

A PHOTOMICROGRAPHIC METHOD FOR THE DETERMINATION OF PARTICLE SIZE OF PAINT AND RUBBER PIGMENTS.* †

BY

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WHEN a biologist desires to measure the diameter of a tissue cell or the length of a bacterium he may use for his purpose a filar micrometer eyepiece calibrated by means of a stage micrometer. Aside from a certain amount of facility required for the manipulation of this instrument his task is a comparatively easy one. Objects like cells, etc., possess, as a rule, a high degree of uniformity with the consequence that a fairly accurate average diameter may be obtained with relatively few measurements. Further than this it is not a vital issue with the biologist if his average measurement, so obtained, happens to deviate from the most probable value by the apparently insignificant amount of one- or two-tenths microns.

On the other hand, the microscopist who wishes to determine the average particle size of a paint or rubber pigment has a problem to deal with which, in a sense, is diametrically opposite to the case just cited. Here, even in the most uniform pigments, will be found particles ranging from the nearly or quite ultra-microscopic to those with a diameter many times as great. Hence, it sometimes becomes necessary to measure thousands of particles, if a high degree of accuracy is required, in order to obtain a value that closely approximates the true average. To try to accomplish this with a filar micrometer would not only consume an unwarranted amount of time but the process itself would become so tedious that it would discourage, at the start, anyone who attempted to solve the problem in this manner.

Then again, the matter of accuracy assumes here a truly important rôle. A few years ago the technical advisor who would

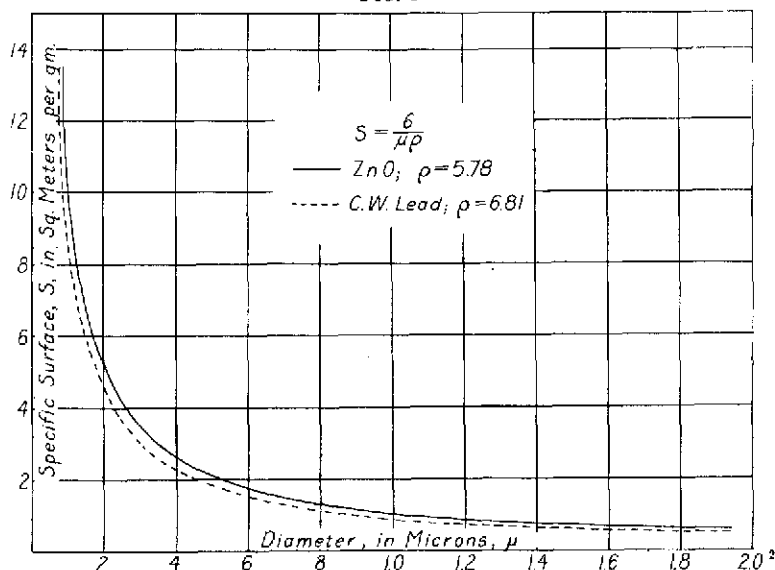
* Communicated by the Author.

† The expression "Particle Size" is used in reference to diameters, as customary amongst paint and rubber technologists.

condemn a consignment of pigment on a matter of one or two-tenths microns (if he were able to detect it) would have been considered hypercritical to say the least. But let us see if such a hasty conclusion arrived at without due consideration, is justifiable or not.

The character and behavior of fine pigments depends to a large extent on the magnitude of their specific surface.¹ Assuming the particles to be spheres, simply for the sake of simplicity—

FIG. 1.



Curves for zinc oxide and corroded white lead, showing relationship between specific surface and diameter of particle.

and this assumption cannot fundamentally alter the argument—it can be shown that,

$$\rho S \mu = 6 \dots \dots \dots (1)$$

where, ρ = density of material.

S = specific surface (square metres per gram of material).

μ = diameter of particle in microns.

¹ Specific surface is inversely proportional to the "diameter" of the particle or to "particle size." Such qualities of a pigment as tint, brightness, hiding power, and oil absorption, in paints, and resistance offered to abrasion in rubber are functions of particle size. It would be a great mistake, however, to assume that these qualities depended *entirely* on particle size. Other factors enter in, such an index of refraction, density, color, forces of adhesion and surface tension.

² If μ is the harmonic mean of the three dimensions, then this equation will hold for any rectangular parallelepiped. Pigment particles roughly approximate this form and that of spheres.

Plotting the equation for zinc oxide ($\rho = 5.78$) and lead carbonate ($\rho = 6.81$) gives the two curves illustrated in Fig. 1. It should be noted that when the pigments are comparatively coarse, from $.8\mu$ in diameter upward, a difference of $.1\mu$ or $.2\mu$ has but little effect on the magnitude of the specific surface. From $.8\mu$ downward, however, the reverse of this condition becomes true. In the case of very fine pigments such as zinc oxide it will be found possible to purchase on the market various grades of material some of which will measure $.6\mu$ and others only $.3\mu$ —a total range of but $.3\mu$, yet one sufficiently great to cause a difference of 100 per cent. in the specific surface. Studying the situation from this point of view will show that the investigator who considers the importance of one- or two-tenths microns is not so fastidious after all.

As a matter of fact the author feels no hesitancy in predicting that within the next few years the manufacturer of fine pigments who wishes to maintain his position in a keenly competitive field will find it necessary not only to become acquainted with the particle size of his products to the first, but even to the second, and probably the third, decimal place in microns.

THE METHOD.

The fundamental idea involved in the method is by no means a new one. In all probability it has been employed many times by various investigators and for numerous purposes; yet the author is not aware of a single case where it has been sufficiently developed in detail so as to make it of practical importance in the special line of work to which it is here applied.³

Briefly stated, the pigment is prepared in such a manner so that a photomicrograph, at a known magnification, can be taken, showing *clearly and distinctly the individual particles*, which are then measured from the negative by a method to be described presently.

³ The method of grain measurement employed by metallographers is fundamentally similar to the photomicrographic method of particle measurement. Note on grain size, by G. H. Gulliver, *J. Inst. of Met.*, 1918.

"The Determination of Grain Size in Metals," by Zay Jefferies, A. H. Kline, and E. B. Zimmer, *Trans. Am. Inst. Mining Engineers*, 1917.

PREPARATION OF THE SAMPLE FOR PHOTOGRAPHING.

About a milligram of the pigment is placed on the centre of a microscope slide to which is added a drop of redistilled turpentine. The slide is to be held at the two ends between the thumb and first finger; a glass rod, with smooth, straight sides, so that it will come in close contact with the glass, is now used to disperse and rub out into an extremely thin layer the material in the turpentine. This is best accomplished by a forward and backward motion of the rod in the direction of the length of the slide and extending over the central area only. The rubbing must cease at a certain critical stage, when there still remains sufficient turpentine unevaporated to prevent the mount becoming "streaky," and yet not enough to float the particles which would allow them to flocculate. By a slightly upward flourish of the rod on the last stroke the mount can be made wedge shape, that is, dense in one part and thin in another, with all intermediate grades of density between. In this way it becomes possible to select a section for photographing that will show neither too many particles nor too few per given unit area.⁴

The next step, after the material is properly dispersed, is to completely remove the remaining turpentine. This should be done by laying the slide on a hot plate, the temperature of which is sufficiently high to cause evaporation within forty or fifty seconds. Care must be taken that volatilization is complete. This is satisfactorily ascertained by noticing if any odor of turpentine remains after heating. The particles will now be found to be cemented to the glass and should remain in this condition, if a reasonable amount of care is exercised in handling the slide. When suffi-

⁴ This method of dispersing the particles is to be used principally with the finest pigments, such as zinc oxide, lithopone, white lead, etc. In the case of these materials it will be found impossible to produce any *grinding* effect that will cause the *individual* grains to be broken up into smaller ones. This is on account of the fact that neither the glass slide nor the rod are optically flat, and consequently they are unable to come in close contact with each other except at a very few points.

With coarser materials such as clays, barytes, asbestine, etc. (which will probably feel gritty), only the slightest possible pressure must be brought to bear upon them with the dispersing rod for here there is some danger of a real grinding effect becoming manifest. Fortunately, these materials are so large that flocculation does not prevent the outline of the particles from being seen and a measurement made, hence, very little rubbing is necessary.

ciently cooled a small drop of glycerine is placed on the centre of the mount and then covered with a thin slip. The excess glycerine must be carefully squeezed out at the sides of the cover glass and absorbed by filter paper. The mount is finished in the usual manner with a ring of Brunswick black.

If the above instructions have been properly carried out, and the mount now held to the light, the pigment, if its index of refraction is high, will just be perceptible as a faint cloud; if its refractive index is low, the pigment will be entirely invisible, except with a microscope.

Upon microscopic observation three essential conditions should be manifest. They are—

1. The particles will be in one plane.
2. They will be free from Brownian motion.
3. They will be dispersed, showing individual grains instead of aggregates and flocculates. (Compare Figs. 8, 9, 10 and 12 with Fig. 7.)

THE PHOTOGRAPHY.

It is not the purpose of the present paper to describe the method of using a photomicrographic apparatus. It is also hardly necessary to add that unless one has acquired considerable facility in the manipulation of such apparatus it would not pay to attempt its application in the measurement of particle size.

In regard to the present problem, however, it must be stated that all photographs are made with transmitted light, and that this light is to be absolutely axial. Obliquity of illumination will give a distorted image, causing an appreciable error in the results.

The beginner will find it advantageous to start with a fine-grained contrast plate, using hydroquinone developer. After he has obtained experience in handling these materials successfully, he should then try his ability with panchromatic plates and develop with pyro. There are plates of this kind made especially for photomicroscopy which give great detail together with sufficient contrast.

THE MAGNIFICATION.

Generally, in photomicrographic work, definition of structure is the one essential quality most desired. However, as the structure of a pigment particle will give us no information in regard to its size, the factor, definition, may be neglected here to a

certain limited extent.⁵ On account of this fact it has been found an advantage to employ a magnification which otherwise would be too high if the best definition is to be obtained. Nevertheless, care must be taken that the photographic image of the particle gives edges sharply enough defined so as to make a satisfactory measurement possible.

With a 2 mm. apochromatic objective a magnification of 1500 diameters will be most convenient for pigments such as zinc oxide, lithopone, red oxide of iron, sublimed white lead, corroded white lead, Mathewson white lead, etc. Lower magnifications are used, naturally, with coarser materials. The method of measuring magnification is given under the section entitled "Errors."

MEASUREMENTS.

As previously pointed out, it sometimes becomes necessary to measure a thousand or more particles in order to obtain a sufficiently accurate average diameter. This demands a rapid method of measurement, if the work is not to become too irksome. The method is as follows: The negative, which must show from 200 to 250 distinct particles, is placed in a stereopticon and an image of it thrown on a screen, so situated that the total magnification of the original particle will be from 20,000 to 25,000 diameters. The image of the particles is measured with a millimetre rule. Particles which are out of focus to any extent at all, as the case will be with those around the border of the negative, must be neglected. In order to eliminate the possibility of duplication and skipping, the area of the screen is divided into small squares.

It is neither necessary nor desirable to consume time in estimating the fractional part of millimetres. These small errors are just as liable to be positive as negative, and it is reasonable to believe that their sum approaches zero as the number of measurements increases.

The length of time required for the measurement of a single particle should be approximately two seconds. As the readings are called off an assistant may take them down on an adding machine regulated to record number of items, so that by the time the measurements are finished their average can be determined directly.

⁵ But to no greater extent than is shown in the photomicrographs, Figs. 8 to 13.

If the probable error and the uniformity coefficient are desired, a permanent record of each particle is made by the method

FIG. 2.
Particle Measurement Record Sheet

Millimeters. mm.	12-17-20										Frequency, f.	fxmm	v	v ²	f x v ² (Σ v ²)
1															
2															
3															
4															
5															
6											8	48	4.44	19.71	157.68
7											6	42	3.44	11.83	70.98
8											19	152	2.44	5.95	113.05
9											53	471	1.44	2.07	109.71
10											82	820	.44	.19	15.58
11											46	506	.56	.31	14.26
12											34	408	1.56	2.43	82.62
13											12	156	2.56	6.55	78.60
14											5	70	3.56	12.67	63.35
15											2	30	4.56	20.79	41.58
16											2	32	5.56	30.91	30.90
17											1	17	6.56	43.03	43.03
18											1	18	7.56	57.15	57.15
19											1	19	8.56	73.27	73.27
20											1	20	9.56	91.39	91.39
21											1	21	10.56	112.40	112.40
22											1	22	11.56	134.60	134.60
23											1	23	12.56	158.80	158.80
											276	2881			1449

Magnification, 20,000 diameters.

$$\text{Average particle size} = \frac{2881}{276} \div 20,000 = 0.522 \mu$$

$$P_{AD} = \pm .6745 \sqrt{\frac{1449}{276 \times 275}} = \pm .093$$

$$P_A = \pm .005 \mu$$

Total probable error by Eq. XI, 1.37 %

$$\text{Coefficient of Uniformity, } U = \sqrt{\frac{276}{2 \times 1449}} = .309$$

employed in Fig. 2. The illustration is self-explanatory. Each stroke corresponds to a particle. The first column gives its measurement in millimetres at 20,000 diameters.

THE AVERAGE DIAMETER.

It is not always an easy question to decide which direction through the particle is its most representative "diameter." In measuring particles which approximate spheres in form, the best rule is to take only the horizontal direction. As the pigment grains will be orientated in every possible way on the screen, an average thus obtained will be, from a large number of measurements, not only the diameter of the average particle, but also the "average diameter" of this most representative particle.⁶

In the case of pigments composed of needle-shaped crystals, it is necessary to calculate the harmonic mean of the three dimensions of each particle. The negative, of course, is able to show only the length and width, and therefore the third dimension must be estimated. Fortunately most acicular crystals encountered in practice are either tetragonal or hexagonal and so the third dimension will be equal to the smaller of the two measurable ones. The average diameter will be the average of the harmonic means.

ERRORS.

The result of a series of measurements, giving an average particle size, will be of little value unless it is known just how much reliability may be placed upon it. In order to ascertain this, it is necessary to make a complete study of the various errors encountered throughout the process. These errors are given in Table I; and below are subjoined comments upon those requiring explanation.⁷

⁶ If the average particle volume is desired to be known it is necessary to base calculation on some assumption as to the shape of the particles. It is usually customary to assume that they are spherical in form. It should be noted, however, that by this method of particle measurement it is not necessary to fall into the error of using the *cubed average diameter* in place of the *average of the cubed diameters*. In order to avoid this mistake it is only necessary to replace the column $f \times \text{mm.}$ in Fig. 2, by $f \times \text{mm.}^3$. If the work is made systematic and a table of cubes is employed no insurmountable difficulties should be encountered in doing this.

⁷ It is not to be inferred from the above statement that Table I includes every existing source of error. Manifestly it would be impossible to create such a table. It is believed, however, that this section omits no source of error which it is reasonably possible to study. Consequently it must be emphasized that where the expression *total error* is used, it is "total" only insofar as it includes the errors listed above.

TABLE I.

Errors and Mistakes Encountered in the Photomicrographic Method for Determining Particle Size.

(I) Errors in Magnification.	<ol style="list-style-type: none"> 1. Calibration of stage micrometer. 2. Measurement of image of micrometer on glass focusing screen. 3. Measurement of bellow's length. 4. Determination of the stereopticon magnification (a. The ruled lines; b. image on screen). 5. Distortion of image on focusing screen.
(II) Errors in Obtaining Average Diameter of Particle Aside from Errors in Magnification.	<ol style="list-style-type: none"> 1. Errors due to the fact that the number of measurements cannot be infinitely great. 2. Errors from disregarding fractional parts of millimeters in measuring image of particle. 3. Errors arising from the fact that the largest particles do not always occur with the proper frequency on a single negative showing but 200-300 particles. 4. Errors from poor judgment in selecting representative section for photographing. 5. Errors from diffraction effects, when particles, the diameters of which are less than the resolving power of the objective are photographed. 6. Errors due to distortion of the photographic emulsion, upon drying.
(III) Negligible Errors.	<ol style="list-style-type: none"> 1. Errors in the ruling of the millimeter scale for determining bellow's length. 2. Errors in the ruling of the scale used in measuring the image of the stage micrometer. 3. Errors in the comparator.
(IV) Mistakes.	<ol style="list-style-type: none"> 1. Poor focusing. 2. Oblique illumination. 3. Insufficient and excessive illuminations. 4. Underdevelopment and overdevelopment of negatives.

(I) 1, 2, 3. The magnification of the microscope is determined in the usual manner with a calibrated stage micrometer.

Instead, however, of using but a single determination, a number of such are made at various bellow's lengths.

Taking as the bellow's length, B. L., the distance between the smallest circle of light projected by the microscope,⁸ and the ground glass surface on which the image is ultimately focused, a linear relationship will exist between B. L. and the magnification of the microscope, D_m , so that,

$$\frac{D_m}{B. L.} = K \quad (\text{constant})$$

If, then, K should be known for any particular set of lenses, the magnification is easily determined from B. L. In calibrating the stage micrometer used in this work there was a probable error of 5.0 per cent. in the 0.01 mm., and 0.5 per cent. in the 0.10 mm. division. Obviously the larger divisions were the more desirable ones to use. Note carefully, however, the remarks given under "Distortion" in regard to the use of these large divisions.

Writing for $D, \frac{I}{.1000}$, where I is the length of the image on the focusing screen of the .1000 mm. division, we have

$$K = \frac{I}{B.L. \times .1000} \dots\dots\dots (II)$$

If P is the probable error, then,

$$\left(\frac{P_K}{K}\right)^2 = \left(\frac{P_I}{I}\right)^2 + \left(\frac{P_{B.L.}}{B.L.}\right)^2 + \left(\frac{.0005}{.1000}\right)^2 \dots\dots\dots (III)$$

Assuming, for the moment, that an actual error exists in the calibration of the micrometer, then its effect will be to produce a constant error in K, and consequently can in no way influence the "smoothness" of the D.-B. L. curve.

Therefore, only the slight inaccuracies in the measurements of I and B. L. will cause points to deviate from this curve.

By repeated experiment it was found that with no more elaborate apparatus than a thin-edged rule and a small hand lens, I could be determined to within 0.1 mm.; also, with suitable precaution the bellow's length could be measured to about ± 1.0 mm.

In view of these facts it is obvious that that part of the error in the magnification due to the inaccuracies in the measurements of I and B. L. must be quite small; hence, the probable error will

⁸ The eye-point.

not be appreciably affected if each point on the D.-B. L. curve is given equal weight.

Granting this, then for n points on the curve, equation (III) may be written,

$$\left(\frac{P_K}{K}\right)^2 = \frac{1}{n} \left(\frac{P_I}{I}\right)^2 + \frac{1}{n} \left(\frac{P_{B.L.}}{B.L.}\right)^2 + \left(\frac{.0005}{.1000}\right)^2 \dots \dots \dots (IV)$$

Should n be as great as 10, then the first two terms on the right-hand side of the equation may be considered negligible for practical purposes, and the error in K becomes equal to the error in the calibration of the micrometer.

With a 2 mm. Zeiss apochromatic objective and a 6X compensating ocular, K was found to be $25.96 \pm .13$.

(1) 4. An easy method for determining the stereopticon magnification, and one used by the author, is to cut two fine parallel lines in the gelatin on a photographic plate, previously exposed to light and developed to a good density. Next measure the perpendicular distance between these lines with a comparator. By means of the stereopticon an image of the lines is now thrown on the screen and measured and the magnification, D_s , determined directly.

If R represents the distance between these rulings and the subscripts I and N refer, respectively, to image and negative, then,

$$D_s = \frac{R_I}{R_N} \dots \dots \dots (V)$$

and,
$$\left(\frac{P_{D_s}}{D_s}\right)^2 = \left(\frac{P_{R_I}}{R_I}\right)^2 + \left(\frac{P_{R_N}}{R_N}\right)^2 \dots \dots \dots (VI)$$

The distance, R_N , need be determined but once, by taking the average of a number of comparator readings. The distance, R_I , however, varies with every readjustment of the stereopticon screen and on this account it is probably more convenient to take but a reading or two and allow for a probable error of 0.5 mm. Actual experiment will indicate that this value is about correct.

If D is the total magnification on the stereopticon screen (20,000 to 25,000 diameters for the finest pigments), then,

$$D = D_m \times D_s \dots \dots \dots (VII)$$

But $D_m = K \times B.L.$

Then the total error in magnification is,

$$\left(\frac{P_D}{D}\right)^2 = \left(\frac{P_K}{K}\right)^2 + \left(\frac{P_{B.L.}}{B.L.}\right)^2 + \left(\frac{P_{D_s}}{D_s}\right)^2 \dots \dots \dots (VIII)$$

The B. L. which enters the third term in equation VIII is usually obtained from but a single measurement and has a probable error of about ± 1.0 mm. Note that this is not the same measurement of B. L. which enters into the determination of K.

In the results of the work presented in this paper the value of P_D was found to be ± 0.78 per cent. at 20,000 diameters.

For the calculation of the total error of average particle size, see Section (II), 1.

(I) 5. The direct method of determining magnification described under Section (I), is applicable only when apochromatic lenses are employed.

With a 2 mm. achromatic objective, distortion in the outer zones is so great that an accurate direct determination of magnification becomes impossible. When it is desired to work with such lenses, the following plan must be adopted: Produce a D. B. L. curve, using a low-power objective (16 mm.), together with the ocular that is to be used later on in conjunction with the 2 mm. objective. With this combination of lenses the rulings of the 0.10 mm. division will no longer fall in the outer zones of the field, and will, therefore, be practically free from distortion. Next determine the relative magnifying power of the 2 mm. with that of the 16 mm. objective. This is easily accomplished with a filar micrometer eye-piece, using some suitably mounted object, such as a fragment of a diatom, with sharp edges sufficiently close together.

The relative magnification of the high-power objective, multiplied by the value of K derived for the 16 mm. lens, will give the desired value for K.⁹

(II) 1. It is obvious that the greater the number of measurements from which the average diameter is derived, the nearer will this average be to the true value. As the number of measurements must of necessity be finite, there will always be a probable error due to this fact. This error is calculated from the equation,

$$P_{A_D} = \pm .6745 \sqrt{\frac{\sum v^2}{n(n-1)}} \dots\dots\dots (IX)$$

where P_{A_D} is the probable error of the average at magnification,

⁹ Even in the case of apochromatic objectives where distortion appears to be negligible, it is advisable to employ this method of determining magnification as a check on the direct method.

D ; v is the amount the particle differs in diameter from the average, and n is the number of particles measured.

The actual size of the average particle is,

$$A_t = \frac{A_D}{D} \dots\dots\dots (X)$$

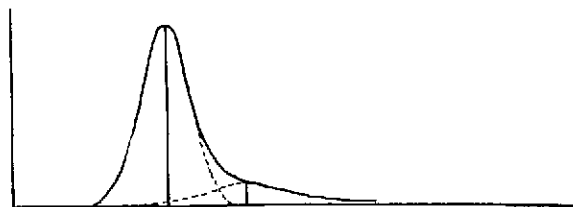
from which the total probable error, derived from the entire process of particle measurement, is obtained, thus:

$$\left(\frac{P_{A_t}}{A_t}\right)^2 = \left(\frac{P_{A_D}}{A_D}\right)^2 + \left(\frac{P_D}{D}\right)^2 \dots\dots\dots (XI)$$

The value of P_D is given by equation VIII.

(II) 3. If we have a pigment following a smooth curve law

FIG. 3.



The type of frequency distribution apparently caused by a mixture of two grades of the same pigment.

of distribution, and if it is found that in this material a particle of certain size should occur but once in a thousand times, then it ought not to appear at all on a negative containing but 200-250 particles. In actual practice such irregularities do happen and affect the average unfavorably. Therefore, in order to secure the most consistent results possible, a criterion of rejection is necessary.

There would be no difficulty in devising a suitable criterion if the curve followed the law of probability to its extremities. Unfortunately it does not always do this, and in such cases is apparently compound and derived from a mixture of different grades of the same pigment. (See Fig. 3.)

The use of any criterion of rejection, based on the mathematics of the probability curve, would therefore eliminate *entirely* the lower right-hand branch of such a curve with the result that the average obtained would be far below its most probable value.

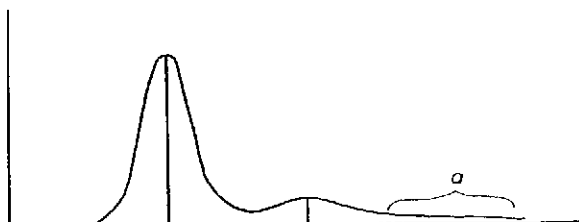
As the equation of a frequency distribution like that shown in Fig. 3 cannot be ascertained, the criterion of rejection, or more

accurately speaking a *method* of rejection, will necessarily be a somewhat arbitrary one.

METHOD OF REJECTION.

The method is to effect the extremity of the curve only. It is applicable when the pigment gives evidence of a smooth, continuous frequency distribution. When it is obvious that the material is composed of two or more grades of the same substance with widely different averages, as shown in Fig. 4, the rejection may

FIG. 4.



A frequency curve showing a mixture of ingredients with widely different average particle size. The method of rejection is applied to the portion of curve marked a.

be applied only to the right-hand branch of the curve furthest from the origin.

Take the following example of the extremity of any suitable curve:

Frequency :	12	10	8	5	2	0	2	0	1	8	1	3
Millimeters :	15	16	17	18	19	20	21	22	23	24	25	26

It will be noted that from mm. 19 to mm. 26 the curve is practically straight and approximately parallel to the millimetre axis. This section may, therefore, be "smoothed" without introducing appreciable error. Bearing in mind that in measuring the images of large particles, such as mm. 21 for instance, there is liable to be an error of ± 1 mm., then it is reasonable to believe that one of the 21's is perhaps either a 20 or a 22. A 21 should be cancelled and either a 20 or 22 inserted; it does not matter which one is selected.

Upon further examination it appears that there are probably seven 24's too many and two 26's. Eliminating these and rewriting, we have:

Frequency :	12	10	8	5	2	1	1	0	1	1	1	1
Millimeters :	15	16	17	18	19	20	21	22	23	24	25	26

There is still the vacancy at 22 to be accounted for. As 23, 24 and 25 each occur, it is more probable that there should be a 22 rather than a 26. Again rewriting, gives us the final form of the curve:

Frequency:	12	10	8	5	2	1	1	1	1	1	1
Millimeters:	15	16	17	18	19	20	21	22	23	24	25

This distribution is far more rational than the one first given, and is certainly to be preferred. Rejection need not be applied where the method of determining particle size is to be employed only for routine purposes.

(II) 5. With glass lenses and white light, particles as small as 0.30μ will appear *clear*, centred with a black outline or circumference. Those a little less than this in diameter, however, will give for their image a *solid* black dot, resembling on the negative, in appearance and size, the diffraction disks produced by particles very much smaller.

There is consequently a limit, governed by the particle size, below which the method of measurement, described in this paper, is no longer applicable. Recourse must be had then to the use of ultra-violet light and quartz lenses, if we are to measure with reasonable accuracy pigments less than 0.30μ in diameter. Fortunately, for the method, pigments finer than this are exceptionally rare.

(II) 6. F. E. Ross has shown that tanning developers, such as pyro-elon and caustic hydroquinone, cause, upon the drying of the negative, contraction of the image. If it is found necessary to use these developers it is perhaps better to make measurements on the wet negative, care being taken that the heat of the stereopticon does not harm the gelatin emulsion in any way.

WHAT IS MEANT BY "PARTICLE SIZE."

We can speak definitely of the "diameter" of a sphere. If we have, say, a pound of fine spherical shot, each shot equal in regard to volume, then if the diameter of one shot is known it can be stated that the length of this diameter is the "particle size" of the entire one pound of material.

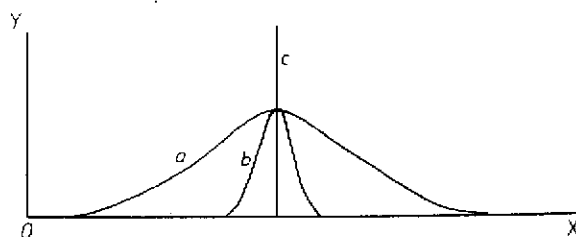
However, in the case of paint and rubber pigments we are dealing neither with spheres nor a perfectly uniform substance, hence the meaning of particle size is less definite here than in the previous illustration.

As pointed out, it is convenient to take as the "diameter"

of a particle that dimension which bears to specific surface the simple relationship shown in equation I. With this much established, let us examine further the significance of the expression "particle size."

If it is stated that the particle size of a sample of zinc oxide is 0.52μ , then it is meant that this is the diameter of the *average* particle. Such a fact may be used to determine specific surface, but aside from this it gives but a poor visualization of the texture of the material, for it neither discloses whether the oxide is composed entirely of particles 0.52μ in diameter nor whether it is a

FIG. 5.



Frequency curves for two pigments of the same average particle size but possessing different uniformities. Under the microscope, pigment *a* will appear to have a greater average diameter than *b*.

mixture ranging from ultramicroscopic particles to grains as coarse as sand and averaging 0.52μ .

This difficulty can be overcome in the following manner: *The Coefficient of Uniformity*: If we have two different pigments giving frequency distribution *a* and *b* (Fig. 5), it would be natural to decide, after a simple comparison under the microscope, that material *a* is the coarser of the two, yet upon actual measurement it will be shown that both pigments have the same average particle size. The reason for this misjudgment is due to the fact that material *a* contains some very large particle which are quite easy to see and consequently attract the eye, while the smaller ones, which it also contains, are difficult to find, and likely to be overlooked.

If this difference between *a* and *b* could be stated mathematically, then such an expression, together with the average diameter, would *completely* express the "particle size" of any given pigment. Fortunately this is quite possible to do, with a fair degree of success.

No doubt the reader has realized that this difference between *a* and *b* is simply one of degree of uniformity and that *b* is the more uniform of the two; and also that the "broader" the curve

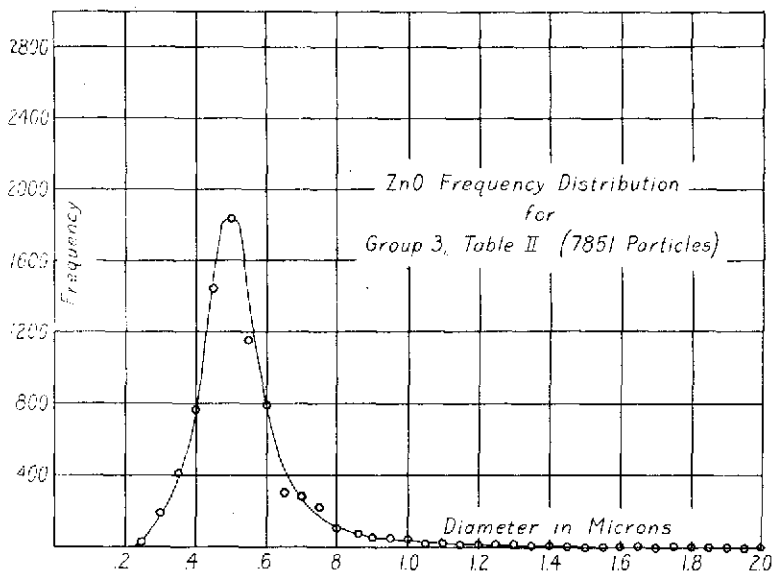
the less uniform the material. This characteristic is governed by the so-called "precision" coefficient, but here it will be referred to as the *uniformity* coefficient and designated by the letter U thus :

$$y = ce^{-U^2(x-a)^2} \dots\dots\dots (XII)$$

where c is the maximum value of y and a is the diameter of the average particle.

If all the particles of a pigment were equal in diameter, then

FIG. 6.



Frequency distribution for an average grade of zinc oxide. The measurements were taken from the 30 negatives recorded in Table II.

their frequency curve would be the straight verticle line c (Fig. 5); the uniformity would be perfect and U equal to infinity. Similarly, if no two particles were the same, U would become zero and the curve found to coincide with the x axis.

In practice, U is determined from the following equation :

$$U = \Delta x \sqrt{\frac{n}{2 \sum y^2}} \dots\dots\dots (XIII)$$

where Δx is the difference between two consecutive values on

the x axis (*i.e.*, the millimetre axis) and should be made equal to unity for convenience; n is the number of particles measured and v the difference (in millimetres) between the particle and its average (at magnification, D , for convenience).

When the curve is symmetrical, U may be used, by substituting its value in equation XII, to find the percentage of any size particle present. This will give us a better idea of the nature of the material than the simple statement of the diameter of the average particle.

As the case sometimes happens, the curve will be asymmetrical, and under such conditions it is no longer permissible to employ U for the purpose just outlined. It should then be called the "Equivalent Uniformity Coefficient" and written U_e . It still remains, however, a constant of the material, and as such is useful for control and identification purposes.

The uniformity of an asymmetrical pigment¹⁰ is equivalent to the uniformity of a symmetrical one having the same values for n and Σv^2 as those possessed by the asymmetrical material.

SOME RESULTS OF MEASUREMENTS.

The author's chief interest has been in the measurement of zinc oxide; hence in deciding upon a material to be used in testing the photomicrographic method of measurement this pigment was selected.

For routine work one negative showing approximately 250 particles¹¹ will usually give results sufficiently accurate; for a critical test, however, more negatives are required. The measurements presented below are the results of a far more extensive investigation than is ever likely to be found necessary in practice.

Five different bags of the same make of zinc oxide were sampled. Three mounts were made from each sample. Two photomicrographs were taken from each mount, giving a total in all of 30 negatives. The number of particles measured was 7851, and the time of measurement seven hours.

The measurements are given in Table II, in groups of 200-

¹⁰ One giving an asymmetrical frequency curve.

¹¹ This does not include the marginal particles which are distorted and out of focus.

TABLE II.
Results of Measurements on 30 Negatives in Groups of 200-250, 1200-1500 and 7851 Particles.

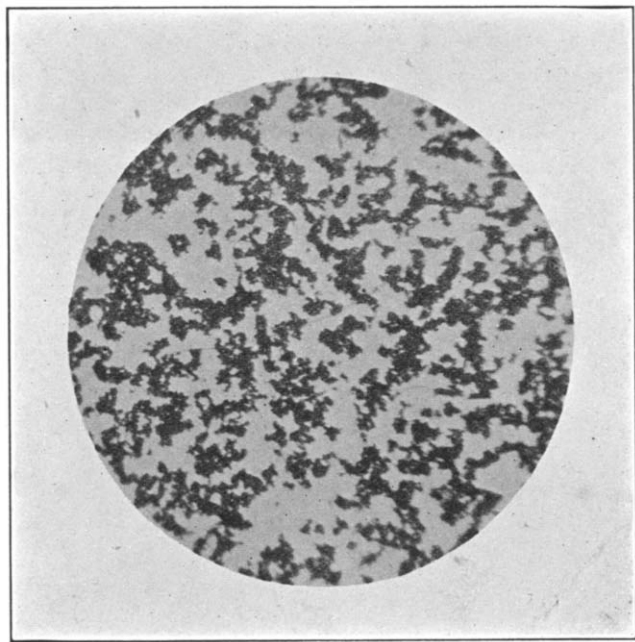
200-250 Particles			1200-1500 Particles			7851 Particles		
Av. Diam.	Prob. Error	Unif. Coef.*	Av. Diam.	Prob. Error	Unif. Coef.	Av. Diam.	Prob. Error	Unif. Coef.
<i>First Negatives.</i>			<i>1st 5 Negatives Combined in 1 Curve.</i>			<i>30 Negatives Combined in a Single Curve.</i>		
1A	±.007	.207						
2A	.010	.161	.543	±.004	.183			
3A	.007	.219						
4A	.005	.263						
5A	.005	.257				.5340	±.0013	.207
<i>Second Negatives.</i>			<i>2nd 5 Negatives Combined in 1 Curve.</i>					
1A	±.009	.163						
2A	.010	.150						
3A	.007	.226	.547	±.004	.185			
4A	.006	.232						
5A	.007	.216						
<i>First Negatives.</i>			<i>1st 5 Negatives Combined in 1 Curve.</i>					
1B	±.005	.320						
2B	.008	.168						
3B	.005	.309	.539	±.003	.223			
4B	.005	.292						
5B	.007	.238						

<i>Second Negatives.</i>		<i>2nd 5 Negatives Combined in 1 Curve.</i>	
1B .527	±.005	.287	
2B .496	.005	.339	
3B .522	.005	.296	
4B .501	.005	.273	
5B .543	.006	.291	
<i>First Negatives.</i>		<i>1st 5 Negatives Combined in 1 Curve.</i>	
1C .538	±.007	.203	
2C .531	.005	.270	
3C .532	.005	.271	
4C .556		.186	
5C .504	.4	.354	
<i>Second Negatives.</i>		<i>2nd 5 Negatives Combined in 1 Curve.</i>	
1C .520	±.006	.267	
2C .518	.004	.359	
3C .524	.007	.201	
4C .519	.006	.240	
5C .515	.005	.310	
Av. Probable Error ±1.13%		Av. Probable Error ±.56%	
Total Error, Including Error in Magnification ±1.37		Total Error, Including Error in Magnification ±.82%	

* Strictly Speaking. U_e

250, 1200-1500, and 7851 particles. The probable errors shown in the columns are due to the fact that the average diameter is derived from a finite number of particles. These errors are calculated from equation IX. The "total errors," given at the foot of the columns, include the errors in magnification and are derived from equation XI.

FIG. 7.



Timinox, 250 Diameters.

This is the type of pigment photomicrograph commonly found in the literature on paint. It is *not* suitable for particle measurement. The magnification and resolving power, under which the photomicrograph was taken, were both very much too low. It is impossible to detect individual particles. In addition the pigment is not dispersed.

Rejection, discussed under section (II)₃, was applied in each individual case. As particles which would be rejected in a small group of 250 would probably be retained in the two larger groups, the values in these latter ones were recalculated each time, that is, the average diameter, $.543\mu$, given in the second group, for instance, is not necessarily the average of the first five diameters, shown in the first group, etc.

The groups are progressive and show the increase in accuracy and reliability with increasing number of measurements.¹²

In Table III are presented the results on the measurements of a variety of the most generally used pigments in the paint and rubber industries. Lamp black and gas black are omitted, however, as it has been impossible to secure negatives of these materials that were sufficiently satisfactory for measurement.¹³

Fig. 7 is the type of photomicrograph which is worthless for particle measurements. The pigments is not only flocculated but no individual particles are shown with certainty and distinctness. The magnification also is much too low. This is the kind of photograph found in technical books on paint.

Fig. 8 shows the type of photograph which must be secured if it is desired to make measurements by the method described in this paper.

¹² If the uniformity of a material is known, then it is possible to calculate before hand just how many particles it is necessary to measure in order to reduce the probable error to any desired amount. If n is the number of measurements required and P_A the desired probable error, then,

$$n = \left(\frac{.4769 \Delta x}{U P_A} \right) \dots\dots\dots (XIV)$$

If $D = 20,000$, then $\Delta x = 1/20,000$ mm. As P_A is given in microns, Δx will be .05 μ . It must be noted that P_A is not the *total* probable error, *i.e.*, it only includes the error given in section (II) 1. All other errors are independent of n .

¹³ It may be stated as a general fact that most technologists who have to deal with fine grained materials have neither the knowledge nor the technique necessary to enable them to make a successful microscopic examination of their products; hence many guesses, far from the truth, have often been given out as to the absolute and relative sizes of pigments. The author has had samples of materials presented to him by technologists who claimed that they were substances too fine to be seen with the microscope, yet in some cases the lowest power objectives were sufficient to resolve them into individual particles. In the case of gas black we are dealing with the finest grained material met with in the paint and rubber industries and, therefore, it is doubtful if there are many technologists capable of handling a pigment of this kind. In all probability the gas black particles are not colloidal, *i.e.*, less than 0.10 μ in diameter. They are translucent and are of a brownish gray color. Their size lies most likely between 0.10 μ and 0.20 μ . This estimate does not take into consideration the very large particles of adamantite which all gas blacks contain.

TABLE III *

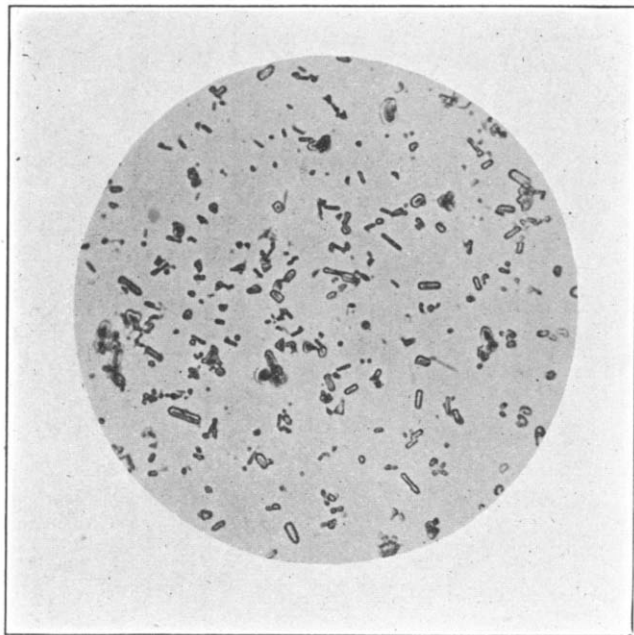
Name	Type	Sample	Negative	Diameter	U
Zinc Oxide	French Process	A		.36	
		B		.39	
		B		.40	
		C		.44	
Zinc Oxide	American Process	A		.46	
		B		.42	
		C		.46	
		D		.42	
		E		.42	
		F		.48	
		G		.46	
		H		.48	
		I	1	.46	
			2	.48	
		J	1	.40	
			2	.38	
Lithopone		A		.33	
		B		.38	
		C		.38	
		D	1	.40	
			2	.37	
			3	.40	
		E	1	.32	
			2	.36	
		F		.50	.210
Iron Oxide	Unadulterated	A		.43	.245
		B		.46	.351
		C		.54	.368
		D		.51	.230
		E		.58	.263
		F		.44	.188
Sublimed White Lead		A		.67	.132
		B		.65	.119
Basic Carbonate of Lead	Carter Process	A		1.03	.067
Basic Carbonate of Lead	Old Dutch Process	A		.75	.086
		B		1.21	
Basic Carbonate of Lead	Mathewson Process	A		1.95	.032
		B		2.39	
Barytes		A		5.33	.045

*The measurements given in this table refer to the average individual particle and do not take into consideration undispersed aggregates.

CONCLUSION.

Those who have devoted much time to the study of particle size will realize that fine-grained materials are of three types, and that each type requires a different method of attack in order to secure particle measurement.

FIG. 8.



Low Leaded Zinc Oxide, 1500 Diameters.

This photomicrograph is well suited for measurement. The crystalline outlines of a number of the particles are clearly shown.

Type A.—Colloidal particles.

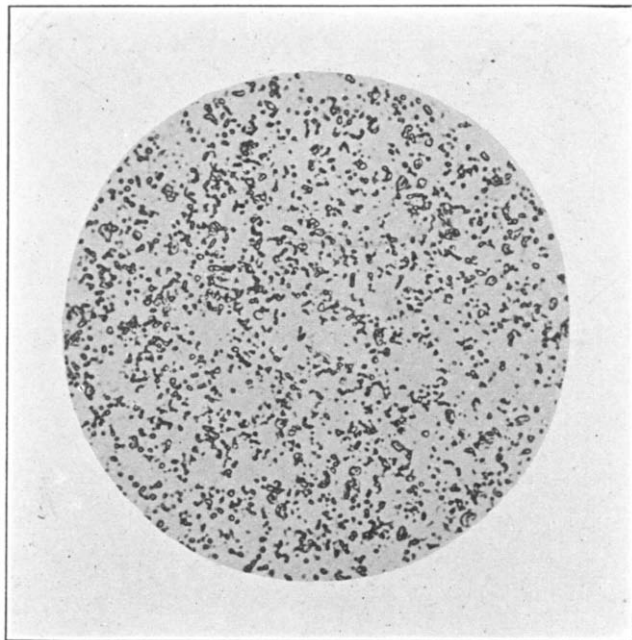
Type B.—Fumed products and fine precipitates such as zinc oxide and lithopone, etc. This type comprises the paint and rubber pigments.

Type C.—Clays and ground materials such as barytes, asbestine, etc. This type includes the so-called "inerts."

A number of methods have been developed for the measurement of colloidal particles. The photomicrographic method is not applicable to this type and therefore it will not be discussed here.

It is hardly necessary to state that the photomicrographic method has been developed expressly for the measurement of particles included under Type B. If applied to any other type it will not be found satisfactory, at least not without special treatment of the sample.

FIG. 9.



French Process Zinc Oxide, 1500 Diameters.

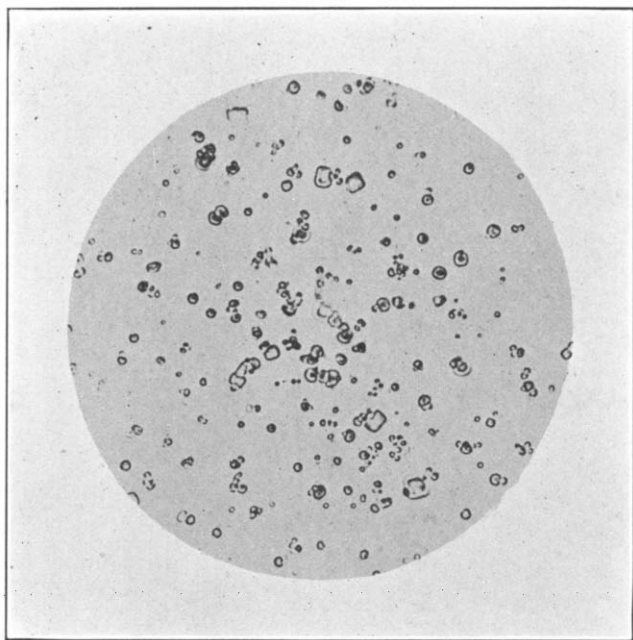
This particular sample of French Process Zinc Oxide approaches the limit of fineness to which the photomicrographic method is applicable. To go below this will require quartz lenses and ultra-violet light.

It seems to the author that the method of grain size determination by the use of a Zeiss-Thoma Counting Chamber employed by Curt Kühn¹⁴ is ideally suitable for Type C, and not for Type B, as Curt Kühn himself uses it. This method necessitates the use of an objective of long working distance giving both low resolving power and magnification. Experience will soon convince one that under such conditions a large percentage of Type B pigment will escape notice altogether and in addition it

¹⁴ *Zeitschrift für Angewandte Chemie*, March 16, 1915.

will not be possible to decide whether flocculates composed of two or three grains are single particles or not. Evidently some such state of affairs did occur for Curt Kühn gives his finest grained lithopone as 372 billion particles¹⁵ per gram, whereas for a lithopone as coarse as 0.40μ and density 4.30, there will be found to be no less than 6850 billion per gram. Similarly for

FIG. 10.



Sublimed White Lead, 1500 Diameters.

A good photomicrograph for measurement.

iron oxide, Curt Kühn gives 308 billion, while this pigment, even when as coarse as 0.50μ and with a density of 5.15, will have 2980 billion per gram. Also with lamp black; here his result is 960 billion as against 19,000 billion, assuming the lamp black particle to be as large as 0.40μ (and it is doubtful if it even attains so large a size). From these facts it does not seem advisable to recommend Curt Kühn's method for Type B pigments.

¹⁵ Particles assumed to be spherical and $U = \infty$.

TABLE IV.*

Showing Relationship of Diameter, Specific Surface, Number of Particles per Gram and Mass of Particle for Zinc Oxide.

Dia. in Microns, μ	Specific Surface in Sq. Meters	Number of Particles per gram, in Trillions	Mass of Particle in Grams
0.70	1.48	.96	1.045×10^{-12}
0.60	1.73	1.54	$.650 \times 10^{-12}$
0.50	2.08	2.64	$.379 \times 10^{-12}$
0.40	2.60	5.17	$.193 \times 10^{-12}$
0.30	3.46	12.24	$.082 \times 10^{-12}$
0.20	5.20	41.40	$.024 \times 10^{-12}$
0.10	10.38	331.20	$.003 \times 10^{-12}$

Specific Surface, surface per gram of material, (S).

Number of particles per gram = $\frac{S}{\pi \mu^2}$ trillion = n.

Mass of 1 particle = $\frac{1}{n} \times 10^{-12}$ grams.

* Particles assumed to be spherical and $U = \infty$.

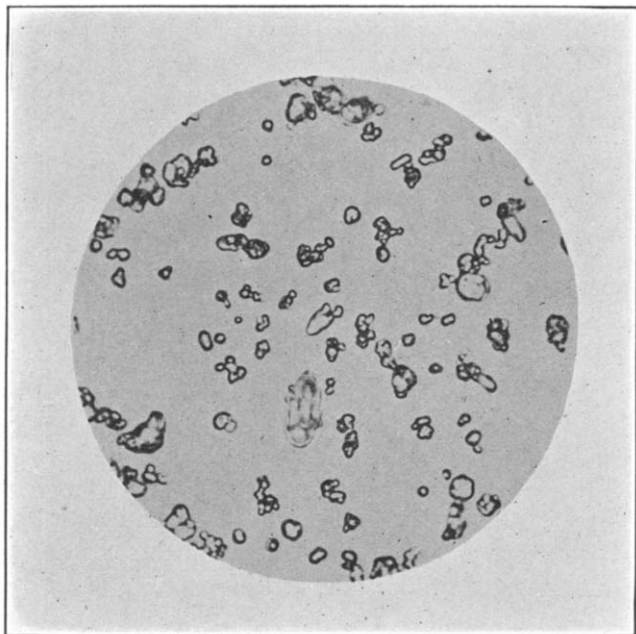
The foregoing paragraphs will probably suggest the question, that if increasing the magnification (550 diameters) employed in the Zeiss-Thoma Chamber method to that used by the photomicrographic method, reveals finer particles and distinguishes between flocculates and individual grains, how do we know that a further increase in microscopic efficiency would not again produce similar results? The answer will depend entirely on the nature of the material examined. For pigments, just on the border line of resolvability, half the particles produce so much defraction that a measurement of their size depends more on an estimate of the intensity of their image than anything else, and hence an increase of resolving becomes a necessity if we desire an accurate measurement of this pigment.

On the other hand, pigments as coarse as $.50\mu$ would probably reveal nothing further. This is apparent from the sharp declivity of the left-hand branch of the probability curve. (See Fig. 6.) In this case the number of particles not revealed on the negative is negligible. If this branch of the curve follows the probability law, then it is always possible to calculate the theoretical number of particles missing, and so further increase the range over which the photomicrographic method is applicable.

The question has often been asked, how is it possible to know,

upon examining a pigment under the microscope, whether one really sees individual particles or simply aggregates? There are a number of ways of deciding upon this. First, most pigments are crystalline, and if it is possible to see the crystal outlines, even if only a relatively few particles, it is reasonable to believe that the remaining portion of the pigment is of the same order of

FIG. 11.



Old Dutch Corroded White Lead, 1500 Diameters.

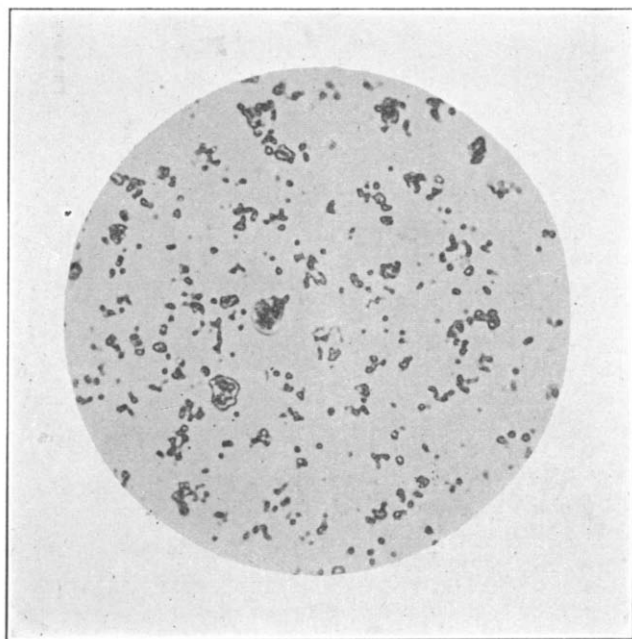
Even though this material is badly flocculated the clear outlines of most of the particles are sufficiently well shown so as to make possible a successful measurement.

magnitude and what we are able to see, therefore, must be, in general, individual particle. Secondly, an individual particle by transmitted light should and does look *clear and transparent*, except of course at its boundary, which appears black. Under transmitted light aggregates are always black, regardless of their color. (See Fig. 7.) Thirdly, individual particles in a number of pigments will show a *uniform extinction of their entire face*, when rotated between crossed nicols. Aggregates do not extinguish uniformly on account of the fact that the individ-

ual grains of which they are composed are differently orientated with respect to their optic axis.

In conclusion the author wishes to acknowledge his indebtedness to Mr. Roger Graver for his assistance in producing the many excellent negatives required for this work, and to Mr. Arthur F.

FIG. 12.



Pure Iron Oxide, 1500 Diameters.

As some of the smallest particles shown here are seen to be "clear centered," it is therefore demonstrated that the resolving power and magnification of the microscope are sufficient to show the individual grains of this pigment. On account of this fact the very smallest particles, appearing to be dark centered, are also in all probability individual particles.

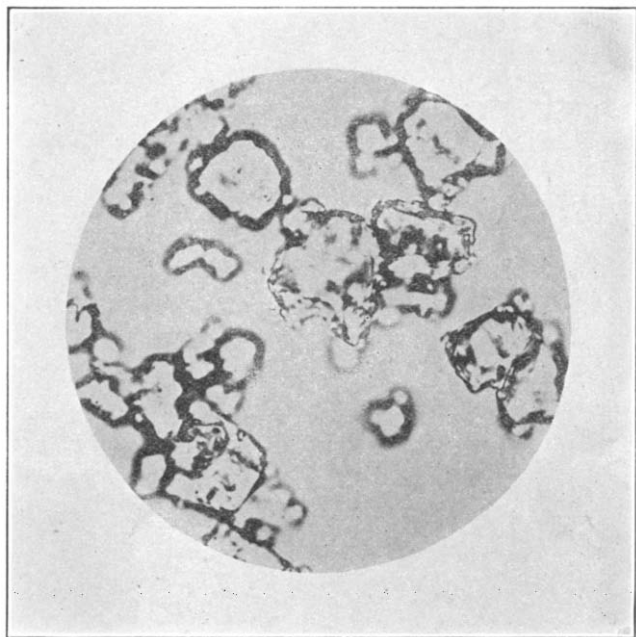
Frantz for his assistance with the innumerable computations that were demanded in the preparation of this paper.

SUMMARY.

1. A method of determining the "diameter" of paint and rubber pigments, by first taking a photomicrograph of the sample, at a carefully ascertained magnification, and secondly again enlarging by means of a stereopticon and then measuring the particles on the projecting screen, is described. It comprises:

- (a) The method of dispersing and mounting the pigment so as to make it suitable for photomicroscopy.
- (b) The method of determining the magnification of the microscope and stereopticon.
- (c) The method of measurement.

FIG. 13.



Barytes, 1500 Diameters.

On account of the low uniformity of barytes it would take about 20 times the number of particles shown here in order to make a successful particle measurement of it.

- (d) The calculation of the probable error.
 - (e) The determination of the uniformity coefficient.
2. The meaning of "particle size" is discussed. That dimension which bears the simplest relationship to specific surface has been selected as the "diameter" of the particle.
 3. The results of the measurements of various pigments are given in tables.