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E. I. du Pont de Nemours & Company

F & F, Research & Development Division

Experimental Station Laboratory

Memorandum Report

DISPERSION QUALITY TEST FOR PRODUCTION CONTROL

Particle Size Index

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Prepared by A. B. J. Rodrigues (mcc)
A. B. J. Rodrigues

Approved by Frank N. Jones
F. N. Jones

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INTRODUCTION

Tinting Strength, the currently accepted standard of mill-base quality, is a measure of the color intensity to be expected from a given mill base. It is a function of pigment particle size and of pigment loading in the mill base but doesn't provide a direct measure of either quantity. It could be an effective production control test but being lengthy and tedious is not often used. Also, its accuracy is dependent on the availability of a uniform standard white or black tinting lacquer and on precisely weighed quantities.

The dry film Particle Size Index (P.I.) test (Ref. 1, 2) is rapid and simple to perform and can accurately predict Tinting Strength of mill bases prepared to formula card specifications. However, it measures particle size alone, neglecting pigment loading. This severely limits its applicability as a control test in production. This report studies an extension to the dry P.I. test to include pigment concentration in the measurement.

OBJECTIVES

The commercial objective is to control mill base production by prediction of tinting strength via particle size index.

The immediate technical objective is to modify the dry film Particle Size Index test to measure both particle size and pigment loading in mill bases so that it may be used for production control.

SUMMARY AND CONCLUSIONS

A wet test was developed to supplement the dry film Particle Size Index test (Ref. 1, 2) so that P.I. could correlate with Tinting Strength of a mill base even when pigment concentration is unknown due to inaccurate loading of ingredients into the premix tank.

The P.I. test is superior to Tinting Strength measurement as a control tool because:

- It is not dependent on uniform properties of test materials. (Can-to-can variations of the "standard" white tinting lacquer used in the Tinting Strength test may cause deviations greater than 3 units.)
- It does not require elaborate materials.
- It is less susceptible to "operator errors."
- It is more reproducible.
- It is easy to run and quick.

Implementation of the P.I. test would require an initial investment in spectrophotometric equipment and generation of calibrative graphs for each mill base.

P.I. has the potential for on-line prediction of Tinting Strength.

ACTION TAKEN OR PROPOSED

This project has demonstrated that the dry film P.I. test can predict Tinting Strength of a mill base. However, implementation of this simple test would require strict control of premix tank loading.

Use of an additional optical density measurement on the liquid dispersion would allow prediction of Tinting Strength of all transparent pigment mill bases. This test should be given serious consideration as a production control tool.

Elimination of the dry film test completely while taking optical density measurements on the liquid dispersion at two wavelengths (maximum and minimum light absorption) has potential as an extremely effective on-line control test. Further investigation of this would be necessary.

This project has been terminated.

PATENT STATUS

No patent action has been taken.

PUBLICATION STATUS

Publication of these results may be considered if the test is not used by Production.

ACKNOWLEDGMENTS

Helpful discussions were held with I. C. Chu, W. P. Dolan, A. R. Hanke and M. H. Schaffer. Technical assistance was provided by J. W. Harriz and R. A. Lambert.

DISCUSSION

I. Theory

A. Particle Size Index

The Mie Theory predicts the scattering effect of spheres of a size commensurate with the wavelength of light incident on them. Combining this theory with Lambert's Law it can be shown (Ref. 3) that optical density is given by:

$$O.D. = \ln I_o/I = c \times k$$

where I_o = intensity of incident light

I = intensity of transmitted light

c = particle concentration

k = extinction coefficient = d x f (λ, particle size)

d = path length of light through the dispersion of particles (pigment)

λ = wavelength of incident light

k is also a function of the pigment refractive index, but this is a constant for a given pigment.

The dry P.I. test consists of measuring optical densities at two different wavelengths on a 1-mil dry film of the mill base. The P.I. is the ratio of these optical densities:

$$P.I. = \frac{(O.D.)_1}{(O.D.)_2} = \frac{\text{conc.} \times k_1}{\text{conc.} \times k_2} = \frac{k_1}{k_2} = \frac{d \times f(\lambda_1, \text{ particle size})}{d \times f(\lambda_2, \text{ particle size})}$$

$$= f(\text{particle size}), \lambda_1 \text{ and } \lambda_2 \text{ being fixed.}$$

Theoretically, any two wavelengths may be chosen. In practice, the test is most sensitive if the wavelengths at which the particular pigment exhibits maximum and minimum absorption are chosen, since the change of optical density with respect to wavelength is greatest in these regions of the spectrum.

B. Determining Pigment Concentration

Pigment concentration of a dispersion is given by

$$c = \frac{O.D.}{k}$$

If the dispersion is in the liquid state in an optical cell of fixed path length, then at any given wavelength, k is a function of particle size alone. P.I. is also a function of particle size only. Therefore, k may be expressed as a function of P.I. The relationship between P.I. and k must be predetermined for each pigment. Then, knowing the P.I. and the optical density at a specified wavelength, pigment concentration in a dispersion can be calculated from the above equation.

C. Relationship to Tinting Strength

Tinting Strength is the coloring power of a given quantity of pigment or dispersion. Standards are established for each mill base and deviations from standard are expressed as percentage units strong or weak, i.e., one tinting strength unit is the change in coloring power of a mill base corresponding to a change of 1% pigment in the mill base. Obviously deviations in degree of pigment dispersion (particle size) will also result in different tinting strengths. Thus, pigment loading being held constant, tinting strength may be directly related to P.I. Tinting strengths determined from this relationship can then be corrected for pigment concentration deviations determined as in (B).

II. Application

According to the preceding theory, P.I. can be determined directly from two optical density readings on a liquid dispersion in an optical cell* of fixed path length. However, some pigments flocculate rapidly in a liquid dispersion, causing a shift in the optical density. W-505, phthalocyanine blue pigment, is notorius for its flocculation

*Optical cells used are available from F. N. Jones.

tendencies. Successive optical density readings on a dispersion of this pigment at a wavelength of 6150 Å (point of maximum absorption) varied by as much as ± 3%. P.I.s determined on a series of 42-1505 mill bases of varying grinding time did, in general, decrease with increasing grinding time but sensitivity of the test was low (Table I). P.I. determined by the dry test method was more sensitive and had better reproducibility (Table II).

A ± 3% error in concentration determination is unacceptable. However, optical density measured at the wavelength of minimum absorption (4970 Å for W-505) was found to be less sensitive to pigment flocculation and reproducible within ± 0.5%. This measurement could be used to accurately determine pigment concentration.

W-818, Monastral Violet, is a relatively stable pigment. Successive optical density readings on a 42-818 dispersion were reproducible at both the minimum and the maximum absorption points over a period of a week. However, on standing for two weeks there is a large change in the optical density at the wavelength of maximum absorption (5800 Å) while the reading at the minimum (4650 Å) is satisfactorily stable. This change in optical density at the peak is due to flocculation. It can be eliminated by subjecting the dispersion to a shearing action. However, this procedure is unreliable. Thus, it is recommended that P.I. be determined from a dry film of the mill base, while pigment concentration is determined from the optical density of the liquid dispersion at the wavelength of minimum absorption.

Each dispersion must initially be calibrated as follows:

(a) Determine the relationship between dry film P.I. and Tinting Strength for the mill base when the mill base meets formula card specifications for pigment loading. Figure 1 is an example of this for 42-785 Monastral Green mill base.

(b) Establish the relationship between P.I. and optical density at a specified light path length for the mill base. This should be determined at the wavelength of minimum light absorption, e.g., 5300 Å for 42-785 (Figure 2).

Tinting Strength of a test mill base may then be determined as follows:

1. Determine the dry film P.I. of the mill base.

2. Determine the "apparent" Tinting Strength from relationship (a) above.

3. Determine the expected optical density from relationship (b) above.

4. Measure the true optical density of the test mill base at the same wavelength and light path length as used in (b).

5. The percentage difference between the true and the expected optical density is the percentage difference of the true pigment concentration from that specified on the formula card. This number is added to the "apparent" Tinting Strength of step (2) to give the true Tinting Strength of the mill base.

This procedure is illustrated in Table III for 42-785 samples milled at the Philadelphia Plant.

III. Advantages of Particle Size Index over Tinting Strength Measurement

The P.I. test:

- Is not dependent on uniform properties of test materials.
- Does not require elaborate materials.
- Is less susceptible to "operator errors" than the Tinting Strength test.
- Is easy to run and quick.

Tinting Strength measurement requires addition of a "standard" white (sometimes black) tinting lacquer to the test mill base. Can-to-can variations of this "standard" white may cause deviations greater than 3 tinting strength units. Operator technique, degree of rejuvenation of test and standard mill bases are additional variables so that measurements are reproducible only within $\pm$ 3 units (Ref. 4).

Two series of 42-785 mill bases were prepared by W. P. Dolan (Philadelphia Plant) on a continuous 47-Process laboratory unit, varying stay-time from 2 to 24 minutes. Tinting Strengths of these mill bases measured using different batches of "standard" white tinting lacquer (code LS-76226) are plotted against stay-time in Figure 3. An exact correlation between Tinting Strength and stay-time cannot be expected, but the wide scatter in the data points is greater than acceptable. P.I. measurements on the same mill bases are plotted against stay-time in Figure 4. A comparison of the two figures clearly shows the superior reproducibility of P.I. measurement.

Tinting Strength measurement requires precise weighing out of the test mill base, the standard white tinting lacquer, a lacquer clear and a reducing thinner. These must be uniformly mixed and filtered. This is sprayed out on panels which are baked. After cooling, G reflectances are measured on these panels and Tinting Strength is calculated by comparison with a standard. This is a lengthy and tedious process which takes about two hours in a plant control lab.

The dry P.I. test does not require precise measurements in diluting the mill base with a clear. A 1 mil drawdown of the diluted mill base dries in a few minutes and is ready for optical density measurements. The only precise weighing necessary is in dilution of the mill base for the wet optical density reading. Conversion of P.I. into Tinting Strength is a simple calculation if appropriate charts are prepared for each mill base. This could be further simplified by use of a programmed desk computer. The entire measurement with calculations and clean-up of optical cells can be performed in about 40 minutes.

An initial investment in spectrophotometric equipment would be necessary. The Cary 14 UV-vis-near IR spectrophotometer was used in this investigation. However, the instrument required for a control lab would have to cover only the visible region of the spectrum, and it would not require continuous optical density recording or automatic variation of wavelength. Use of a sonic bath would facilitate clean-up of the optical cells.

P.I. may not be applicable in testing dispersions of some coarse inorganic pigments such as W-355, as it is not very sensitive in the region of greatest interest (tinting strength of the standard) (Ref. 2). However, these pigments are easy to disperse and a control test is not as essential in their manufacture.

P.I. has the potential for on-line determination of Tinting Strength. A sample of the mill base leaving the sand grinder could be run through a flow-through optical cell and optical densities measured at two specified wavelengths. P.I. could be measured directly on the liquid dispersion which being freshly milled, will not have flocculated.

REFERENCES

1. Chu, I. C., ESR-69-27.

2. Rodrigues, A. B. J., ESR-69-51.

3. Chromey, F. C., J. Opt. Soc. Am., 50, 730 (1960).

4. Wilson, R. P., private communication, October, 1969.

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TABLE I

P.I. OF 42-1505 MILL BASES*
(MEASUREMENTS TAKEN ON DILUTED LIQUID DISPERSION)

Sample No.	Tinting Strength	$(O.D.)_{6150\ \mathring{A}}$ 0.05 mm. path	$(O.D.)_{6150\ \mathring{A}}$ (average)	$(O.D.)_{4970\ \mathring{A}}$ 1 mm. path	$(O.D.)_{4970\ \mathring{A}}$ (average)	$P.I. = \frac{(O.D.)_{4970\ \mathring{A}}}{(O.D.)_{6150\ \mathring{A}}}$
1	12.7_W	1.21 1.17	1.19	1.34 1.29	1.31	1.11
2	12.6_W	1.18 1.20	1.19	1.28 1.28	1.28	1.07
4	10.5_W	1.21 1.24	1.22	1.27 1.28	1.28	1.05
5	3.5_W	1.34 1.36	1.35	1.32 1.33	1.33	0.986
6	5.5_W	1.23 1.29	1.26	1.27 1.28	1.28	1.02

Note: 6 gms. of mill base were diluted with 80 gms. of clear.
6150 Å is the wavelength of maximum absorption.
4970 Å is the wavelength of minimum absorption.

*Samples supplied by W. P. Dolan, Philadelphia.

TABLE II

P.I. OF 42-1505 MILL BASES*
(MEASUREMENTS TAKEN ON DRY 1 MIL FILMS OF MILL BASE)

One part of mill base was diluted with two parts of clear (by volume).
Two 1 mil drawdowns were prepared from each diluted mill base.

Sample No.	Stay-Time (Minutes)	Tinting Strength	$(O.D.)_{peak}$	$(O.D.)_{trough}$	P.I.	Average P.I.
1	2.4	12.7_W	3.13 2.40	 0.996	 4.16	4.16
2	3.9	12.6_W	2.47 2.80	0.997 0.109	4.04 3.90	3.97
3	7.9	10.6_W	2.36 2.31	0.089 0.083	3.77 3.60	3.69
4	10.0	10.5_W	2.34 2.63	0.081 0.090	3.46 3.42	3.44
5	20.0	3.5_W	3.01 3.14	0.095 0.097	3.16 3.09	3.13
6	17.9	5.5_W	2.46 2.60	0.082 0.098	3.34 3.38	3.36
7	14.1	6.1_W	2.63 2.46	0.085 0.080	3.23 3.25	3.24

*Mill bases supplied by W. P. Dolan, Philadelphia.

TABLE III

PREDICTION OF TINTING STRENGTH VIA PARTICLE SIZE INDEX

Sample No.	(1) P.I. 1 mil Dry Film	(2) Apparent Tinting Strength from Fig. 1	(3) Expected Optical Density from Fig. 2	(4) $(OD)_{5300\ \text{Å}}$ 1 mm. path	(5) Conc. Deviation from Standard $\frac{(4)-(3)}{(3)} \times 100$	True Tinting Strength (2) + (5)	Measured Tinting Strength Phila. Plant	Measured Tinting Strength ESL
3795	5.96	-4.4	2.67	2.93	+9.7	5.3_s	2.4_s	0.8_s
4060	6.44	-6.2	2.75	2.61	-5.1	11.3_w	9.1_w	12.7_w

*Measurements were made at the Philadelphia Plant and at the Experimental Station Laboratory by different operators using different cans of "standard" white tinting lacquer.

FIGURE 1

P.I. VS. TINTING STRENGTH FOR 42-785 MILL BASE

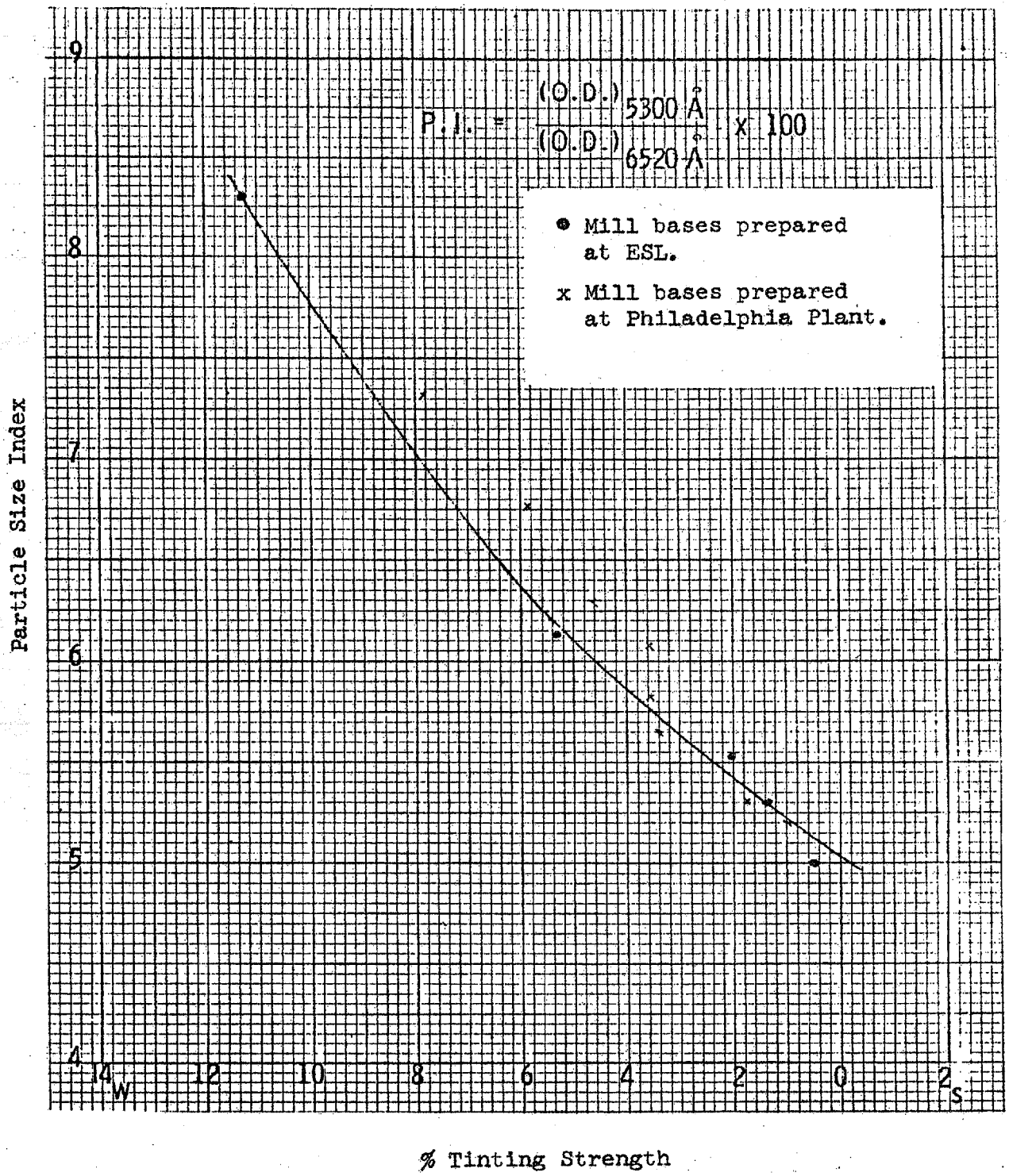
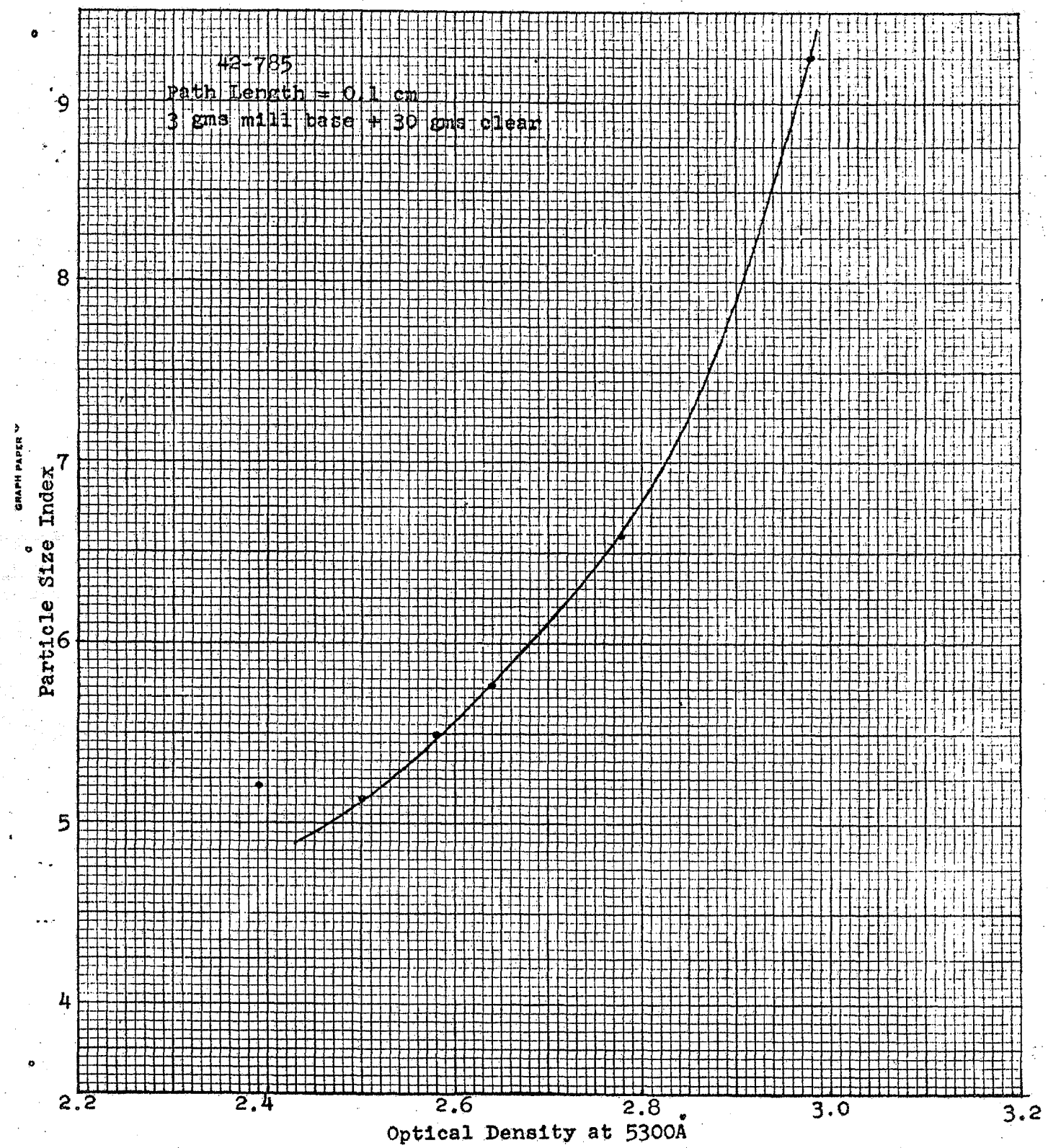


FIGURE 2



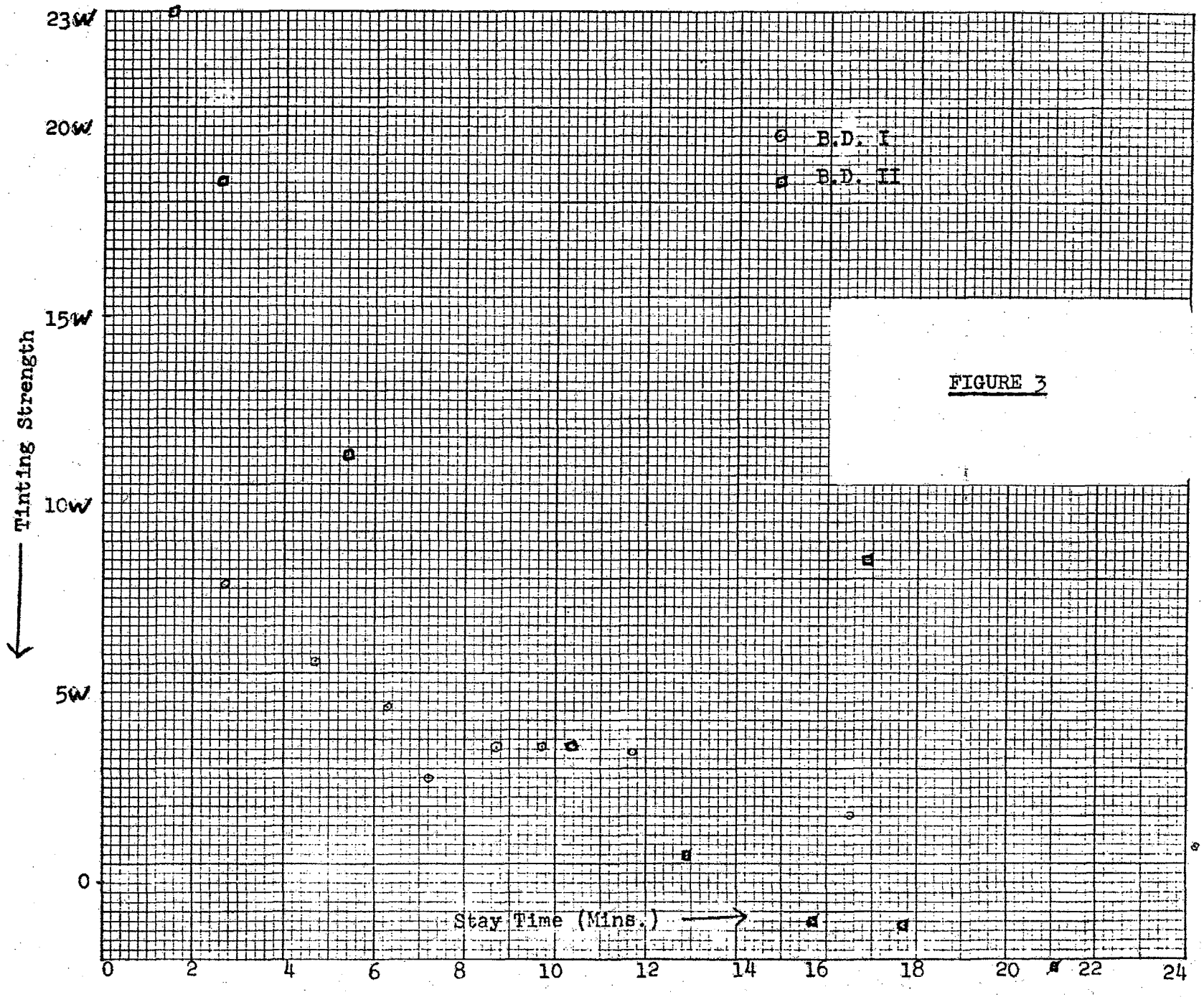


FIGURE 3

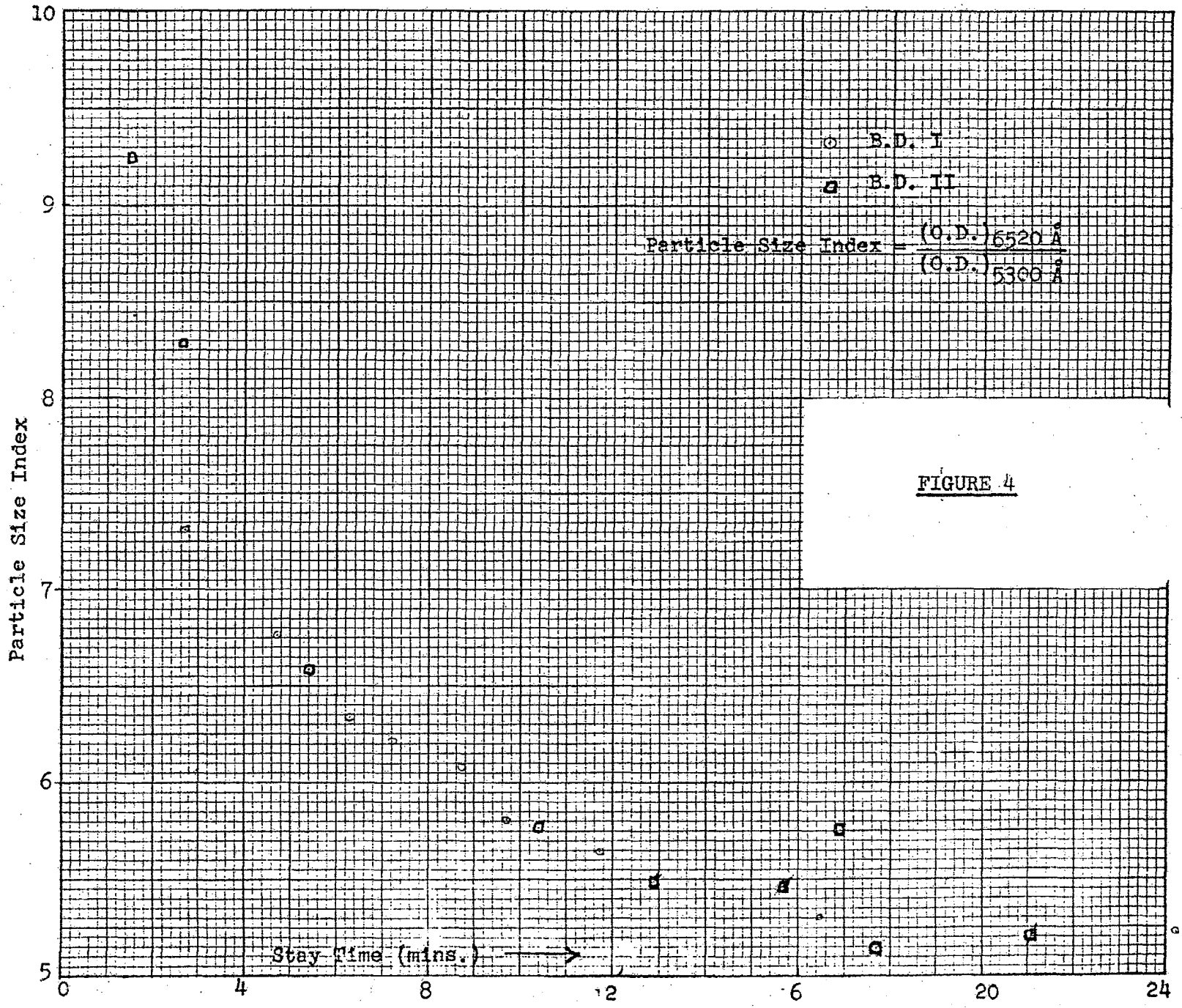


FIGURE 4

ABSTRACT

A test based on light scattering properties of pigment particles was developed to predict the Tinting Strength of mill bases via optical density readings on a dry film of the mill base and on the liquid dispersion itself. This Particle Size Index test was found to be simple, quick, less susceptible to "operator errors" and more reproducible than direct Tinting Strength Measurements.

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