PbO_2, g/cc	Apparent Density of PbO_2, g/cc	Absolute Density of PbO_2, g/cc	Weight of Composition per inch, grams	Average Burning Time, sec/inch	Burning Rate, g/sec
Manufacturer L						
Sample #1	2.0	2.63	9.28	3.85	0.843	4.57
Sample #2	1.65	2.17	-	3.85	0.989	3.89
Manufacturer M						
Sample #1	0.51	1.38	7.86	3.25	0.628	5.18
Sample #2	0.52	1.41	-	3.25	0.643	5.06
Sample #3	0.6	1.44	-	3.25	-	-
Manufacturer N						
Sample #1	0.32	1.43	6.82	3.00	0.619	4.85
Sample #2	0.52	1.38	7.91	3.25	0.676	4.82
Sample #3	0.66	1.36	8.00	3.25	0.761	4.27
Sample #4	0.59	1.92	7.70	3.25	0.626	5.19
Manufacturer O						
Sample #1	1.5	2.83	7.99	3.45	0.66	5.18
Manufacturer P						
Sample #1	2.38	2.26	7.92	3.386	1.140	2.97
Sample #2	1.20	1.68	-	3.386	-	-
Manufacturer Q						
Sample #1	0.60	1.72	8.89	-	-	-

TABLE VI

Differential Thermal Analysis Peaks For
Lead Dioxide Samples From Six Domestic Manufacturers

Lead Dioxide Source and Sample	Endothermic Peaks Run #1	Run #2
Manufacturer L		
Sample #1	465	465
	510	515
	645	630
Sample #2	475	480
	525	520
	645	640
Manufacturer M		
Sample #1	416	416
	460	460
	640	610
Sample #2	422	415
	460	455
	635	627
Sample #3	427	425
	465	460
	635	627
Manufacturer N		
Sample #1	412	400
	450	440
	610	615
Sample #2	410	420
	445	450
	615	615
Sample #3	420	427
	460	465
	625	620
Sample #4	435	420
	463	456
	507	610
	635	
Manufacturer O		
Sample #1	450	450
	485	485
	615	605
Manufacturer P		
Sample #1	465	435
	485	480
	525	535
	635	610
Sample #2	428	430
	478	480
	540	540
	605	590
Manufacturer Q		
Sample #1	448	448
	493	495
	537	533
	612	615
Sample #2	440	430
	490	485
	525	510
	627	615

TABLE VII

DIFFERENTIAL THERMAL ANALYSIS PEAKS FOR 2:1 LEAD DIOXIDE-SULFUR MIXTURE UTILIZING LEAD DIOXIDE SAMPLES FROM SIX DOMESTIC MANUFACTURERS

Lead Dioxide Source & Sample	Endothermic Peaks		Exothermic Peaks	
	Run #1	Run #2	Run #1	Run #2
Manufacturer L				
Sample #1	110	140	340*	335*
Sample #2	110	110	305*	307*
Manufacturer M				
Sample #1	115	145	125* ign.	155* ign.
			140	148
Sample #2	110	115	202* ign.	220* ign.
			125	147
Sample #3	98	110	200* ign.	200* ign.
Manufacturer N				
Sample #1			100	90
	135	-	142* ign.	135* ign.
			130	105
Sample #2	405*	425*	140*	135* ign.
			130	105
	420		200	
Sample #3	450	425*	265*	275* ign.
			92	90
Sample #4	110	100	140* ign.	135* ign.
Manufacturer O				
Sample #1	115		165	170
	203	115	210* ign.	210* ign.
Manufacturer P				
Sample #1			125	145
	90	112	312	310
				100
				165
Sample #2	440*	425*	150* ign.	275* ign.
Manufacturer Q				
Sample #1	97		125	110
	415	135	275*	150
	443			180
				293* ign.
Sample #2	125	112	97	92
	450*	435*	150	145
			165	155
			230	225
			310*	305*

TABLE VIII

CALORIFIC VALUES FOR THE HEATS OF REACTION OF DIFFERENT RATIOS OF LEAD DIOXIDE AND SILICON

Ratio of PbO_2 to S:	Heat of Reaction in cal/g				
	Manuf L	Manuf M	Manuf N	Manuf O	Manuf P
9.5 : 0.5				301.1 302.0	
9.0 : 1.0	483.6 480.3	460.8 458.1	446.1 443.3	440.5 441.3	485.4 488.9
8.7 : 1.3				493.1 489.7	
8.5 : 1.5				501.1 500.0	
8.0 : 2.0	483.2 490.4	477.9 468.0	484.9 486.9		506.7 505.7
7.5 : 2.5				441.0 443.0	
7.0 : 3.0	423.7 421.4	395.8 413.2	422.0 423.0		444.6 450.4
6.0 : 4.0	353.9 347.0	341.5 355.6	354.5 359.6		364.8 362.7
5.0 : 5.0	295.8 299.0	291.0 288.9	301.1 297.5	292.0 291.7	311.3 309.8
4.0 : 6.0	241.9 240.1	233.3 231.2	233.3		246.2 230.2
3.0 : 7.0	166.2 172.2	155.9 156.7	183.4 177.7	179.8 178.0	165.8 162.2

TABLE IX

CHEMICAL ANALYSIS OF ELEVEN LEAD DIOXIDE SAMPLES FROM SIX DOMESTIC MANUFACTURERS

Manufacturer and sample	Purity o/o PbO_2	Insoluble in H_2O_2-HNO_3	Soluble in H_2O	Pb, o/o	Theoratical PbO_2 based on o/o Pb
Manufacturer L					
Sample 1	94.3	0.05	1.2	86.0	99.2
Sample 2	94.8	0.08	0.0	84.2	97.2
Manufacturer M					
Sample 1	92.2	0.01	0.74	84.6	97.7
Sample 2	89.7	0.06	0.0	84.8	97.8
Manufacturer N					
Sample 1	89.4	0.05	0.0	83.9	97.0
Sample 2	79.5	0.13	0.0	84.9	97.9
Sample 3	85.1	0.04	0.39	85.2	98.3
Sample 4	96.3	0.01	0.13	85.8	99.1
Manufacturer O					
Sample 1	95.9	0.0	0.35	85.5	98.7
Manufacturer P					
Sample 1	95.9	0.0	1.4	86.1	99.3
Manufacturer Q					
Sample 1	98.1	0.0	0.10	85.9	98.6

TABLE X

d - SPACINGS OBTAINED FROM X-RAY DIFFRACTION PATTERNS OF LEAD DIOXIDE SAMPLES FROM FIVE DOMESTIC MANUFACTURERS

Manuf L	Manuf M	Manuf N	Manuf O	Manuf P
3.50	3.50	3.48	3.50	3.49
-	-	3.12	3.14	3.12
2.79	2.79	2.78	2.79	2.79
2.47	2.47	2.47	2.47	2.47
1.85	1.85	1.85	1.85	1.85
1.75	1.75	1.74	1.75	1.75
1.69	1.69	1.69	1.69	1.69
1.56	1.56	1.56	1.57	1.57
1.52	1.52	1.52	1.52	1.52
1.48	1.48	1.48	1.48	1.48
1.40	1.40	1.40	1.40	1.40
1.27	1.27	1.27	1.27	1.27
1.23	1.23	1.24	1.24	-
1.21	1.21	1.21	1.22	1.21
1.17	1.17	1.16	1.17	1.17
1.15	1.15	1.15	1.15	-
1.13	1.13	1.13	1.13	
		1.11	1.11	
		1.10	1.10	

ASTM POWDER DIFFRACTION DATA CARDS FOR LEAD DIOXIDE

8-185

d	3.50	2.80	1.96	3.50	PbO_2	PbO_2
I/I₁	100	100	100	100	Lead (IV) Oxide	Plattnerite

Rad. CuKα λ 1.542 Filter Ni Dia. 60cm
Cut off 16 I/I₁ Visual estimate
Ref. G. F. Claringbull, British Museum

Sys. Tetragonal S.G. D_{4h}^{14} - $P4_2/mnm$
a 4.941 b₀ 3.374 A C 0.6831
α β γ Z 2 Dx 9.63
Ref. Dorinville, J.Chem.Soc. 211 (1932)

εα nωβ 2.30(Li) εγ Sign -
2V D9.42 mp Color Jet to brownish black
Ref. D_{4h}

Sample from Leadhills, Lanarkshire (BM 56917)
D.T. 312° (760mm); Sol. in HCl. Analysis in Min. Mag. 7 53 (1886).

Replaces 1-0171

d Å	I/I₁	hkl	d Å	I/I₁	hkl
[illegible]	[illegible]	110	1.001	20	213
[illegible]	100	101	0.973	[illegible]	[illegible]
2.48	70	200	.942	40	332
2.71	10	210	.912	70	431,406
[illegible]	100	211	.933	20	[illegible]
1.754	40	220	.929	40	
1.633	40	002			
1.569	40	310			
1.527	70	112			
1.484	70	301			
1.399	50	202			
1.276	70	321			
1.240	30	400			
1.220	50	222			
1.177	20	330			
1.152	70	312			
1.134	70	411			
[illegible]	40	420			
1.102	40	331			
1.008	80	431			

11-548

d	3.50	2.46	2.79	2.30	β-PbO_2 (corrosion product)
I/I₁	100+	90	80	100+	Beta Lead (IV) Oxide

Rad. λ Filter Dia.
Cut off I/I₁ Visual
Ref. Burbank, J. Electrochem. Soc. 104 492 (1957)

Sys. Tetragonal S.G. $P4_2/mnm$ (136)
a 4.99 b₀ 3.37 A C 0.685
α β γ Z Dx 9.63
Ref. Ibid.

Sample is an anodic corrosion product of Pb and was obtained in acid medium at elevated potentials.

d Å	I/I₁	hkl	d Å	I/I₁	hkl
3.50	100+	110			
2.79	80	101			
2.46	90	200			
1.85	30	211			
1.75	30	220			
1.49	50	002			
1.356	30	310			
1.319	30	112			
1.246	30	301			
1.197	30	202			
1.273	30	321			
1.238	30	400			
1.214	30	222			
1.152	30	312			

11-549

d	3.12	2.74	2.63	3.83	α-PbO_2
I/I₁	100	70	70	12	Alpha Lead (IV) Oxide

Rad. CuKα λ 1.5418 Filter Ni Dia. 366 mm
Cut off 4.31 I/I₁ G.C. diffractometer
Ref. R.A. Gross, Australian Defence Scientific Service, Defence Standards Laboratories, Dept. of Supply, Melbourne Australia

Sys. Orthorhombic S.G. Pccn (60)
a 4.938 b 5.939 c 5.484 A 0.8316 C 0.9237
α β γ Z 4 Dx 9.875
Ref. P. Ruetschi and B.D. Cahan, J. Electrochem. Soc. 104 406-413 (1957)

High-angle reflections taken from Zablocki et al., Doklady Akad. Nauk SSSR 73 559 (1950).
D.S.L. sample prepared by method of S.E. Cleaves, J. Electrodeposition Tech. Soc. 12 26 (1937).
Ruetschi and Cahan give a line at 3.53 A which probably arises from some β-PbO_2.

Replaces 10-258

d Å	I/I₁	hkl	d Å	I/I₁	hkl
3.83	12	110			
3.12	100	111			
2.97	15	080			
2.74	70	002			
2.63	70	081			
2.46	30	200			
2.23	6	112			
2.02	6	022			
1.89	30	220			
1.84	45	130,202			
1.79	30	221			
1.64	15	113			
1.54	17	222,023			
1.53	30	311,132			
1.47	30	041,312			
1.37	15	312			
1.31	15	223			
1.24	30	330			
1.22	30	241,400			
1.20	60	204,313			

APPENDIX II

KEY WORDS

Lead Dioxide

Structural Variations

Chemical Reactivity

Density

Reactivity of Lead Dioxide

Crystallinity

X-Ray Diffraction Patterns

Fractionations

Reaction Rate

Kinetics

Surface Area

Rate Calorimeter

Delay Burning Rate

UNCLASSIFIED
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5. AUTHOR(S) *(Last name, first name, initial)*

RIPLEY, WILLIAM L. and LIPSCOMB, CHARLES A.

6. REPORT DATE 13 June 1968	7a. TOTAL NO. OF PAGES 90	7b. NO. OF REFS
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13. ABSTRACT

A study is made of the performance characteristics of lead dioxide specimens from five U. S. manufacturers. Reactivity data is obtained using temperature-time curves, pressure-time curves, and burning rate of delay bodies. The relationship of chemical and physical properties of lead dioxide to its performance in the various tests, and the relationship of the various performance tests to each other, are considered.

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14 KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Lead Dioxide						
Structural Variations						
Chemical Reactivity						
Density						
Reactivity of Lead Dioxide						
Crystallinity						
X-Ray Diffraction Patterns						
Fractionations						
Reaction Rate						
Kinetics						
Surface Area						
Rate Calorimeter						
Delay Burning Rate						
William L. Ripley						

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