

Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be “used for any purpose other than private study, scholarship, or research.” If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of “fair use” that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select “Pages from: first page # to: last page #” on the print dialog screen

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

POWER REQUIREMENTS IN PIGMENT COMMINUTION

BY

JOSEPH T. GILDERSLEEVE

A THESIS
SUBMITTED TO THE FACULTY OF
THE DEPARTMENT OF CHEMICAL ENGINEERING
OF
NEWARK COLLEGE OF ENGINEERING

IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE
IN CHEMICAL ENGINEERING

NEWARK, NEW JERSEY

1956

4676-11-11

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____

NEWARK, NEW JERSEY

JUNE, 1956

ABSTRACT

The results of this work prove that the relation between total work and surface area developed in the wet grinding of pigments is an exponential function. The following equations were experimentally determined for the pigments studied:

$$\text{For Zinc Oxide:} \quad P = .090 (\Delta s)^{1.05}$$

$$\text{For Titanium Dioxide:} \quad P = .086 (\Delta s)^{1.072}$$

$$\text{For Calcium Carbonate:} \quad P = .107 (\Delta s)^{0.98}$$

This work shows that in the grinding of sub-sieve size pigments the Rittinger and Bond theories which state that surface area developed is directly proportional to total work, are not valid and cannot be applied.

It is also shown in another plot that when a surface area developed versus total work plot is made with all the pigments starting from the same surface area, the ratio of their y-intercepts, where $\Delta s = \log 1 = 0$, are related to the ratio of the mineralogical hardness of the pigments. In fact the straight lines of the pigments fall in the order of their hardness. Since $\Delta s = 0$ refers to the unground pigment, the only plot it can have any significance in is a plot where the grinds have the same starting point.

A study was also made of each of the grinding variables and their effect on the development of surface area.

Thus by the use of a simple method of measuring surface area and a measurement of power expended, these equations can be used to predict power requirements to obtain a specific grind.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the aid of Mr. R. W. Jamieson, Technical Director of Benjamin Moore & Co., by extending the use of the Benjamin Moore & Co. laboratory facilities and materials. He also wishes to thank Professor G. C. Keefe for his suggestions and guidance in this work.

TABLE OF CONTENTS

Page No.

I. <u>Introduction</u>	1
II. <u>Theory of Operation</u>	
A. Theory of Comminution	3
B. Theory of Air Permeability	5
III. <u>Experimental Apparatus</u>	
A. Design of Permeameter and Method of Operation	10
B. Grinding Equipment and Power Measurement	16
C. Pigments Studied	20
D. Variables Studied	24
IV. <u>Experimental Results</u>	26
V. <u>Conclusions</u>	31
VI. <u>Recommendations</u>	33
<u>Appendix</u>	
Tables of Data	35
Graphs	44
<u>Bibliography</u>	47

<u>No.</u>	<u>LIST OF FIGURES</u>	<u>Page No.</u>
1.	Photograph of Permeameter	12
2.	Photograph of Plug Forming Equipment	12
3.	Drawing of Equipment	13

LIST OF TABLES

1.	Permeameter Data on Runs with Zinc Oxide	35
2.	Permeameter Data on Runs with Zinc Oxide and Titanium Dioxide with Variables other than Time	36
3.	Permeameter Data on Runs with Titanium Dioxide and Calcium Carbonate	37
4.	Power Readings on Westinghouse Watthour Meter for Slurries of Zinc Oxide, Titanium Dioxide and Calcium Carbonate grinding in a Pebble Mill	38
5.	Data on Surface Development and Power Expended(Zinc Oxide)	39
6.	Data on Surface Development and Power Expended (Titanium Dioxide and Calcium Carbonate)	40
7.	Effect of Variables on Surface Developed	41
8.	Results of Log-Log Plots of Surface Developed vs Power and Time consumed	42
9.	Data used in plotting all pigments starting from the same base Surface Area	43
10	Results of Log-Log plot with all pigments starting from the base Surface Area	43

LIST OF GRAPHS

1.	Plot of Time of Grind versus Surface Area Developed	44
2.	Plot of Total Work (Power) versus Surface Area Developed	45
3.	Plot of Total Work versus Surface Area Developed with all pigments referred to the same starting surface area	46

I. INTRODUCTION

In the paint industry one of the most important operations is the grinding of pigments. In contrast to the minerals field where much of this grinding is done dry, paint manufacturers invariably grind pigments in some liquid. The lack of information on this type of grinding has led the author to reexamine the current theoretical approaches. It was found that the theories of Rittinger, Kick and Bond are of little use in this type of work as they fail to predict the time necessary to reach a certain average particle size or the power necessary to develop a certain amount of surface area.(1)

In approaching this study three facets of the problem were kept in mind, first how to measure the surface developed, second how to measure the power and third which mill would give the greatest surface development. For the routine measurement of pigment surfaces the air-permeability apparatus in the form used by Carman (1) is very satisfactory, especially when the apparatus is standardized with the results obtained through the more reliable absorption of gases method.

Power measurements were made with a Watt-Hour Meter through which the power supplied the rollers was measured. This instrument was capable of reading the small difference in power which were handled. Readings were taken with the mill empty and loaded, with the various pigment slurries and at the various speeds. The difference between no load and loaded readings were taken as the power used to develop surface.

The pebble mill was chosen as the most efficient mill in developing surface, especially for a water system which was studied.

Among the variables studied were mill time, wetting and antifoam agents, grinding media, speed of the mill and solids of the slurry. Three widely different pigments were studied, Zinc Oxide, Titanium Dioxide and Calcium Carbonate.

The pigments were ground, dried and measured and the surface area developed correlated to the power input and time of grind.

II THEORY OF OPERATION

A. Theory of Comminution

Energy requirements are a matter of considerable concern in size reduction as the energy consumption represents a large portion of the total cost in such operations. In the past Kick's law and Rittinger's law have stood as the laws of grinding but with Bond's 3rd Law of Comminution there are now three such concepts.

Rittinger's theory postulates that the useful work done in crushing and grinding is directly proportional to the new surface area produced and inversely proportional to the product diameter. Speaking of this law Gaudin says: "The efficiency of a comminution operation is the ratio of the surface energy to the kinetic energy expended."(10) By this theory, even the best values for surface energy indicate that 99% of the work input is wasted. Bond also points out that Rittinger's theory ignores the distance factor (particle deformation before breakage) although work is the product of force multiplied by distance. All size reduction of solids, by whatever means, starts with an initial crack which spreads through and across the particle by the flow of resident energy to the crack tips.(1)

Kick's theory is based primarily on the stress-strain diagram of cubes under compression. It states that the work required is proportional to the reduction in volume of the particles.(12)

But Bond contends neither Rittinger's theory (concerned only with surface) nor the Kick theory (concerned only with volume) can be completely correct. The Bond theory states that the total work useful

in breakage is (a) inversely proportional to the square root of the diameter of the product particles, (b) directly proportional to the length of the crack tips formed, and (c) directly proportional to the square root of the surface area formed.

Bond's equations on his 3rd Theory of Comminution are:

$$W_t = W \left(\frac{\sqrt{F}}{\sqrt{F} - \sqrt{P}} \right)$$

$$W_i = W \left(\frac{\sqrt{F}}{\sqrt{F} - \sqrt{P}} \right) \sqrt{\frac{P}{100}}$$

If F and P are in inches:

$$W_i = W \left(\frac{\sqrt{F}}{\sqrt{F} - \sqrt{P}} \right) \sqrt{\frac{P}{.003937}}$$

Or by simplifying the second equation:

$$W_i = W \left(\frac{\sqrt{R}}{\sqrt{R} - 1} \right) \sqrt{\frac{P}{100}}$$

where:

W_t = work input to reduce from infinite feed

F = diameter which 80% of feed passes (microns)

P = diameter which 80% of product passes (microns)

W_i = work index, total kw-hr per ton to reduce from infinite to 80% passes 100 microns (65% passes 200 mesh)

W = work input kw-hr per ton

R = reduction ratio, F/P

The work index can be calculated from laboratory tests or from plant operation using the last three equations where W, F and P are known. When the work index is known the work input required for any size reduction can be calculated. The work index therefore is an all inclusive constant containing surface area, grindability and the other properties of the material and the performance of the mill on which the

index has been calculated. The term 80% passes is the most significant method of expressing a screen analysis in one term; it can be found easily from the plotted size distribution.(1)

Since most of this work has been done in the minerals field it pertains to larger particles than are usually found in paint pigments. Here the larger portion is sub-sieve sized particles and this study was undertaken to see if any or all of the above theories hold in the sub-sieve range.

B. Theory of Air Permeability

If a fluid is percolated through a porous medium of uniform cross-sectional area, A , and thickness, L , the rate of flow, Q/t , is given by the equation,

$$u = Q/tA = K_1 \Delta^P / n L$$

Where:

u = apparent linear rate of flow in cm/sec

Q/t = rate of flow in milliliters per second

A = cross-sectional area in square centimeters

K_1 = proportionality constant representing the permeability of the porous medium

Δ^P = pressure difference driving the fluid through the medium, in grams per square centimeter

n = viscosity of the fluid, in poises

L = thickness of the porous medium in centimeters

The proportionality constant, K_1 , is a specific property of the porous medium which is independent of the dimensions of the latter, of the pressure difference, and of the viscosity of the fluid. It has been shown theoretically (5) that if the porous medium consists

of a bed of rigid grains, K_1 is calculable in terms of the porosity of the bed and of the specific surface of the solid particles. The resulting equation is:

$$K_1 = g \epsilon^3 / 5S_0^2 (1-\epsilon)^2$$

where:

- g = acceleration due to gravity (980 cm/sec/sec)
- ϵ = porosity or fractional void of the bed
- S_0 = specific surface of the powder in square centimeters per cubic centimeter

The porosity function, $\epsilon^3/(1-\epsilon)^2$, gives the important relationship between permeability and porosity for any given powder. Conversely, if K_1 and ϵ are known, it is possible to calculate S_0 by the equation: (17)

$$S_0 = \frac{g \epsilon^3}{5K_1 (1-\epsilon)^2} = 11 \frac{1}{K_1} \times \frac{\epsilon^3}{(1-\epsilon)^2} = 11 \frac{t\Delta P A}{Q L n} \times \frac{\epsilon^3}{(1-\epsilon)^2}$$

It has long been known that when the mean free path of molecules of a gas flowing through a capillary is an appreciable fraction of capillary diameter the rate of flow is greater than given by Poiseuille's law. (14) This is regarded as a "slip" at the capillary walls and the theory of the slip correction term was worked out by Maxwell. (4) In its application the slip term enabled specific surfaces calculated by the normal Kozeny equation as shown above to be corrected; but in the case of pigments, the uncorrected surface is often several times smaller than the corrected surface, i.e. the slip term is not a correction but is the main term.

When the mean free path is many times greater than the capillary diameter, molecular flow is obtained. This has been studied both theoretically and experimentally by Knudsen who obtained the law: (15)

$$Q/t = 8/3 \quad 2RT/\pi M \cdot A^2/p \cdot Lp/L$$

When this term is used as a correction for the Kozeny equation it extends its use to pure molecular flow in porous media. Carman and Arnell (4) take a value of 0.5 for k_0/k and then

$$Q_1 L p_1 / t A \Delta p = p F_1 / 5 n S_0^2 + 0.96 F_2 / S_0 \sqrt{RT/M}$$

As the above equation is a quadratic in S_0 , the direct solution would give a very clumsy expression for S_0 . It was found better to break up the calculations from the experimental data into stages.

First, if one ignores the slip term, a specific surface S_k is obtained, this being the uncorrected surface obtained with the normal Kozeny equation,

$$S_k^2 = t A \Delta p / Q_1 L p_1 \times F_1 p / 5 \eta$$

Next, if the Kozeny term is ignored, a specific surface S_m is calculated, which would be the corrected surface if pure molecular flow occurred in the plug,

$$S_m = t A \Delta p / Q_1 L p_1 \times 0.96 F_2 \sqrt{RT/M}$$

The final form of the equation is,

$$S_0 = S_m / 2 + \sqrt{S_m^2 / 4 + S_k^2}$$

For routine measurements calculations are not laborious. If a plug of fixed dimensions is used L and A are constants for a particular apparatus and it is also most convenient to keep Q_1 constant. For a given material, it is desirable to use always the same weight, so that ρ and the two porosity functions F_1 and F_2 are always the same. If air alone is used M is constant and on any particular day p_1 , n and RT can be taken as constant. Indeed, for most routine work no serious error is introduced by choosing values of these quantities which correspond to normal laboratory conditions and assuming them

constant. This leaves only t , Δp and p to be inserted in the equations. Since the product $t\Delta p/p_1$ is common to both equations it is evaluated. Pressures were measured in mm of Hg, and these values can be inserted in $t\Delta p/p_1$ directly, since this involves a ratio of pressures; but, for p , the value in mm of Hg must be multiplied by 1333 to convert to dynes/cm².

The symbols used in the above equations are:

p_1 and p_2	Pressures on each side of plug, in dynes/cm ²
Δp	Pressure difference $p_1 - p_2$; dynes/cm ²
p	Mean pressure $\frac{1}{2}(p_1 + p_2)$, dynes/cm ²
Q_1	Volume gas in ml flowing in time t , measured at p_1
t	Time of measurement, sec.
L	Length of plug or circular capillary, cm
A	Cross-section of plug or circular capillary, cm ²
η	Viscosity of gas, poises
T	Absolute temperature, °K
R	Gas Constant 8.31×10^7 in cgs units
M	Molecular weight of gas
ϵ	Porosity, $(1 - W/\rho AL)$
F_1 and F_2	Porosity functions $(\epsilon^3/(1-\epsilon)^2)$ and $(\epsilon^2/(1-\epsilon))$
W	Weight of the plug in grams
ρ	Density of the powder, gr/ml
k	Constant in Kozeny equation
k_0	Corresponding constant for viscous flow in straight capillaries

S_o	Specific surface in cm^2/cm^3 , i.e. cm^{-1}
S_k	Specific surface in Kozeny equation, cm^{-1}
S_m	Specific surface in molecular flow equation, cm^{-1}

The introduction of the term for slip flow and molecular flow into the Kozeny equation for gas permeability provides a quick, simple and reliable routine method for measuring the surface of pigments. Owing to variation with porosity, permeability surfaces have been based on the concept of a normal porosity range which for uniform equidimensional particles is $\epsilon = 0.4$ to 0.5 . For non-uniform particles it can be less and for acicular, platy or skeletal particles it can be considerably higher. For this reason pigments were chosen which did not fall into this latter category as the porosities attainable are not applicable in the Kozeny type equation.

The permeability surface provides a quick, simple and reliable method for obtaining the surface of pigments. The absorption method is more accurate but is quite unsuited for routine. (3) (7)

III EXPERIMENTAL APPARATUS

A. Design of Permeameter and Method of Operation

The outstanding features of the air permeability apparatus for measuring the surface area of pigments are: (a) formation of a self-supporting plug of pigment in a precision-bored tube with a small hand-press, and (b) direct measurement of air flowing through the plug with a graduated tube.(2) The formation of a self-supporting plug offers no difficulties with paint pigments or finer particles. The main advantage of (b) is that the permeability apparatus is very simple and gives direct readings of the volume of air passing through the plug for very small rates of flow under a constant pressure head. A serious error in previously used apparatus is that as the confining liquid rises up the measuring tube air enclosed between the liquid surface and the plug expands, since its pressure decreases. This is easily overcome by leveling the liquid inside and outside the tube. The error increases with the enclosed volume and in this modified apparatus has been reduced to a minimum. It must be emphasized that the pressure drop across the plug is generally so large that it is little changed by the head of liquid rising in the measuring tube, so that the error is not due to change in the mass rate of flow through the plug, but in time taken for a given volume to be recorded.

The equipment for this test is shown in Figures 1 and 3. The plug of compressed pigment is in the small tube located within the glass bulb at the top of the pipette. The top end of the plug is connected to the glass tubing and pressure tubing by means of a

rubber stopper. The pressure tubing is connected to a manometer and a pump for maintaining a constant pressure difference across the plug. In the laboratory a Cenco-Pressovac $\frac{1}{4}$ Pump was used which gave a constant 12 mm of Hg vacuum which was checked after each run with a manometer.

To maintain the gas confined in the graduated measuring tube, made from a 10 ml. pipette, constantly at atmospheric pressure, the confining liquid is allowed to flow from a reservoir and is controlled by a screw-clip so that the levels in the two arms of the small manometer remains the same. The side-arm and stop-cock is used for introducing the air and to avoid complications from vapors from the confining liquid, dibutyl phthalate was used in the open end manometer and mercury was the confining liquid and was used in the closed end manometer. The closed end manometer permits a continuous check on the constant vacuum and can be used to check when the equipment has reached equilibrium. The glass tube with the cotton plug is a safety device for non-plug forming pigments so they will not be sucked into the vacuum pump.

The plug forming equipment consists of a stainless steel tube which has an internal diameter of 0.636 cm and the plug was formed by compressing the pigment between stainless steel plungers of $\frac{1}{4}$ " stock in a hand press. The sliding fit plungers are fixed into the jig, giving a fixed length when they are squeezed in a vice until the plunger ends remain flush with the end faces of the jig.(fig. 2) Details of this hand press were obtained from the New Jersey Zinc Company.

Figure 1

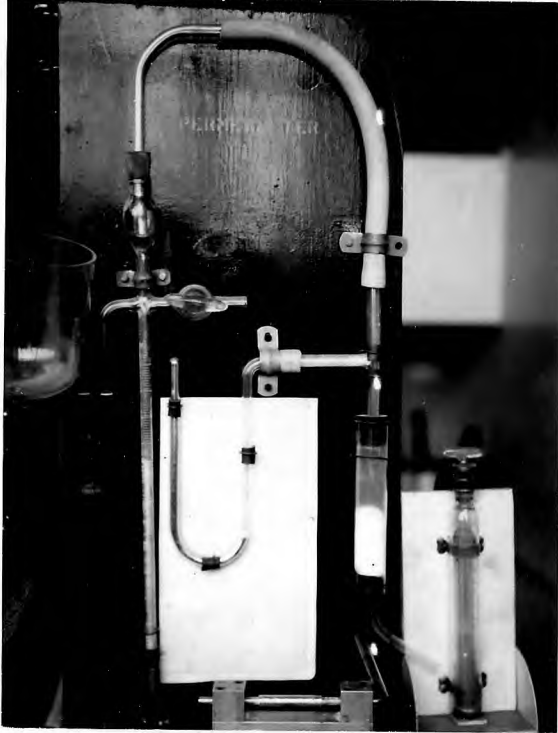


Figure 2

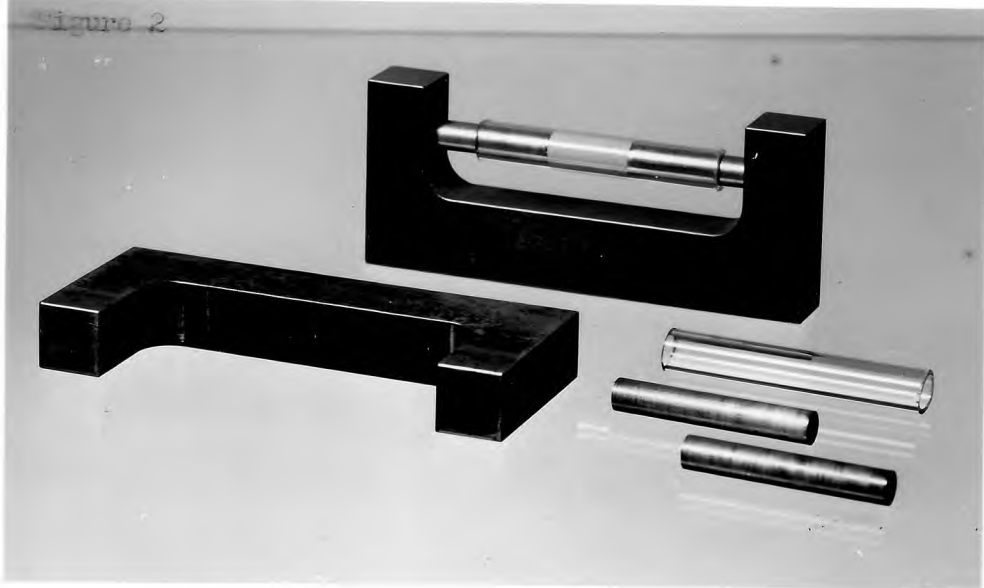
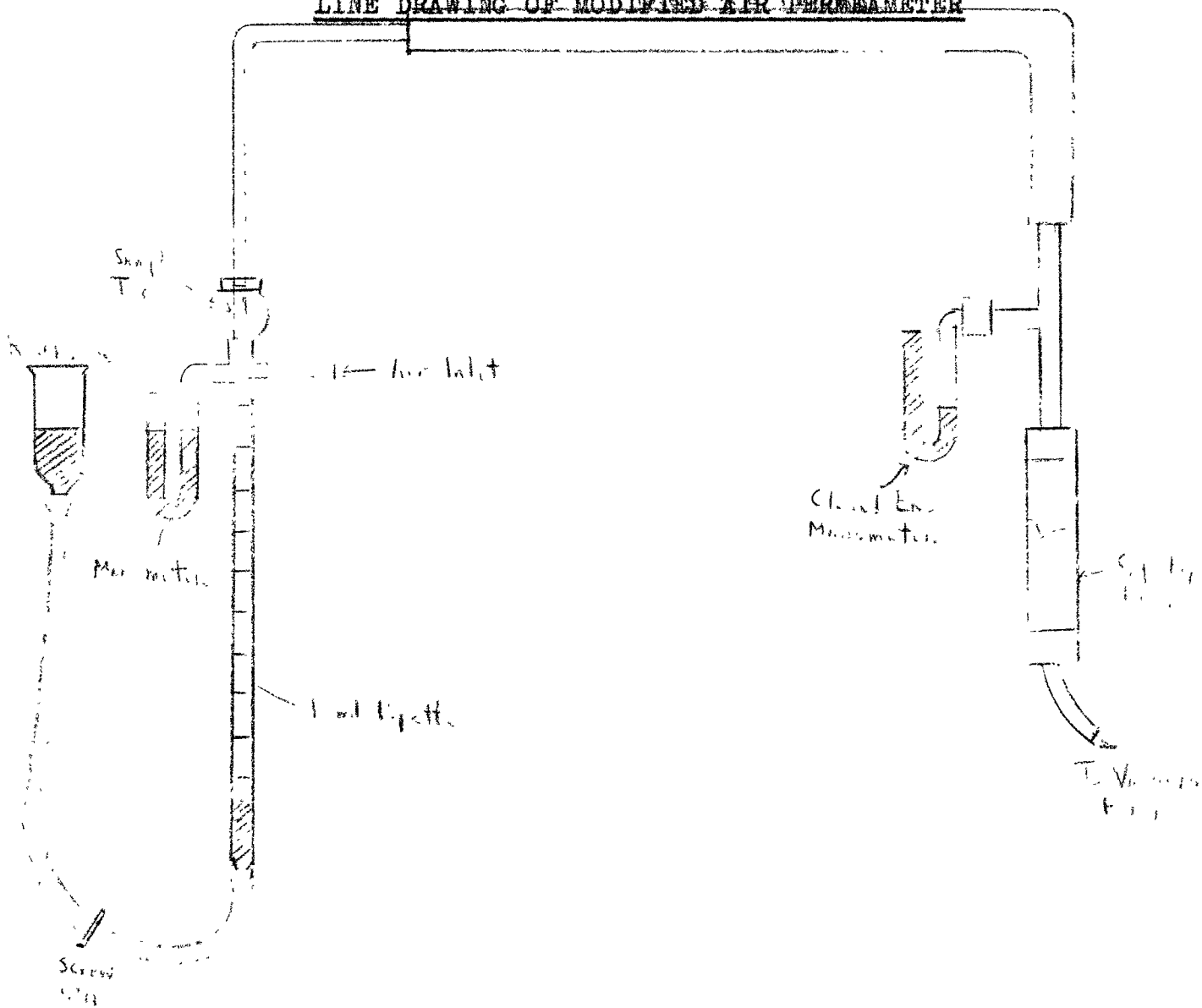


FIGURE 3

LINE DRAWING OF MODIFIED AIR PERMEAMETER



Procedure:

1. Weigh the clean, dry sample tube.
2. Weigh out in a tared aluminum dish a sample of the pigment equal to some intermediate amount which will give porosity of 0.4 to 0.5 in the plug. Break up any lumps by means of a spatula. The pigment plug is prepared by transferring small portions of the pigment to the sample tube of which one end has been closed by the insertion of the plunger. The other plunger is inserted and the pigment squeezed by hand pressure. A small funnel is helpful in making these additions. Additional portions of the pigment are added at alternate ends of the tube, pressure being applied after each addition, until all the pigment is in the tube. The assembled tube and plungers are placed in the jig and slowly compressed in a vise until the plunger's ends are flush with the side of the jig. The plungers are removed and any feather edges of pigment at the ends of the tube are cleaned out. The tube with the plug of pigment is weighed. The difference between this weight and the weight of the empty tube, is the weight of the pigment plug.

One end of the tube containing the pigment plug is inserted into the end of the rubber stopper of the permeameter and the rubber stopper pressed carefully into place. The vacuum pump is started and allowed to run until practically all the air in the connections up to the plug has been removed, as indicated by the closed end manometer. The stopcock is closed slowly and the mercury allowed to rise a short distance in the calibrated tube; meanwhile the open end manometer is kept level by means of the screw-clip. At a suitable distance, after the rate of rise of the mercury has become constant, the stopwatch is

started as the mercury level passes a graduation line. The seconds required for the mercury to travel one and two cubic centimeters are recorded.

The stopcock is opened, the vacuum pump stopped, the sample tube reversed, and the determination repeated. The two sets of results should check very closely. If significant differences occur, a complete new determination is made.

3. Surface determination on the standardizing sample of Kadon XX?

Zinc Oxide:

Weight of tube and pigment 17.0515 grams

Weight of tube 15.4970 grams

W = 1.5575 grams

$$\epsilon = 1 - W/pAL = 1 - 1.5575/5.606 \times .318 \times 1.63$$

$$\rho = 5.606 \text{ gr/ml}$$

$$\epsilon = 1 - .536 = .464$$

$$A = .318 \text{ cm}^2$$

$$F_1 = \epsilon^3 / (1 - \epsilon)^2 = .100 / .287 = .348$$

$$L = 1.63 \text{ cm}$$

$$F_2 = \epsilon^2 / (1 - \epsilon) = .215 / .536 = .405$$

$$p_1 = 753 \text{ mm Hg}$$

$$t_{\Delta p} / p_1 = 202 \times 741 / 753 = 198.5 \text{ sec}$$

$$p_2 = 12 \text{ mm Hg}$$

$$s_m = (0.96 \sqrt{\frac{8.31 \times 10^7 \times 298}{29}} \times \frac{.318 \times .405}{2 \times 1.63} \times 198.5)$$

$$\Delta p = 741 \text{ mm Hg}$$

$$s_k^2 = \left(\frac{.2 \times .318 \times .348}{(2 \times 1.63 \times 10^3 \times 10^{-3})} \right) \times 198.5 \times 382.5 \times 1333$$

$$Q_1 = 2 \text{ ml}$$

$$s_m = 2.2 \times 10^5 \text{ cm}^{-1}$$

$$t = 202 \text{ sec}$$

$$s_k^2 = 38.2 \times 10^8 \text{ cm}^{-1}$$

$$\eta = .18 \times 10^{-3} \text{ poises}$$

$$s_o = \frac{2.2 \times 10^5}{2} \sqrt{\frac{1.85 \times 10^{10}}{4} \div 38.2 \times 10^8}$$

$$s_o = 1.1 \times 10^5 \div 1.262 \times 10^5 = 2.362 \times 10^5 \text{ cm}^{-1}$$

$$s = s_o / \rho = \frac{23.62 \text{ m}^2/\text{cc}}{5.606 \text{ gr/cc}} = 4.22 \text{ m}^2/\text{gr}$$

Standardization: The above computations cover a sample which was supplied the author by the New Jersey Zinc Sales Company. The specific surface of this sample of XX-2 Zinc Oxide was checked in their laboratory using both the Air Permeability and the Nitrogen Absorption methods and found to be 4.2 sq.m/gr. This checks very well with the value of 4.22 m²/gr as shown above. This sample was used to check the accuracy of readings on the modified air permeameter as suggested in the literature.(4)

B. Grinding Equipment and Power Measurement.

Pebble mills have been widely adopted for pigment dispersion in the last two decades. In the most commonly used design, a cylindrical chamber, mounted horizontally, is partially filled with pebbles or porcelain balls together with the components of the mixture for grinding. Rotation of the cylinder causes the balls to be lifted to the point where they cascade, rolling over each other, crushing any particles caught between the contacting balls and subjecting the mixture to a highly turbulent shearing action in the spaces between the balls.(18)

The efficient use of pebble mills requires the balance of a number of variables. Although the analysis of performance of any given mill operation is difficult, requiring in some cases careful and systematic observation over an extended series of trial runs, there are, nevertheless, data from standard practice and experimental work which can be applied to many special cases. It can be seen that the construction of the mill and its driving mechanism establishes permissible loads and speeds, but other conditions well within the

control of the operator determine actual grinding efficiency.

The pebble mill which has a non-ferrous lining of porcelain and the grinding media of flint or porcelain pebbles was chosen for this work. Since the vehicle for the slurries studied was water, work could not be done with the ball mill and its metal mill and grinding media, since rusting would cause contamination.

The speed of the mill is one of the important operating factors in the operation of the pebble mill.. The following equation expresses the relation between mill diameter and the speed at which the balls would be held by centrifugal force to the interior of the mill cylinder: (9)

$$S = K / \sqrt{D}$$

S = mill speed RPM

K = constant

D = diameter of mill ft.

This speed has been designated as the "critical speed" and has been quite generally adopted as the reference point in describing mill operation. Theoretically, the balls in a rotating mill centrifuge if the speed exceeds that given by the equation: (6)

$$S = 54.19 / \sqrt{r}$$

r = radius of mill ft.

$$S = 54.19 / \sqrt{.172} = 54.19 / .414$$

$$r = \frac{4.125}{2 \times 12} = .172 \text{ ft.}$$

$$S = 130 \text{ RPM for the lab pebble mill}$$

It should be noted that this equation is based on a mill containing the balls only with no grinding charge present. When the latter is introduced, the limiting speed is lower in value. The amount of the decrease from the critical speed will depend directly on the

viscosity of the grinding charge. It is obvious that the lower the viscosity, the nearer the speed may be to the critical speed value, and the higher the viscosity, the greater the deviation therefrom.(13)

Commercial practice has been based on the properties of the mixture being ground and the characteristics of the grinding media. Commercial mills for pigment dispersion thus usually operate at speeds 50 to 65 percent of critical speed.(8) In the case of the laboratory pebble mill this gives operating speeds of 65 to 75 RPM.

The recommended ball load is 40 to 55 per cent of the total mill volume. Higher loads reduce the cascading giving in effect a choked mill. Lower loads may contribute to slipping of the ball charge with excessive wear and deformation of the grinding media.(6) The laboratory mill was loaded to 50 per cent of its total volume or about one pint of pebbles.

The optimum dispersion volume is 18 to 20 per cent of mill volume.(8) A charge which is slightly in excess of that which fills the ball voids is most rapidly dispersed. This is the type of charge used on the laboratory mill and amounted in each case to about one half pint.

The pigment slurries were kept as simple as possible to keep the variables at a minimum. They consisted of:

	<u>53.8% Mix</u>	<u>63.7% Mix</u>	<u>37.3% Mix</u>
Pigment	240 gr	290 gr	170 gr
Water	200 cc	150 cc	270 cc
Tamol 731 (25%)	3 cc	3 cc	3 cc
Nopco JMK	3 gr	3 gr	3 gr

The grinding equipment used was the Paul O. Abbe Single Tier Jar Rolling Mill (Revo-Charge Motor Drive) described as follows:

<u>H.P.</u>	<u>Floor Space</u>	<u>Height</u>	<u>Rolls</u>
1/3	13" x 72"	16"	3" x 48"

The jars are easily placed on or removed from the rollers and no bands are required to hold them in place. Standard rollers are steel, the rubber covering of which is carefully ground to size. All rollers are directly driven to insure positive action and eliminate danger of binding.

The jar mill is a straight side porcelain jar cemented in a steel can for protection against breakage. Its dimensions are:

<u>O.D.</u>	<u>Outside Height</u>	<u>I.D.</u>	<u>Inside Height</u>	<u>Operating Capacity</u>
5.13"	5.50"	4.125"	4.125"	0.25 gal.

The main grinding media was Selected French Flint Beach Pebbles with a long diameter averaging about 3/4 inches and a short diameter averaging about 1/2 inch. Beach pebbles, rounded and free of pits, have long been employed as grinding media. In this work Borondum Cylinders of high density ceramic with 3/4 inch diameter and 3/4 inch height; and spherical 1/2 inch diameter porcelain high density balls, were also studied.

Power requirements were measured on a Westinghouse Watt-Hour Meter, Type OB, Single Phase, $K_n = 1/3$, 5 amps, 115 volts. The constant of this meter was 3.56×10^{-4} kw-hr per revolution of the wheel and the number of seconds per revolution was checked using a stop-watch. This meter was connected directly to the line and the mill drew its power through it.

Power readings were taken with the mill loaded with its ball charge and this figure subtracted from the readings obtained when the pigment slurry was also present. The difference between these two readings gave the power used in developing surface area. These readings were so small that any heating losses were not considered as they were constant for any set of runs and would have made the power readings that much smaller.

The method of making the grinds consisted of first slurring the pigment in the water and agents under a high speed agitator and adding this slurry to the pebble mill which had been loaded with the ball charge. The jar mill was then put on the rollers and allowed to grind for the predetermined time. After this period was completed the jar mill was removed from the rollers and the slurry removed from the mill. The power was checked and recorded for the run. The slurry was then spread out in shallow trays and allowed to dry in a constant temperature-humidity room for 24 hours. It was then used to prepare a plug to be run in the permeameter.

C. Pigments Studied

This study covered three widely different pigments in order to get a wide range of values. It was the plan that by testing pigments of widely different hardness, specific gravity and reactivity, a correlation would be obtained that would hold over the entire range.

The first pigment studied was a Zinc Oxide, which is a white pigment, nodular in shape. It has high brightness, its refractive index is 2.08. It is relatively low in tinting strength and hiding

power but has special properties which make it a very desirable pigment. It is relatively opaque to ultraviolet light. It is slightly chemically reactive and forms reaction products with paint vehicles. The chemical reaction is taken advantage of in paint formulation to obtain certain properties in some paints but excludes its use in some types.(16) Listed below are some of the constants on:

XX-2 Zinc Oxide (New Jersey Zinc Company)

Particle Shape	Nodular
Insoluble in HCl	.03%
SO ₃ (total S as)	.25%
Water at 110°C	.20%
Water soluble salts	.57%
PbO (total Pb as)	.19%
ZnO	over 98.00%
Oil Absorption	8.2 cc
One pound bulks	.0214 gal
Mho Hardness	4 - 4.5
Specific Gravity	5.606

The second pigment studied is the most important white pigment, Titanium Dioxide. Its most outstanding property is its extreme opacity, which is much higher than that of any other white pigment. Tinting strength as determined by the Reynolds method ranges from 1200-1300 and one pound of pigment in linseed oil will hide 115 square feet of black surface. It has an index of refraction of 2.70, average mean particle size diameter of 0.3 microns and a total dry brightness of 98 to 99 per cent. It is very resistant to acids and alkalies, it

is not discolored or otherwise affected by gases, and is non-reactive with practically all types of vehicles or media in which white pigments are used.

The Titanium Dioxide used in this study had the following constants:

Titanox RA (Titanium Pigment Corp.)

Crystal		Rutile	
Refractive Index		2.70	
Specific Gravity		4.2	
1 lb bulks	.0286 gal	lbs per solid gal.	34.99
Tinting Strength		1600	
Oil Absorption		17-19	
Mho Hardness		6-7	7-7.5 single crystal
TiO ₂ (min)		97.0%	
SiO ₂		0.15%	
Fe ₂ O ₃		0.006%	
Al ₂ O ₃		1.3%	
Sb ₂ O ₃		0.02%	
Mn		.1 - .2%	
Pb		0.015%	
Average Particle Size: Mean Diameter Microns		0.3 - 0.4	
Transmission Range		420. - 600 mm	
Thermal Conductivity:			
cal/cm/sec °C	perpendicular to c axis	.0124-.0136	
	parallel to c axis	.0200-.0216	
Specific Heat	c/g	.1707-.179	
kg cal/mol/°C	200-1000°C	13.2	
Coefficient of linear expansion @ 25°C	a axis	7.19 x 10 ⁻⁶ /°C	
	c axis	9.94 x 10 ⁻⁶ /°C	

Molal Heat Capacity (25°C)	13.16 cal/°C
Dielectric Constant	114
parallel to c axis	500 kc 190
Power loss parallel to c axis	500 kc 0.025
Electrical conductivity(room temp)	0.2-1.0 x 10 ⁻¹⁰ mho per cm
Melting Point	1825°C

The Third pigment examined is a white extender pigment, natural whiting, Calcium Carbonate. It varies from pure white to dirty cream in color. It is a bulky pigment, quite stable to light, and is unaffected by hydrogen sulfide. It is practically insoluble in water but more soluble in water containing carbon dioxide forming calcium bicarbonate. It is soluble in all dilute acids with the evolution of carbon dioxide. The calcium carbonates exhibit little covering power in wet oil or varnish films. Their oil absorption varies widely and is dependent on particle size and surface treatment, which may change the characteristics of the pigment markedly to improve gloss, increase ease of wetting, prevent penetration and lower oil absorption. (16)

The calcium carbonate used was Calwhite. It is a high brightness, relatively low particle size natural calcium carbonate pigment produced from pure crystalline marble. It is manufactured under rigid control by a system of water grinding and centrifugal classification. Some of its other properties are listed below:

Calwhite (Georgia Marble Co.)

Dry brightness	96%
Hardness (Mho)	3.0
Oil Absorption G-C	23-25
pH	9.1 - 9.2

Specific Gravity	2.71
Particle Size distribution	2-30 microns
	75% minus 10 microns
Mean particle size	6.5 microns
Specific Resistance	20,000 ohms
Bulking Value	
One pound bulks	0.0443 gal
Weight per solid gallon	22.57 lbs

Typical Chemical Composition:

CaCO_3	98.00%
MgCO_3	1.01%
Al_2O_3	0.02%
Fe_2O_3	0.08%
Mn	Trace
SiO_2	0.38%
Cu	None
Moisture	0.40% (max)

D. Variables Studied

While this study pertained to surface area and power requirements, it was felt that several of the operating variables other than time should be checked in order to get the optimum grind on each run. This was accomplished by checking the effect of five other variables on the Zinc Oxide and Titanium Dioxide grinds.

The first variable studied was mill speed. Operating within the 50 to 65 per cent of critical speed range mentioned in section B, runs

were checked at 65 RPM, 75 RPM and 85 RPM. The time, mix and all other conditions remained constant.

In the first runs because of the water system and the fact that the wetting agent was a detergent type material there was some foaming. This foaming would have cushioned the cascading of the pebbles and cut down on grinding efficiency. Therefore an antifoam agent was added, a silicone soap, Nopco JMK (Nopco Chemical Co.) and also checked in a grind to note its effect on the development of surface area.

Also checked was the effect of the wetting agent. This was done by running the organic, anionic, Tamol 731 (Rohm & Haas) against an inorganic agent, Potassium Tripolyphosphate and also a grind with no wetting agent. Tamol 731, which is the sodium salt of a carboxylated polyelectrolyte, was chosen from among many organic types because of its good performance in the type of system being studied. The mix was kept thin to prevent rheological side effects. (13)

With a 24 hour grind, using flint pebbles, Tamol, Antifoam and 65 RPM, the solids effect was checked. Slurries with about 40, 50 and 60 per cent solids were ground to determine its effect on surface development.

Finally the grinding action of the random shaped flint beach pebbles was compared with that of uniformly shaped cylinders of a high density ceramic and spherically uniform porcelain balls.

IV. EXPERIMENTAL RESULTS

At the outset it was necessary to drop one of the pigments which had been chosen for this study, Silver Bond Silica. It was found that this pigment when ground did not form a self-supporting plug and this would have made it impossible to measure surface area by means of the air permeameter.

Investigation of the possible sources of error in the use of the permeameter equations showed the following: (11)

<u>Variable</u>	<u>Accuracy Assumed in Measuring</u>	<u>Max. % deviation in s_0</u>
Volume of Air (Q_1)	± 0.1 ml	± 1.0
ΔP	± 25 mm Hg	± 1.7
Time (t)	± 1 sec	± 0.4
Length of Plug (L)	± 0.01 cm	± 0.3
Area of Plug (A)	$\pm 2.3 \times 10^{-3}$ cm ²	± 0.5
Porosity of Plug (ϵ)	$\pm 2.3 \times 10^{-3}$ cm ²	± 2.0
	± 0.01 cm (L)	± 2.0
	± 0.001 gr (W)	± 0.5
	± 0.02 gr/ml (ρ)	± 1.2

Since this method is also dependent on the porosity of the plug being between 0.4 and 0.5, it was first determined what the range would be in weight for each pigment, as follows:

$$W = \rho A L (1 - \epsilon) = 0.5 \rho A L \text{ --- } 0.6 \rho A L$$

For Zinc Oxide: 1.455 gr --- 1.745 gr

For Titanium Dioxide: 1.09 gr --- 1.31 gr

For Calcium Carbonate: 0.70 gr --- 0.84 gr

An average of the above high and low figures was taken and that was the amount weighed out for compression into the plug.

The power requirements were found to be the same for each type of pigment slurry as the viscosity for each was just about the same due to the solids content and the efficient job done by the wetting agent.(13) The slurries were in reality practically water thin and because of this there was no measurable difference in their power requirements. These power requirements were measured at each speed but since most of the data was run at 65 RPM, the optimum grind speed, they were the only readings required. Only the actual work used in grinding was used and this is why the power readings were so low. Work done in revolving the mill and the pebbles was not considered as having part in the development of surface.

The drying of pigments had to be handled very carefully as it was found that if they were heat forced or allowed to pack the results would be erratic due to cindering or flocculation. It was also not possible to dry them in the laboratory on days when the humidity was high as they carried over surface water which caused the plug to be impervious to the air stream flowing through it. It was found that the best method was to spread a thin layer of the ground slurry on a large tray and dry in a constant temperature-constant humidity room(77°F - 50% R.H.) In this way all the pigment grinds reached the permeameter in the same condition and moisture content was the same for all samples.

In an attempt to check the theories of Rittinger and Bond, the power expended in each grind was first plotted on arithmetic graph

paper against the surface area developed and the square root of the surface area developed. Since each of the pigments failed to yield a straight line relationship, we found that the Rittinger and Bond theories of direct proportionality did not hold. The data was also plotted on semi-log paper and again did not yield straight lines. This proved the relationship was not of the type, $y = n 10^{mx}$, where m and n are constants.

The data when plotted on log-log paper yielded straight lines with each of the pigments, as shown in Curve 2. This meant they were power functions of the general type $x = A y^n$. These lines cross each other because of their different slopes and the lines and the equations derived therefrom show no correlation with other properties of the pigments such as specific gravity, hardness or grinding resistance. The equations from this plot are as follows:

$$\text{For Titanium Dioxide:} \quad P = .086 (\Delta s)^{1.072}$$

$$\text{For Zinc Oxide:} \quad P = .036 (\Delta s)^{0.678}$$

$$\text{For Calcium Carbonate:} \quad P = .076 (\Delta s)^{0.894}$$

However, when each of the pigments was plotted on log-log paper starting with the same surface area (that of Titanium Dioxide) it yielded a family of straight lines extending radially from the same origin and displaced in the order of their hardness. The y-intercepts where $\Delta s = \log 1 = 0$, which can be considered the condition of the pigments before grinding, were in ratios very close to the ratios of the Mohs hardness of the pigments. Since this did not show up on the previous plot, it points out the fact that the $\Delta s = 0$ intercept only have significance where all the Δs start from the same place, in other

words where all the $\Delta s = 0$ have the same base surface area.

In this plot the surface areas and power required to develop them for the pigments which did not start at the same particle size as the Titanium Dioxide, were obtained by interpolating the original experimental data as shown in Curve 2. The plot of these interpolated values of Zinc Oxide and Calcium Carbonate and the experimental values for Titanium Dioxide is shown in Curve 3.

From this set of curves were obtained the following equations:

$$\text{For Titanium Dioxide:} \quad P = .086 (\Delta s)^{1.072}$$

$$\text{For Zinc Oxide:} \quad P = .090 (\Delta s)^{1.05}$$

$$\text{For Calcium Carbonate:} \quad P = .107 (\Delta s)^{0.98}$$

The very important relation between the y-intercept and the mineralogical hardness of the materials is listed below:

	<u>Hardness</u>	<u>Ratio</u>	<u>y-intercept</u>	<u>Ratio</u>
For Titanium Dioxide:	6.0		16.8	
		1.41		1.33
For Zinc Oxide:	4.25		12.6	
		1.41		1.37
For Calcium Carbonate:	3.0		9.2	

In the study of the relation of time of grind to surface area developed, the function was again a power one as shown in Curve 1. Equations for this correlation of time of grind to surface area developed are:

$$\text{For Titanium Dioxide:} \quad t = 22 (\Delta s)^{.609}$$

$$\text{For Zinc Oxide:} \quad t = 11 (\Delta s)^{.60205}$$

$$\text{For Calcium Carbonate:} \quad t = 20 (\Delta s)^{.869}$$

The check on the grinding variables was made by comparing the surface areas developed when each in turn was removed or replaced.

The results checked for both pigments studied, Titanium Dioxide and Zinc Oxide. They showed that for this particular system and the particular mill, the best way to develop optimum grinding conditions was to grind at 65 RPM with 53.8 per cent solids, adding Tamol and Antifoam, the grinding media to be flint beach pebbles. These were the conditions under which all of this experimental data covering grinding time and power effect on surface area development was collected.

A check of the results obtained with the air permeameter against those obtained by other investigators showed the results were in the same range and in most cases comparable where the same type of pigment was studied. This served as a double check on the validity of the surface area results which had already been checked using the standardizing Zinc Oxide. In the Carman paper (4) the values of s_0 of Zinc Oxide as obtained by air permeability were $1.49-1.77 \text{ cm}^{-1} \times 10^5$ and by Nitrogen Absorption $1.81 \text{ cm}^{-1} \times 10^5$. The values obtained in this experiment for a particular grade of Zinc Oxide range from 1.5325 to $2.342 \text{ cm}^{-1} \times 10^5$. In the case of Titanium Dioxide, Carman shows a range of 3.26-3.82 on air permeability and 4.4 on nitrogen absorption, while the experimental values ranged from 2.006 to 2.892. With the Calcium Carbonate, Carman had no figures for natural Calcium Carbonate, just the precipitated type which is much finer. A letter from the pigment supplier quotes a figure of .21 which compares to the experimental range of .1684 to .753. This type of check cannot be held too closely since this paper deals with a specific pigment while Carman's paper does not identify the types studied. In dealing with Zinc Oxide it could be nodular or acicular, fine or coarse grade; with Titanium it could be Rutile or Anatase; Calcium Carbonate could be natural or precipitated.

V. CONCLUSIONS

In the field of wet pigment grinding the theory of grinding has not kept pace with the practical developments. The theories of Rittinger and Bond, developed for use in dry grinding of larger sized materials, cannot be used when studying sub-sieve size pigments. Experimental results indicate the development of surface area in this range is a more complicated phenomena than the direct relationship of total area developed to power expended as postulated by Rittinger. Here, too, the formation of crack tips as mentioned by Bond is difficult to imagine in particles which are less than a micron in diameter.

To fill the need for some method of predicting the power requirements to develop a certain amount of surface area, the following equations were derived from the plots of the experimental results:

$$\text{For Zinc Oxide:} \quad P = .090 (\Delta s)^{1.05}$$

$$\text{For Titanium Dioxide:} \quad P = .086 (\Delta s)^{1.072}$$

$$\text{For Calcium Carbonate:} \quad P = .107 (\Delta s)^{0.98}$$

In the log-log plots from which these equations were developed, the y-intercepts (where $\Delta s = \log 1 = 0$) of the three straight line plots were in the same order and ratio as their hardness. These lines were based on all the pigments having the same starting surface area. When the pigments started from different surface areas the correlation did not hold. Therefore the $\Delta s = 0$ point, or the unground pigment starting point, only has significance when all the pigments are studied from the same base.

With these equations one could predict the power necessary to reduce a certain feed pigment to a definite surface area or to a certain average particle size by use of the equation:

$$d_{av} = 6 / \rho s$$

$$d_{av} = \text{average particle diameter, cm}$$

$$\rho = \text{density gr/cc}$$

$$s = \text{specific surface cm}^2/\text{gr}$$

These equations could also be used in testing the efficiency of a grinding operation, for when a grind did not bring up the predicted surface area, it would be necessary to check the grinding variables to see where they could be changed to get the optimum grind.

In some cases the time of grind alone would be very valuable information in scheduling production and the following equations derived from plots of these experimental results can be used to predict the mill time on the pigments studied:

$$\text{For Titanium Dioxide: } t = 22(\Delta s)^{.609}$$

$$\text{For Zinc Oxide: } t = 11(\Delta s)^{.60205}$$

$$\text{For Calcium Carbonate } t = 20(\Delta s)^{.869}$$

This work has given the paint manufacturer a simple method of evaluating his grinding procedures and bringing them up to the point of optimum grind by the use of a simple set of measurements.

VI. RECOMMENDATIONS

Fine pigment grinding in water or solvent systems, using small amounts of wetting agents, is quite widely used today. Pebble mills are one of the popular mills in this type of operation, especially in the grinding of Whites. Since the mill time and power consumption are the all important factors in this type of grinding, any method of cutting down either would be a decided advantage.

Using the author's equations on production size mills the manufacturer could check the efficiency of his grinding methods and in the cases where an optimum grind is not being obtained, check out the variables involved and their effect on surface development.

In this type of grinding also, the paint manufacturer should make a study of the mineralogical hardness of the pigments, as well as their starting particle size range, with a view to simplifying the grinding procedure by replacing coarser pigments with finer ones and harder pigments with softer ones, whenever it is feasible.

APPENDIX

Legend: T - Tamol
A - Antifoam
P - Pebbles

TABLE 1

35

PERMEAMETER DATA ON RUNS WITH ZINC OXIDE (Specific Gravity: 5.606)

Variable	P ₁	P ₂	ΔP	P	t				$\frac{t \Delta P}{P_1}$	$s_m \times 10^5$	$s_k^2 \times 10^8$	$s_o \times 10^5$	m^2/gr	Wt. plug gr.	RPM	SOLIDS	ADDITIVES
Grind Time	mm Hg	mm Hg	mm Hg	mm Hg	sec	ϵ	F ₁	F ₂		$\frac{cm}{cm}$	$\frac{cm^{-1}}{cm^{-1}}$	$\frac{cm^{-1}}{cm^{-1}}$					
0 hrs	756	12	744	384	140.6	.448	.2895	.364	138.2	1.385	22.4	1.5325	2.73	1.6018	65	53.8%	T A P
4 hrs	753	12	741	382.5	143.	.476	.393	.4325	140.8	1.67	30.6	1.835	3.27	1.5200	65	53.8%	T A P
8 hrs	753	12	741	382.5	152.3	.478	.402	.437	150.	1.80	40.0	2.0	3.57	1.5186	65	53.8%	T A P
12 hrs	756	12	744	384	168.	.471	.371	.420	165.4	1.908	34.2	2.074	3.88	1.5397	65	53.8%	T A P
16 hrs	753	12	741	382.5	173.	.483	.423	.451	170.3	2.11	39.9	2.287	4.08	1.5123	65	53.8%	T A P
20 hrs	756	12	744	384	189.	.474	.385	.4275	186.	2.18	43.5	2.364	4.22	1.5300	65	53.8%	T A P
24 hrs	756	12	744	384	231.5	.449	.301	.367	227.5	2.285	28.1	2.4025	4.28	1.6000	65	53.8%	T A P
36 hrs	756	12	744	384	234.1	.455	.317	.380	231.	2.40	40.7	2.56	4.57	1.5825	65	53.8%	T A P
48 hrs	756	12	744	384	214.	.4825	.423	.451	210.5	2.60	49.5	2.78	4.96	1.5030	65	53.8%	T A P
1 hr	756	12	744	384	172.6	.435	.256	.334	169.7	1.506	24.0	1.65	2.94	1.6431	65	53.8%	T A P
2 hrs	756	12	744	384	195	.418	.215	.301	192.	1.585	22.8	1.7205	3.07	1.6921	65	53.8%	T A P
3 hrs	756	12	744	384	200.	.420	.219	.305	196.5	1.64	23.8	1.77	3.155	1.6859	65	53.8%	T A P
17 hrs	756	12	744	384	172	.488	.444	.465	169.	2.155	41.5	2.3325	4.16	1.4894	65	53.8%	T A P
18 hrs	756	12	744	384	194	.469	.365	.414	191.	2.17	38.5	2.335	4.17	1.5437	65	53.8%	T A P
19 hrs	756	12	744	384	192	.471	.371	.420	189.	2.18	38.8	2.342	4.18	1.5386	65	53.8%	T A P

TABLE 2

Legends: T -Tamol S -Spheres
 A -Antifoam K -Pot. Tripoly.
 P -Pebbles O -Omitted
 C -Cylinders

PERMEAMETER DATA ON RUNS OF ZINC OXIDE AND TITANIUM DIOXIDE WITH VARIABLES OTHER THAN TIME (ALL 24 HOUR GRINDS)

Variable	P ₁ mm Hg	P ₂ mm Hg	ΔP mm Hg	P mm Hg	t sec	ε	Zinc Oxide					s m ² /gr	Weight plug gr.	RPM	Solids	Add.	
							F ₂	F ₂	tΔp D ₁	s _m x 10 ⁵ cm ⁻¹	s _k x 10 ⁸ cm						s _o x 10 ⁸ cm
Antifoam	753	12	741	382.5	152	.462	.307	.390	150.	1.61	27.85	1.767	3.15	1.5686	65	53.8	AO T P
Wetting Agent	762	12	750	387	225	.446	.288	.359	222.	2.185	34.6	2.3345	4.16	1.6108	65	53.8	K A P
"	762	12	750	387	151	.478	.399	.4375	148.8	1.788	32.1	1.954	3.49	1.5177	65	53.8	TO A P
Solids	770	12	758	391	164.2	.452	.309	.373	161.8	1.652	27.3	1.778	3.17	1.5967	65	63.7	T A P
"	770	12	758	391	200.5	.458	.326	.387	197.5	2.094	35.2	2.251	4.02	1.5745	65	37.3	T A P
Grinding Media	762	12	750	387	198.3	.437	.263	.339	195.3	1.81	27.8	1.952	3.48	1.6370	65	53.8	T A S
"	762	12	750	387	165	.467	.361	.389	162.5	1.73	31.8	1.897	3.38	1.5493	65	53.8	T A C
Mill Speed	770	12	758	391	221.4	.447	.292	.362	218.	2.16	34.8	2.31	4.12	1.6094	75	53.8	T A P
"	770	12	758	391	143.8	.506	.512	.535	141.6	2.075	39.75	2.2595	4.09	1.4381	85	53.8	T A P
							Titanium Dioxide										
Antifoam	760	12	748	386	202	.464	.348	.401	199	2.19	38.7	2.355	5.62	1.1653	65	53.8	AO T P
Wetting Agent	760	12	748	386	188	.477	.395	.433	185	2.20	40.8	2.372	5.64	1.1373	65	53.8	K A P
"	760	12	748	386	176.4	.463	.344	.398	174	1.90	33.4	2.06	4.91	1.1659	65	53.8	TO A P
Solids	760	12	748	386	156.8	.487	.436	.497	154	2.055	37.5	2.222	5.29	1.1176	65	63.7	T A P
"	760	12	748	386	210.	.450	.301	.368	207	2.09	34.8	2.245	5.35	1.1978	65	37.3	T A P
Grinding Media	760	12	748	386	256.3	.418	.216	.330	252.3	2.08	30.3	2.218	5.28	1.2651	65	53.8	T A S
"	760	12	748	386	224	.456	.322	.383	221.	1.95	47.0	2.165	5.16	1.1829	65	53.8	T A C
Mill Speed	760	12	748	386	179	.465	.388	.428	176	2.07	38.2	2.238	5.33	1.1626	75	53.8	T A P
"	760	12	748	386	230	.433	.267	.331	227	2.06	33.9	2.215	5.27	1.2353	85	53.8	T A P

Legend: T - Tamol
A - Antifoam
P - Pebbles

TABLE 3

PERMEAMETER DATA ON RUNS WITH TITANIUM DIOXIDE AND CALCIUM CARBONATE

Variable	P_1 mm Hg	P_2 mm Hg	ΔP mm Hg	p mm Hg	t sec	ϵ	F_1	F_2	$\frac{t\Delta p}{P_1}$	$s_m \times 10^5$ $\frac{m}{cm-1}$	$s_k^2 \times 10^8$ $\frac{cm}{cm-1}$	$s_o \times 10^8$ $\frac{cm}{cm-1}$	s m ² /gr	Weight plug gr.	RPM	SOLIDS	ADD.	
Grind																		
Time																		
0 hrs	758	12	746	385	176.5	.458	.327	.387	174.3	1.848	31.7	2.006	4.78	1.176	65	53.8	T A P	
4 hrs	758	12	746	385	152.	.487	.439	.462	150.	1.90	35.6	2.075	4.94	1.116	65	53.8	T A P	
8 hrs	758	12	746	385	155	.489	.448	.468	153.	1.96	38.2	2.140	5.11	1.178	65	53.8	T A P	
12 hrs	758	12	746	385	195	.458	.328	.388	192.5	2.06	35.2	2.22	5.29	1.110	65	53.8	T A P	
16 hrs	758	12	746	385	230	.441	.273	.348	227.	2.16	34.6	2.308	5.50	1.2155	65	53.8	T A P	
20 hrs	758	12	746	385	188	.477	.394	.434	185.5	2.205	44.0	2.389	5.68	1.1363	65	53.8	T A P	
24 hrs	758	12	746	385	241	.444	.284	.356	238	2.325	37.5	2.4775	5.89	1.2071	65	53.8	T A P	
36 hrs	758	12	746	385	210	.489	.409	.444	207.	2.52	47.0	2.692	6.41	1.1292	65	53.8	T A P	
48 hrs	758	12	746	385	228.8	.479	.404	.439	226.	2.72	50.7	2.892	6.88	1.1301	65	53.8	T A P	
									<u>Calcium Carbonate</u>									
0 hrs	756	12	744	384	10	.433	.252	.331	9.73	.088	1.36	0.1684	0.622	0.7908	65	53.8	T A P	
4 hrs	756	12	744	384	19.5	.408	.191	.279	19.18	.1465	2.03	0.25675	0.860	0.8324	65	53.8	T A P	
8 hrs	756	12	744	384	22.	.424	.230	.313	21.6	.1853	2.75	0.2825	1.042	0.8090	65	53.8	T A P	
12 hrs	756	12	744	384	27.	.422	.225	.308	26.6	.2244	3.32	0.3235	1.193	0.8126	65	53.8	T A P	
16 hrs	756	12	744	384	35	.407	.190	.278	34.4	.2610	3.63	0.3615	1.335	0.8337	65	53.8	T A P	
20 hrs	756	12	744	384	39.5	.416	.211	.296	38.4	.3110	4.38	0.4165	1.537	0.8211	65	53.8	T A P	
24 hrs	756	12	744	384	52	.414	.208	.292	51.2	.4090	5.90	0.5225	1.937	0.8243	65	53.8	T A P	
36 hrs	756	12	744	384	68	.410	.198	.285	66.8	.5210	7.53	0.6385	2.355	0.8298	65	53.8	T A P	
48 hrs	756	12	744	384	86	.404	.185	.275	84.6	.6370	8.72	0.7530	2.78	0.8385	65	53.8	T A P	

TABLE 4

POWER READINGS TAKEN ON WESTINGHOUSE WATTHOUR METER FOR SLURRIES OF
ZINC OXIDE, TITANIUM DIOXIDE AND CALCIUM CARBONATE GRINDING IN A

PEBBLE MILL

<u>RPM</u>	<u>Empty Mill sec/rev</u>	<u>Loaded sec/rev</u>	<u>Empty rev/sec</u>	<u>Loaded rev/sec</u>	<u>To Load rev/sec</u>	<u>To Load rev/hr</u>	<u>K kwhr/rev</u>	<u>Total Work kw-hr/hr</u>
85	5.32	5.28	.1880	.1894	.0014	5.04	3.56×10^{-4}	17.9424
75	5.44	5.41	.1838	.1848	.0010	3.60	"	12.8160
65	5.48	5.46	.1825	.1832	.0007	2.52	"	8.9712
<u>RPM</u>	<u>Watts 4 hrs</u>	<u>Watts 8 hrs</u>	<u>Watts 12 hrs</u>	<u>Watts 16 hrs</u>	<u>Watts 20 hrs</u>	<u>Watts 24 hrs</u>	<u>Watts 36 hrs</u>	<u>Watts 48 hrs</u>
85	7.18	14.35	21.55	28.75	35.83	43.15	64.70	86.20
75	5.14	10.25	15.40	20.55	35.65	30.80	46.20	61.60
65	3.565	7.17	10.70	14.26	17.82	21.40	32.10	42.80
<u>RPM</u>	<u>Watts/gr 4 hrs</u>	<u>W/gr 8 hrs</u>	<u>W/gr 12 hrs</u>	<u>W/gr 16 hrs</u>	<u>W/gr 20 hrs</u>	<u>W/gr 24 hrs</u>	<u>W/gr 36 hrs</u>	<u>W/gr 48 hrs</u>
85	.0299	.0599	.0899	.1197	.1492	.1795	.2690	.3590
75	.0214	.04275	.0642	.0857	.1069	.1282	.1923	.2567
65	.01482	.0298	.0446	.0594	.0743	.0892	.1337	.1785

TABLE 5DATA ON SURFACE DEVELOPMENT AND POWER EXPENDED

<u>Grinding Time hrs</u>	<u>Specific Surface m²/gr</u>	<u>Surface Developed m²/gr</u>	<u>Power Expended Watts/gram</u>
	<u>Zinc Oxide</u>		
0	2.73	--	--
1	2.94	0.21	.003705
2	3.07	0.34	.00741
3	3.155	0.425	.011115
4	3.27	0.54	.01482
8	3.57	0.84	.0298
12	3.88	1.15	.0446
16	4.08	1.35	.0594
17	4.16	1.43	.063
18	4.17	1.44	.0668
19	4.18	1.45	.0705
20	4.22	1.49	.0743
24	4.28	1.55	.0892
36	4.57	1.84	.1337
48	4.96	2.23	.1785

TABLE 6

DATA ON SURFACE DEVELOPMENT AND POWER EXPENDED

<u>Grinding Time hrs</u>	<u>Specific Surface m²/gr</u>	<u>Surface Developed m²/gr</u>	<u>Power Expended Watts/gram</u>
<u>Titanium Dioxide</u>			
0	4.78	--	--
4	4.94	0.16	.01482
8	5.11	0.33	.0298
12	5.29	0.51	.0446
16	5.50	0.72	.0594
20	5.68	0.90	.0743
24	5.89	1.11	.0892
36	6.41	1.63	.1337
48	6.88	2.10	.1785
<u>Calcium Carbonate</u>			
0	0.622	--	--
4	0.860	0.238	.01482
8	1.042	0.420	.0298
12	1.193	0.571	.0446
16	1.335	0.713	.0594
20	1.537	0.915	.0743
24	1.937	1.315	.0892
36	2.355	1.733	.1337
48	2.78	2.158	.1785

TABLE 8RESULTS OF LOG-LOG PLOTS OF SURFACE DEVELOPED VERSUS POWER AND TIME CONSUMED

<u>Plot Δs versus</u>	<u>Pigment</u>	<u>t intercept or P intercept</u>	<u>Δs intercept</u>	<u>Slope</u>	<u>Equations</u>
P	ZnO	.036	9.0	0.678	$P = .036(\Delta s)^{.678}$
P	TiO	.086	13.0	1.072	$P = .086(\Delta s)^{1.072}$
P	CaCo	.076	10.0	0.894	$P = .076(\Delta s)^{.894}$
t	ZnO	10.	.23	0.60206	$t = 10. (\Delta s)^{.60206}$
t	TiO	22.	.038	0.609	$t = 22. (\Delta s)^{.609}$
t	CaCo	20.	.065	0.869	$t = 20. (\Delta s)^{.869}$

RELATIONSHIP OF HARDNESS TO Δs INTERCEPT

<u>Pigment</u>	<u>Mho Hardness</u>	<u>Ratio</u>	<u>Δs intercept</u>	<u>Ratio</u>
TiO	6.0	1.41	9.0	1.11
ZnO	4.25	1.41	10.0	1.30
CaCo	3.0		13.0	

TABLE 9

DATA USED IN PLOTTING ALL PIGMENTS STARTING FROM THE SAME BASE SURFACE AREA

<u>Δ_s</u>	<u>ZnO</u>		<u>TiO</u>		<u>CaCO</u>	
	<u>P</u>	<u>Δ_s</u>	<u>P</u>	<u>Δ_s</u>	<u>Δ_s</u>	<u>P</u>
0.18	.018	0.16	.01482		1.22	.1300
0.40	.038	0.33	.0298		2.22	.2350
0.60	.053	0.51	.0446		5.12	.5500
0.80	.072	0.72	.0594			
1.00	.090	0.90	.0743			
		1.11	.0892			
		1.63	.1337			
		2.10	.1785			

TABLE 10

RESULTS OF LOG LOG PLOTS WITH SAME BASE STARTING SURFACE AREA

<u>Pigment</u>	<u>P-intercept</u>	<u>Δ_s intercept</u>	<u>Slope</u>	<u>Equations</u>
TiO	.086	16.8	1.072	$P = .086 (\Delta_s)^{1.072}$
ZnO	.090	12.6	1.05	$P = .090 (\Delta_s)^{1.05}$
CaCO	.107	9.2	0.98	$P = .107 (\Delta_s)^{0.98}$

RELATIONSHIP OF HARDNESS TO Δ_s INTERCEPT

<u>Pigment</u>	<u>Mho Hardness</u>	<u>Ratio</u>	<u>Δ_s intercept</u>	<u>Ratio</u>
TiO	6.0		16.8	
		1.41		1.33
ZnO	4.25		12.6	
		1.41		1.37
CaCO	3.0		9.2	

PLOT OF TIME OF GRIND VERSUS SURFACE AREA DEVELOPED

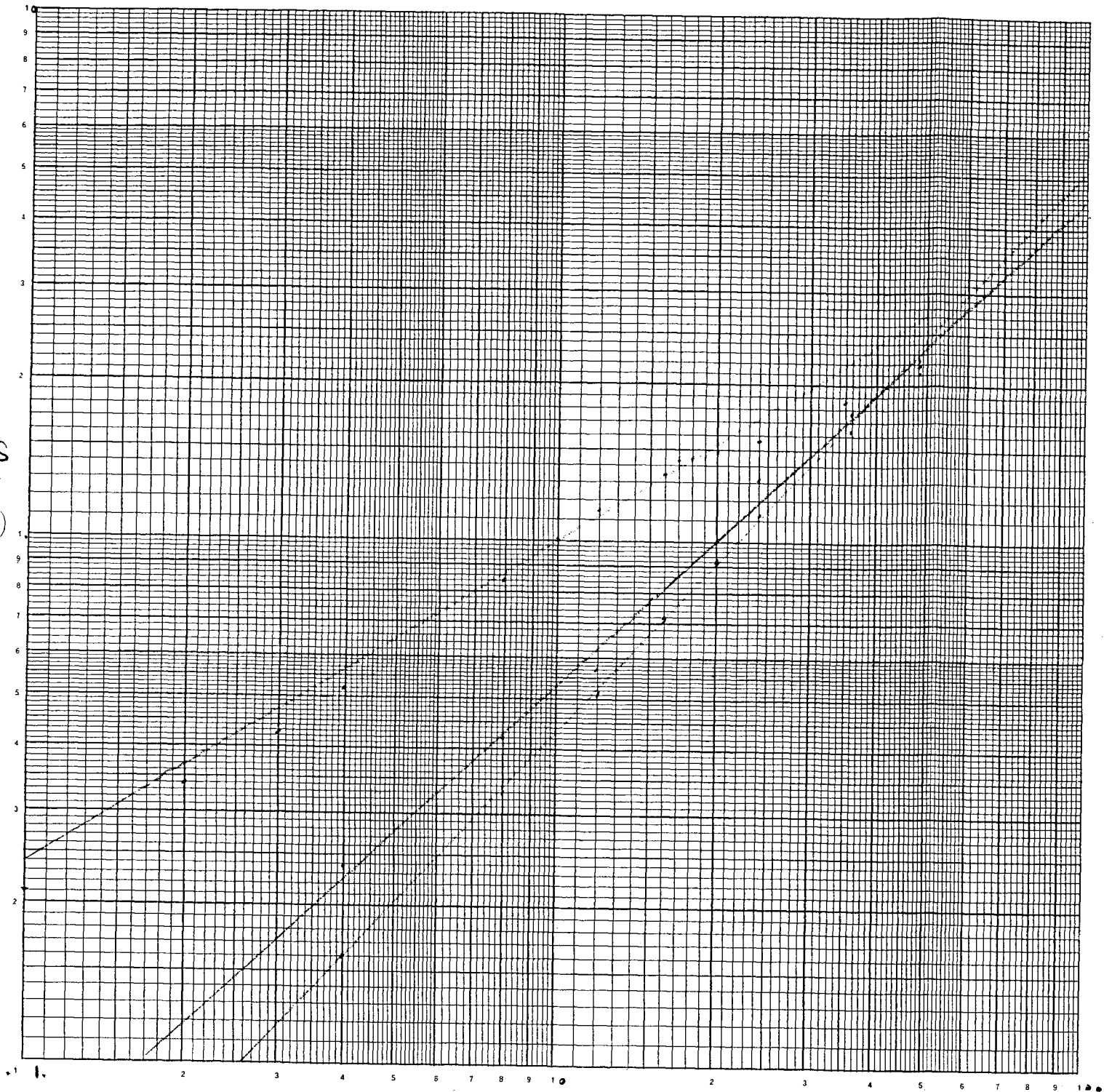
PRINTED IN U. S. A.

ENGINEERS TECHNICAL DATA SYSTEM

ENGINEERS PUBLISHING CO., PHILA., PA.

FORM NO. 226-1G

$\frac{\Delta S}{t^2}$



- - - ZnO
 — TiO₂
 — CaCO₃

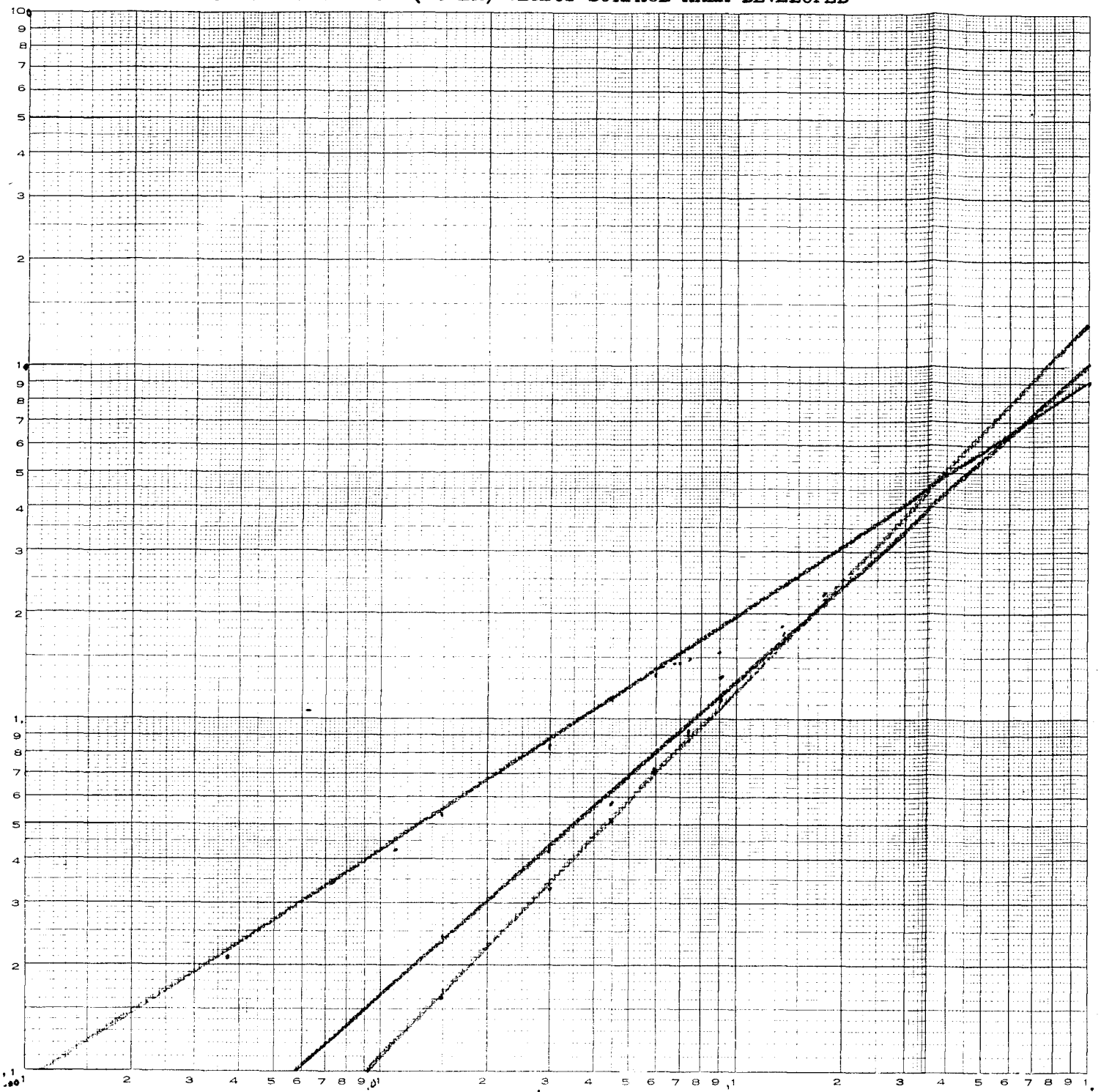
t
hrs

PLOT OF TOTAL WORK (POWER) VERSUS SURFACE AREA DEVELOPED

EUGENE DIETZGEN CO.
MADE IN U. S. A.

ΔS
 $\frac{9/13}{1/4}$

ND. 340-L33 DIETZGEN GRAPH PAPER
LOGARITHMIC
3 CYCLES X 3 CYCLES



- ZnO
- TiO₂
- CaCO₃

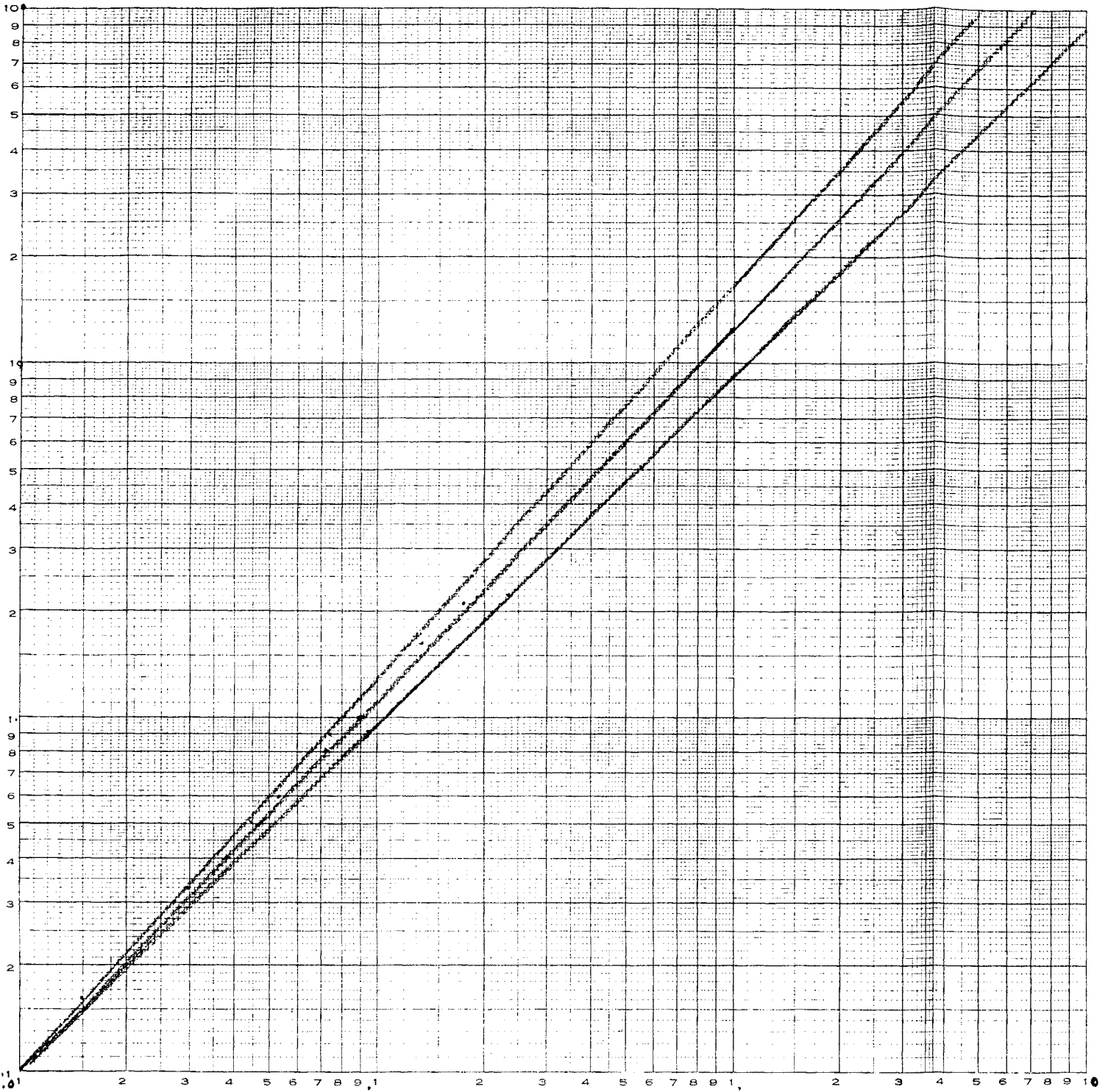
P $\frac{\text{watts}}{\text{gr.}}$

PLOT OF TOTAL WORK VERSUS SURFACE AREA DEVELOPED
ALL PIGMENTS REFERRED TO THE SAME STARTING SURFACE AREA

EUGENE DIETZGEN CO.
MADE IN U. S. A.

NO. 340-L33 DIETZGEN GRAPH PAPER
LOGARITHMIC
3 CYCLES X 3 CYCLES

ΔS
 $\frac{P}{q}$



- ZnO
- TiO₂
- CaCO₃

P $\frac{\text{watts}}{\text{gram}}$

BIBLIOGRAPHY

1. Bond, F.C., Chem Eng., 59, p 242 (1952)
2. Blaine, R.L., ASTM Bull. No. 123, p 51 (1943)
3. Brunauer, S., Emmett, P.H. & Teller, E., J. Amer Chem Soc., 60, 309 (1930)
4. Carman, P.C., Malherbe, P.R., J. Soc Chem Ind., 69, 134-43 (1950)
5. Carman, P.C., Symposium on new methods for particle size determination in the sub-sieve range, ASTM, p 24-33, March 4, 1941.
6. Coghill, W.H. & DeVaney F.D., U.S. Bureau of Mines, Tech Paper 581 (1937)
7. Emmett, P.H., Symposium ASTM, p 95, March 4, 1941
8. Fischer, E.K., Rolle, C.J., & Ryan, L.W., Official Digest Fed P & V Prod Clubs, 20, No. 287, p 59 (1948)
9. Fisher, H.Z., des Vereines deut. Ing., 48, p 437-441 (1904)
- 10 Gaudin, A. M., "Principles of Mineral Dressing" McGraw-Hill Book Co. Inc., New York, N. Y. (1939)
- 11 Gooden & Smith, Ind Eng Chem (Anal Ed) 12, p 479 (1940)
- 12 Gross, J., U.S. Bureau of Mines Bulletin 402 (1938)
- 13 Green, H., Ind Eng Chem,(Anal Ed) 14, p 576-85 (1942)
- 14 Harvey, E. N., Symposium on Paint and Paint Materials, ASTM, p 60, Feb 25, 1947
- 15 Lea, F.M. & Nurse, Symposium Inst of Chem Eng & Soc of Chem Ind, p 47, Feb 4, 1947
- 16 Mattiello, J. J. "Protective & Decorative Coatings" Vol II, John Wiley & Sons, New York, p 32-4, 393 (1942)
- 17 Pechukas A., Gage, F.W., Ind Eng Chem (Anal Ed) 18, p 370 (1946)
- 18 Underwood, C.M., Ind Eng Chem, 30, p 905-8 (1938)