University of Louisville

ThinkIR: The University of Louisville's Institutional Repository

Electronic Theses and Dissertations

1940

The effect of particle size on the tinting strength of a pigment.

Gaylord Barrick 1917-1948

University of Louisville

Follow this and additional works at: <https://ir.library.louisville.edu/etd>

Part of the [Chemical Engineering Commons](#)

Recommended Citation

Barrick, Gaylord 1917-1948, "The effect of particle size on the tinting strength of a pigment." (1940).

Electronic Theses and Dissertations. Paper 1680.

<https://doi.org/10.18297/etd/1680>

This Master's Thesis is brought to you for free and open access by ThinkIR: The University of Louisville's Institutional Repository. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of ThinkIR: The University of Louisville's Institutional Repository. This title appears here courtesy of the author, who has retained all other copyrights. For more information, please contact thinkir@louisville.edu.

UNIVERSITY OF LOUISVILLE

THE EFFECT OF PARTICLE SIZE
ON THE TINTING STRENGTH OF A PIGMENT

A Thesis

Submitted to the Faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

By *Luther*
Gaylord *A...* Barriek
1940

THE EFFECT OF PARTICLE SIZE
ON THE TINTING STRENGTH OF A PIGMENT

Gaylord Barrick

Approved by Examining Committee:

Director *G. C. Williams*

R. C. Trust

H. L. Johnson

J. L. Williams

Guy Stevenson

July 30, 1940

13270

TABLE OF CONTENTS

	Page
Acknowledgment	iii
Abstract	iv
List of Figures	v
List of Tables	vi
Introduction	1
Historical	3
Theoretical	5
Experimental	12
Particle Size Determination	13
Particle Size Separation	21
Tinting Strength Determination	24
Data and Results	25
Interpretation of Results	33
Conclusions	37
Literature Cited	39
Acknowledgment	42
Vita	43

ACKNOWLEDGMENT

**The Author wishes to acknowledge the
kind assistance and helpful guidance
of Doctor G. C. Williams, who
directed this research.**

ABSTRACT

A technique is described for the separation of very fine pigment particles into very narrow size groups. The effect of particle size on the tinting strength of Molybdate Orange and Prussian Blue has been quantitatively determined.

Maximum tinting strength of each pigment was found to occur at a particle size near the wavelength of the color of the pigment.

For particle sizes greater than this optimum size the tinting strength curve was found to follow the mathematically derived equation $T.S. = I_0 \frac{C}{d} (1 - e^{-2kd})$, where I_0 is the intensity of the incident beam, C is a factor involving the indices of refraction of pigment and medium, k is a constant, and d is the diameter of the particle.

LIST OF FIGURES

	Page
Figure 1 Comparison of Mass Tene and Tinting	
Strength	10
Figure 2 Centrifuge Used in this Investigation .	16
Figure 3 Effect of Particle Size on the Tinting	
Strength of Molybdate Orange	27
Figure 4 Effect of Particle Size on the Tinting	
Strength of Prussian Blue	29
Figure 5 Particle Size Distribution of Molybdate	
Orange	31
Figure 6 Particle Size Distribution of Prussian	
Blue	32

LIST OF TABLES

	Page
Table I Tinting Strength of Molybdate Orange .	26
Table II Tinting Strength of Prussian Blue . .	28
Table III Tinting Strength of Para Red	30

INTRODUCTION

The effect of particle size on the tinting strength of a pigment is important from both the theoretical and the practical viewpoints. The paint manufacturer is especially interested in a quantitative evaluation of this factor as it enables him to utilize his pigment more economically and to produce more easily a product according to specifications. It should be borne in mind, however, that there are important factors other than particle size which determine the relative tinting strengths of two samples of the same pigment. A few of these are the relative index of refraction, oil absorption or wetting, dispersion qualities, and opacity.

The effect of particle size on the tinting strength of a pigment has been mentioned in a qualitative way by several authors. Most of them agree that tinting strength increases with subdivision of the particle but suggest that there is a point beyond which further subdivision results in a decrease in tinting strength. The exact location of this optimum particle size has, however, been in some doubt. A study of the quantitative effect of this factor was made the subject of this investigation.

HISTORICAL

Bancroft has found that 8 milligrams of lampblack will stain 10 grams of dolomite of about 40 mesh size while 654 milligrams of lampblack is necessary to stain 10 grams of dolomite of 200 mesh size or less(6). Although his experiment somewhat parallels the objectives of this research, the contrast may not be quite so great in the case of pigments since 40 mesh material may be too large to conform to statistical dispersion and reflection principles.

Joachim says that certain particle sizes produce maximum hiding power while on either side greater or less fineness produces less hiding(12).

Calbeck and Harner who were working on particle size distribution by sedimentation methods mention the fact that two samples of red lead having different size distribution curves had different tinting strengths(3). These workers found that two samples of a pigment may have equal apparent diameters and still have different size distribution curves. Thus the futility in attempting to determine the effect of particle size on the tinting strength using the microscope as a guide to particle size is pointed out.

The specific project undertaken in this research does not seem to have been studied by any previous investigators although the subject has been considered by several men working along related lines.

THEORETICAL

The relationship between particle size and tinting strength of a pigment may be attacked from a strictly theoretical angle if certain simplifications are imposed. The fundamental assumption in the development of this particle size-tinting strength relationship is that tinting strength is proportional to the total amount of light absorbed by a unit volume of the pigment. It is evident, therefore, that tinting strength will be affected by the number of particles per unit volume of pigment and the amount of light absorbed by each particle. The problem was, therefore, reduced to finding a way of expressing these two factors in terms of the dimensions of the particle. It was further assumed that as subdivision of the particle took place the reduced particles were laid side by side on a plane surface. This was assumed in order to prevent an increase in the number of reflecting surfaces. If the number of interfaces were increased, the effect would be complicated by involving the hiding power.

Let a unit volume of a pigment in the form of a cube be divided into 'n' equal cubes which are to be uniform throughout and are laid side by side on a plane mirror surface. The length of each edge of each reduced cube is $n^{-1/3}$ while the cross sectional area of each is $n^{-2/3}$. There are now, however, n equal cubes so that the total cross sectional area is $n^{1/3}$. A comparison of this cross sectional area with the dimensions of the reduced particles indicates that the cross

sectional area of a unit volume of reduced particles varies inversely with the dimensions of the reduced particle, i. e., area equals $1/d$. Also $n^{1/3}$ equals $1/d$.

Next, consider the absorption of light in its passage through a thickness 'd' of the pigment. According to the Lambert absorption law for uniformly absorbing materials I/I_0 equals e^{-kl} where I and I_0 are the respective intensities of the transmitted and incident beams, k is a constant for the material and l is the length of the path(s). Since the light must pass through the particle twice in order to be returned by reflection from the mirror surface below, the intensity of the returning beam must equal $I_0 e^{-2kd}$. Since the incident light minus the returned light equals the absorbed light, the absorbed light is given by $I_{abs.} = I_0 (1 - e^{-2kd})$. The amount of light absorbed per particle is given by $I_{abs.} = I_0 n^{4/3} (1 - e^{-2kd})$. Since there are n particles in the resolved unit volume the amount of light absorbed by that unit volume will be given by $I_{abs.} = I_0 n^{1/3} (1 - e^{-2kd})$. It has been shown, however, that $n^{1/3}$ equals $1/d$ so that the total light absorbed per unit volume of pigment or in other words the tinting strength can be expressed as

$$T.S. = \frac{I_0 C}{d} (1 - e^{-2kd})$$

The factor C has been introduced in order to provide for the effect of the indices of refraction of the pigment and the surrounding medium. This factor is of the form $1 - \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$

where n_2 and n_1 are the indices of refraction of the pigment and surrounding medium respectively. The constant k expresses the opacity of the pigment and is given by $k = \frac{1}{d} \ln \frac{I_0}{I}$ which is another form of Lambert's absorption law. The constant is expressed as a reciprocal length. The numerical value of k increases as the opacity of the pigment increases. Referring to the T. S. expression above, it is apparent that the value of the factor $(1 - e^{-2kd})$ approaches unity and the factor $\frac{I_0 C}{d}$ becomes more and more important as k increases with an increase in opacity. This indicates that particle size has a much greater effect on the tinting strength of an opaque pigment than on that of a relatively transparent one. Further examination of this relationship shows that the maximum value of the tinting strength should occur at zero particle size. This requires that the eye be able to detect light waves of near zero wavelength. However, this is impossible and the maximum must be looked for at a particle size somewhere above a diameter equal to the minimum wavelength of visible light. It is well known that particles equal to or less than the wavelength of the light falling on them tend to scatter that light rather than to reflect or absorb it (2,5). Tinting strength for this reason should be expected to decrease as the particle size is reduced below the wavelength of the light falling on the particle. Furthermore, tinting strength of a blue pigment should be expected to attain a maximum value at

a particle size less than that size for which the tinting strength of a red pigment is a maximum. A normally red pigment may appear orange and finally a light yellow as the particle size is reduced below the wavelength of red light since the particle may still be large enough to reflect orange or yellow light.

The tinting strength expression for the region where the particle size is between the wavelength of the color of the pigment and the lower limit of visible light is difficult to predict. It is highly probable, however, that the tinting strength of a color becomes zero at the lower limit of visible light. The tinting strength as a white may persist long after this point is passed, however. It is well known that certain normally colored substances such as colored glasses or cement clinker become white when finely pulverized (2,5)

Perhaps it should be pointed out that depth of tone of a color is a poor guide to tinting strength. The mass tone of a color may be expressed in a form similar to that for the tinting strength or $M. T. = I_0 C(1 - e^{-2kd})$. This indicates that mass tone increases with particle size. Consider two portions of the same pigment having different particle sizes. The portion having the larger particle size will appear darker by the ratio $\frac{(1 - e^{-2kd_1})}{(1 - e^{-2kd_2})}$ where d_1 and d_2 are respectively the larger and smaller particle sizes. The ratio of the tinting strengths is, however, this ratio multiplied by $\frac{d_2}{d_1}$.

For large values of k the former ratio rarely reaches a value of two or three while the latter may reach values as low as an eighth or a tenth. It is thus shown that a certain group of pigment particles may have a mass tone twice that of another group and yet have a tinting strength only one fifth as great. Perhaps this can better be illustrated by the accompanying curves. Consider particle sizes at A and B. Point x on curve I gives the mass tone at A while y gives that at B. The values of the tinting strength are found on curve II. It is noted that the ratio of tinting strengths is much greater than that for mass tone and that the ratio is inverted.

Fig. 1 Comparison of Mass Tone and Tinting Strength

Examination of the tinting strength expression shows that the amount of light absorbed and therefore the tinting strength varies directly with the intensity of the incident beam. However, the tint of a mixture of a white and a color will appear nearly the same for all intensities since the tinting strength of the white will also vary with the intensity. It should be pointed out that tinting strength as here derived has the dimensions of amount of light absorbed per unit volume while the orthodox tinting strength is a dimensionless ratio. The usual method of comparison of tinting strengths may be expressed as:

$$T.S. = \frac{C_1 d_2 (1 - e^{-2kd_1})}{C_2 d_1 (1 - e^{-2kd_2})}$$

If the standard and the subject color are of the same composition this may be reduced to:

$$T.S. = \frac{D}{d_1} (1 - e^{-2kd})$$

If k is very large D will be very nearly equal to d_2 or the statistical particle size of the standard. This principle will be further illustrated in a later section.

EXPERIMENTAL

Briefly, the method of attack on the problem was a separation of the pigment particles into narrow size groups and the determination of the tinting strength of each group using the untreated original mixture as a standard. Thus physical and chemical homogeneity and uniform particle size within each group were assured.

PARTICLE SIZE DETERMINATION

Several means of particle size determination were available (1,3,9,10,13,14). Many of these methods do not furnish an ultimate means of separating the particles but they do result in the distribution of the various sizes within a given sample of a pigment. As one of the ultimate problems in this research was to be the separation of the particles into narrow size groups, it was desirable to use a method of particle size determination which could also be used as a method of size separation. After examination of the available methods it was decided that a system of fractional sedimentation in a centrifuge could be worked out to serve this double purpose.

Before arrangements were made for equipment to be used, it was necessary to determine the most practical kind of a dispersion for the purposes of this investigation. It was realized that the work could be somewhat expedited if an aqueous dispersion could be used, for the orthodox oil dispersion results many times in discolored material from which

the oil is difficult to remove when it is necessary to determine the weight of a separated pigment. Furthermore, oil viscosities are comparatively high and somewhat variable. It was also found that glycerine could be added to an aqueous dispersion to vary the viscosity and make the operation of the centrifuge more flexible in the particle sizes which could be separated. A prerequisite of an aqueous dispersion was the finding of a wetting agent, since water alone will not wet and disperse the common pigments. It was found that a .25% solution of Aerosol in water was quite suitable as a dispersive medium. This seemed to be the minimum concentration as less concentrated solutions had very little dispersive power on the pigments studied. The mechanism of this dispersive action was not fully investigated but it was considered as due to a lowering of the interfacial tension since agitation produced profuse foaming. Some work has already been done on the subject of aqueous dispersion of pigments but it is not conclusive(4). Such properties as density, viscosity, and pH of the suspension were investigated and found to differ very little from those of plain water.

The use of a centrifuge was found necessary because the speed of gravitational sedimentation was found to be less than agitation due to thermal currents. Therefore, a simple centrifuge was designed and constructed. This machine consisted of a one-quarter inch circular steel plate about eleven

inches in diameter mounted in a horizontal plane on the mandrel of a grinder head which was in turn mounted in rubber against the vertical bracket of the main base. A one-quarter horsepower electric motor with a four step pulley was provided to drive the machine. The plate was provided with six radial compartments each capable of holding a 1.5 x 6.5 centimeter glass vial. These compartments consisted of slots cut in the plate with copper strips along the bottom and spring brass clips on top to hold each vial securely in a horizontal position. Rubber pads in the outer end of the compartments served as cushions for the vials. Speeds of from 1250 to 3000 r.p.m. were obtainable in four steps. This machine is shown in Fig. 2.

The centrifuge used in this work limited the size range to be studied to sizes from about one and one-half micron to about one-quarter micron. This size range was determined by the length of time which the material could be left in the centrifuge. It was desired that no run should last more than thirty minutes nor less than two minutes. The lower limit of a quarter micron could be attained with a speed of 3000 r.p.m. and a period of thirty minutes while the upper limit could be attained at a speed of 1250 r.p.m. and a period of two minutes in the centrifuge. The speed was changed, whenever convenient, to provide a period of about five minutes. The upper size limit was raised in some cases by increasing the

Fig. 2

Centrifuge Used in this Investigation

viscosity of the medium with glycerine.

Calculation of particle size was based on Stoke's law. This law was modified to fit the conditions of the centrifuge. The modification is shown in the following steps:

$$v = \frac{s d^2 \Delta D}{18 \eta} \quad \text{Stoke's law}$$

$$v = \frac{s}{t} = \frac{(F_2 - F_1)}{t}$$

$$a = \frac{w^2 (F_2 - F_1)}{\ln \frac{F_2}{F_1}} \quad \text{Angular acceleration}$$

$$d = \frac{6}{\pi N} \sqrt{\frac{s}{2t \Delta D} \ln \frac{F_2}{F_1}}$$

d - diameter of particle in centimeters

r_2 - outer radius of dispersion in centimeters

r_1 - inner radius of dispersion in centimeters

η - viscosity of suspending medium in poises

t - time of centrifuging in seconds

N - speed of centrifuge in r.p.s.

ΔD - difference in density of pigment and suspending medium

w - angular velocity in radians per second

v - velocity in centimeters per second

s - distance traveled in centimeters

This expression gives the maximum size of particles

left in suspension after the dispersion has been left in the centrifuge for a period of t seconds. A distribution curve can be drawn by determining the weight per cent of precipitated material at intervals of time and plotting against the corresponding diameter. It should be pointed out that this procedure does not result in a true distribution curve since the weight at any diameter will contain all material above that diameter and some material below the diameter. The curve, however, gives a means of comparing dispersions and serves as a guide to the true distribution curve. The method of Calbeck and Harner using a time-weight plot results in a true distribution curve(3). This method requires a large scale plot of the data and the construction of several tangents to this curve extending to the weight per cent axis. The differences in weight per cents intercepted by adjacent tangents are plotted against averages of the two sizes at which the adjacent tangents are drawn. This procedure has a valid theoretical background and should be resorted to where it is necessary to know the actual distribution. This particular section of the research was concerned mainly with the effects of the various treatments encountered on the particle size so that it was not deemed necessary to determine the actual distribution.

Before confidence could be placed in the results of the entire experimental procedure it was necessary to determine whether or not the particle size of the separated material

changed at any point from the beginning of the separation of the particles to the determination of the tinting strength. The effect of wetting with an intermediate drying and the effect of precipitation in the centrifuge were determined by dividing a pigment dispersion into three equal parts, subjecting a part to each of the two treatments and then comparing the approximate distribution curves of each with that of the untreated material.

Five per cent dispersions of Molybdate Orange and Prussian Blue were made up by slowly adding warm Aerosol solution to the proper amount of dry pigment in a steel bottom mixing can and stirring with a heavy glass rod. When the proper amount of solution had been added, the suspension was transferred to a closed can and put on a tumbling mill.

Three hundred milliliters of each dispersion was made up and divided into three equal parts. Each of the 1.5 x 6 centimeter glass vials were filled to a depth of 4.5 cm., were stoppered, and were put into the centrifuge. The centrifuge was operated for a period of one minute at a speed of 1715 r.p.m. after which period one vial was removed and was replaced by a tare. The suspension remaining above the precipitated pigment was removed by means of a siphon tube taking care to keep the tip of the tube just under the surface of the liquid as the suspension was removed so as to not disturb the precipitated pigment at the bottom of the tube. A second

tube was removed after an elapsed time of two minutes, a third at four, a fourth at nine, a fifth at sixteen, and the sixth at twenty five minutes. The procedure of separation of the two phases was repeated for each vial. The tubes and the pigment contained in each were dried in the oven and weighed. The difference in this weight and the weight of the empty tube gave the amount of pigment precipitated in the interval of time that particular tube was in the centrifuge. The second of the three portions of the suspension was dried and then redispersed using warm Aerosol building up again to a five per cent suspension. This portion was treated in the same manner as the one just described. The third portion was treated in the same manner as the first except that the liquid above the precipitated material was discarded while the solid was redispersed and brought down a second time in the centrifuge. Particle sizes corresponding to the length of time each vial was in the centrifuge were calculated and plotted against the per cent precipitated in that interval of time. This section of the work was done by Jenne who also did some work on pH values of the dispersions under treatment at various stages. His work shows that the treatments encountered have very little effect on the particle size since the curves obtained by the above procedure are parallel and coincident within experimental error. The distribution curves for the two pigments studied are included. These are composites of those obtained by Jenne(11)

PARTICLE SIZE SEPARATION

The procedure for particle size separation was somewhat longer than that of the size distribution determination. The theory of the separation procedure may be illustrated by the following case. Suppose one has a mixture containing equal parts of five, four, three, and two micron particles and wishes to produce a cut containing 90% four micron material. Four grams of the mixture is dispersed and put into the centrifuge for a time sufficient to bring down all five micron particles. Since the sedimentation rate is proportional to the square of the diameter of the particle, the suspension above the precipitated material will contain:

0	gms.	5 micron material
9/25	"	4 " "
16/25	"	3 " "
21/25	"	2 " "

This suspension is removed and placed in the centrifuge for a time sufficient to bring down the four micron material.

This time the precipitate contains:

9/25	gms.	4 micron material
9/16x16/25	"	3 " "
1/4x21/25	"	2 " "

This sedimented material is separated from the suspension and is redispersed. The new dispersion is then placed in the centrifuge for a time sufficient to bring down

all four micron material. The sediment this time contains:

$$\begin{array}{rcll} & 9/25 & \text{gms.} & 4 \text{ micron material} \\ (9/16)^2 & \times 16/25 & " & 3 " " \\ (1/4)^2 & \times 21/25 & " & 2 " " \end{array}$$

It can thus be seen that the amount of four micron material remains constant while the amount of smaller material is decreased quite rapidly with the number of times the procedure is repeated. The number of times the procedure must be repeated may be calculated. The 10% impurity in this case may be assumed to be composed of three micron material. Since there will be 9/25 gram of four micron material remaining, it is obvious that the three micron material must be reduced to 1/25 gram. The amount of three micron material remaining after the procedure has been repeated n times is given by $(9/16)^n \times 16/25$ grams. Setting this expression equal to 1/25 gram it is found that the procedure must be repeated five times. The analysis of the sedimented material will show after five treatments:

$$\begin{array}{rcll} .5625 & \text{gms.} & 4 \text{ micron material} \\ .0360 & " & 3 " " \\ .0008 & " & 2 " " \end{array}$$

Repeating the procedure just one more time will reduce the three micron material to about 3.5% and completely eliminate the two micron material.

In actual practice, however, the procedure is complicated by the fact that in most pigments there is a continuous size variation instead of the simple groups as used in the explanation of the separation theory. One must, therefore, start the separation at a size several per cent above that of the desired finished value. Close scrutiny of the foregoing analyses shows that the amount of the material of the size at which the cut is started will be zero in the final product. The amounts of the sizes between this largest and the desired size will, however, increase as one minus the square of the ratios of the individual diameters to that diameter at which the cut was started. This applies only to those particles larger than the desired diameter and can not be eliminated. Those particles less than the desired size can be eliminated to any extent as has been shown. Another practical modification of this procedure was the elimination of the calculation of the number of times the procedure of precipitation and redispersion must be repeated to give the desired purity. The procedure was repeated until the liquid above the separated material became clear indicating that no smaller material was present.

An attempt was made to separate the particles and to determine the effect of particle size on the tinting strength of Para Red in addition to the two pigments already mentioned but excessive bleeding made the results largely unreliable.

DETERMINATION OF TINTING STRENGTH

Tinting strengths were determined by a comparison of the amount of the separated material of a uniform and known particle size which produced a tint identical with that produced by a standard color when each was let down with white paste. The original pigment was used as a standard. The separated pigment and white were weighed onto one of two glass plates tared to within one-tenth milligram while the standard color was weighed onto the other. The bleaching white was then added from a known amount to the standard color until the two tints were matched. The standard color had previously been ground in refined linseed oil while the separated material was rubbed out in linseed oil after it had been weighed onto the plate. The white used was a prepared paste sold for this specific purpose.

Tinting strengths of the separated material were then calculated by the expression:

$$T.S. = \frac{\text{weight standard} \times \text{wt. white to sep. mat.}}{\text{weight sep. mat.} \times \text{wt. white to standard}} \times 100$$

This procedure is a slight variation of the usual method to allow for the comparisons of very small amounts of the pigments.

DATA AND RESULTS

TABLE 1

TINTING STRENGTH OF MOLYBDATE ORANGE PIGMENT

Size Microns	Centrifuge Speed	Time Min.	Separated Color gms.	Bleaching White gms.	Standard Color gms.	Bleaching White gms.	Tinting Strength
.27	2610	4.75	.0040	.2000	.0400	3.1895	63
.35	2610	2.83	.0220	.5000	.0440	1.3580	74
.50	1715	3.30	.0220	.5000	.0440	.6620	151
.64	1715	2.00	.0220	.5000	.0440	.7741	130
.75	1715	1.50	.0200	.5000	.0400	1.0280	97
1.00	2610*	2.95	.0115	.3000	.0460	1.4010	85
1.25	2610*	1.90	.0135	.3000	.0270	.7230	85

Density of Pigment 6.12
 Density of Medium 1.00
 r₂ 12.50 cm.
 r₁ 8.00 "
 η 01 poise

*Viscosity adjusted to .0814 poise with glycerine (55% solution)
 Density of Medium 1.142

Fig. 3 EFFECT OF PARTICLE SIZE ON TINTING STRENGTH OF MOLYBDATE ORANGE

TABLE 2

TINTING STRENGTH OF PRUSSIAN BLUE PIGMENT

Size Microns	Centrifuge Speed	Time Min.	Separated Color gms.	Bleaching White gms.	Standard Color gms.	Bleaching White gms.	Tinting Strength
.200	3000	41.0	.0040	.4000	.0100	1.2140	82
.275	3000	22.0	.0044	.4000	.1800	17.1650	96
.385	3000	11.2	.0060	.4000	.0250	2.3600	71
.55	3000	5.5	.0025	.2000	.0100	1.6360	49
.75	2610	3.9	.0045	.3000	.0250	4.3660	38
1.00	2610	2.2	.0025	.2000	.0100	3.4850	23

Density of Pigment 1.83
 Density of Medium 1.00
 r_2 12.50 cm.
 r_1 8.00 "
 z 01 poise

Fig. 4 EFFECT OF PARTICLE SIZE ON TINTING STRENGTH OF PRUSSIAN BLUE

TABLE 3

TINTING STRENGTH OF PARA RED PIGMENT

Size Microns	Centrifuge Speed	Time Min.	Separated Color gms.	Bleaching White gms.	Standard Color gms.	Bleaching White gms.	Tinting Strength
.25	3000	44.0					
.35	3000	22.5	.0014	.1000	.0880	.5200	121
.50	3000	11.0	.0025	.2000	.0880	.5640	124
.75	3000	4.9					
1.00	3000	2.75	.0095	.3400	.0220	.6390	123

Density of Pigment 1.49
 Density of Medium 1.00
 r_2 12.50 cm.
 r_1 8.00 "
 η 01 poise

Fig. 5 PARTICLE SIZE DISTRIBUTION OF MOLYBDATE ORANGE

Fig. 6 PARTICLE SIZE DISTRIBUTION OF PRUSSIAN BLUE

INTERPRETATION OF RESULTS

The experimental work shows that particle size has a marked effect on the tinting strength of a pigment.

The tinting strength curve for Molybdate Orange shows that the maximum tinting strength of this pigment occurs at a particle size of about .53 micron. The tinting strength in that portion between this size and zero particle size does not decrease quite as rapidly as was expected. This may have been due to the presence of larger material in those groups supposed to contain only .35 and .27 micron material. It was estimated that the presence of only ten per cent of .50 micron material in that group supposed to contain .35 micron particles would increase the tinting strength of that group by about ten per cent.

The portion of the tinting strength curve for sizes greater than that at which the maximum occurred followed very closely the expression $T.S. = \frac{D}{d}(1 - e^{-2kd})$. It was pointed out in a previous section that the statistical diameter D of the standard could be obtained from this relation and thus the absolute tinting strength could be determined. Substitution of values from the curve into the approximate expression $T.S. = \frac{D}{d}$ gives a value of about .85 for the statistical particle size of the standard. The absolute tinting strength of the standard can now be expressed as $T.S. = \frac{I_0 C}{.85}(1 - e^{-1.7k})$.

It should be pointed out that the size separation technique does not require a size distribution curve although

the distribution was used in the discussion of the theory. It was pointed out that the practical modification of the procedure eliminated the need of calculation of purity and with it the need of the distribution curve was eliminated. In fact the author did not determine this curve for either Prussian Blue or Para Red although his associate did determine the curve for the sample of Prussian Blue used.

During the work on the Molybdate Orange separation it was noted that the suspension remaining above the separated material was quite yellowish in the case of the .35 and .27 micron groups. Suspected causes of this discoloration were the affect of some pH change on the chromate or the possibility that the color was shifting toward the yellow due to particle size alone. PH values were checked at several stages in the separation, for various concentrations of the color, and other conditions as were encountered. These measurements showed no change which would account for the color shift. The second possibility was given added strength when it was found that only those sizes less than the wavelength of red light exhibited this phenomenon.

The work on Prussian Blue was interesting since it confirmed the idea that the tinting strength of a pigment reaches a maximum at a particle size near the wavelength of the color of the pigment. The value of D was found from the curve to be about .28 microns. This indicates that the

sample of Prussian Blue used as a standard had an absolute tinting strength roughly three times that of the Molybdate Orange because of a difference in particle size alone. The effects of refractive indices would alter the numerical value of this comparison somewhat, however.

It was pointed out in a previous section that the work on Para Red was hindered by the excessive bleeding of the pigment. The ordinary Para Red is a mixture of isomers many of which are more soluble than the main constituent although it is itself soluble to a considerable extent. It may be said, therefore, that Para Red is more of the nature of a dye than a pigment. Since the tint of a mixture of a dye and a white paste depends only on the concentration of the dye, it might have been expected that the tinting strength of all groups of this material would be the same. During the separation of this material it was noted that the liquid above the sediment never became clear indicating that continuous solution was taking place. The difficulty in trying to separate a soluble material into narrow size groups is evident since particle sizes change throughout the operation. It is possible that an oil technique where the solubility of the pigment is less may yield more satisfactory results.

CONCLUSIONS

Results of the foregoing investigation lead to the following conclusions:

1. A suitable technique for particle size separation has been developed.
2. A logical theory of the effect of particle size on the tinting strength of a pigment has been advanced and supported by the results.
3. The tinting strength of Nolybdate Orange has been found to reach a maximum at about .53 micron particle size.
4. The tinting strength of Prussian Blue reached a maximum at a particle size of about .30 micron.
5. Para Red was unsuitable as a subject in this investigation because its physical properties are not in line with the technique used.

The main conclusion to be drawn is that the tinting strength of a pigment occurs at a particle size near the wavelength of the color of the pigment and that the shape of the curve is in line with that predicted by mathematical analysis.

LITERATURE CITED

- (1) Austin, J. B., Ind. Eng. Chem., Vol. 11, 334 (1939)
- (2) Bancroft, W. D., "Applied Colloid Chemistry", McGraw-Hill Publishing Company, New York, N. Y. p. 248 (1932)
- (3) Calbeck, J. H., and Harner, H. R., Ind. Eng. Chem., Vol. 19, p. 58 (1927)
- (4) Daniel, L. C., India Rubber World, Vol. 101, pp. 50-2 (1939)
- (5) Edser, Edwin, "Light for Students", MacMillan and Co., London, p. 375 (1911)
- (6) Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, and Lacquers", Fifth Ed., Inst. of Paint and Varnish Research, Wash. D. C., p. 48 (1932)
- (7) *ibid.*, pp. 107-135
- (8) Getman, F. H. and Daniels, F., "Outlines of Theoretical Chemistry", John Wiley and Sons, London, p. 93 (1937)
- (9) Hauser, E. A. and Lynn, J. E., Ind. Eng. Chem., No. 5, p. 659 May (1940)
- (10) Hauser, E. A. and Reed, C. E., J. Phys. Chem., Vol. 40, p. 1169 (1936)
- (11) Jenne, L. C., Unpublished Work, University of Louisville, (1940)
- (12) Joachim, Benjamin, "Applied Paint and Varnish Chemistry", American Paint Journal Co., St. Louis, Mo., p. 42 (1934)

- (13) Norton, F. H. and Spiel, S., J. Am. Ceramic Soc., Vol. 1, p. 367 (1938)
- (14) Oden, S., in Jerome Alexander's "Colloid Chemistry", Vol. 1, p. 861 (1926)

ACKNOWLEDGMENTS

The author wishes to thank the Louisville Oil, Paint, and Varnish Production Club for the fellowship grant which made this investigation possible.

He also wishes to thank Mr. Henry L. Beakes for his kind interest and helpful suggestions.

Gaylord Barrick

Gaylord Barrick, son of Bert and Elizabeth Barrick, was born at Brazil, Indiana, on February 11, 1917.

He attended Bee Ridge common school and was graduated from Brazil High School where he became a member of the National Honor Society in 1935.

In September of 1935 he entered Rose Polytechnic Institute. While there he became a member of the Student Branch of A. I. Ch. E. and was elected to Tau Beta Pi in 1939. He was the author of "Heats of Combustion and Formation of Organic Compounds" published in the Rose Technic in November of 1938. His undergraduate thesis was "Heats of Combustion of Some Chlorine, Sulphur, and Metallic Function Organic Compounds". He was graduated with honors from Rose Polytechnic Institute with the degree of Bachelor of Science in Chemical Engineering in June, 1939.

In September, 1939, he was awarded the Louisville Oil, Paint, and Varnish Production Club Fellowship for graduate study in paint technology at the University of Louisville for the year 1939-1940. His graduate thesis was "The Effect of Particle Size on the Tinting Strength of a Pigment". He was graduated in August, 1940, with the degree of Master of Chemical Engineering from the University of Louisville. He will continue graduate work in Chemical Engineering at Purdue University.