Serial No.

Copy No. 1. Numerical File

E. I. DU PONT DE NEMOURS & COMPANY
KREBS PIGMENTS DEPARTMENT
256 VANDERPOOL STREET
NEWARK, NEW JERSEY

CONFIDENTIAL

KW-57-13

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

ULTRA-VIOLET TRANSMISSION OF DISPERSED HYDROUS OXIDES

Period Covered MAY 1950 to AUGUST 1950

FILE: 210.2

DATE: March 15, 1951

210.2

Serial No. KN-51-13

Copy No. 1. Numerical File

Copy to:

#1 - Numerical File
2 - Research Office (210.2)
3 - Library File (210.2)
4 - V. Chalupski - Plant Files
~~5 - E. E. Bolton/T. B. Gallaway/PJM~~
6 - W. E. Spengeman
7 - W. S. Struve/PJM
8 - D. B. Killian/A. Siegel

NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

ULTRA-VIOLET TRANSMISSION OF DISPERSED HYDROUS OXIDES

MAY 1950 to AUGUST 1950

CHARGE: 1101-11-258

SUBMITTED BY: A. R. HANKE DATE SUBMITTED: Jan. 31, 1951

APPROVED BY : B. H. PERKINS 2/12/51 DATE ISSUED: March 13, 1951

INTRODUCTION:

The suggestion that hydrous nickel oxides improve paint film durability by absorbing harmful ultra-violet light prompted this investigation. This report covers the observations of a preliminary nature that were made on the ultra-violet light transmission of various hydrous oxides. No claim is made that the transmission curves obtained have a high precision or that the regions of low light transmissions found are due entirely to light absorption. Light scattering may also be a part of the explanation for low light transmission. In spite of the uncertainty introduced by not being able to distinguish between light absorption and light scattering, the data are still useful in that they establish limiting values for the ultra-violet absorption of the pigments. Thus, if considerable ultra-violet light scattering did exist, the oxides would be even less effective than the data show them to be.

SUMMARY AND CONCLUSIONS:

1. Light transmission data were obtained on the following water dispersions of hydrous oxides:

Iron oxide (III)
Chromium oxide (III)
Titanium oxide (IV)
Nickel oxide (II)
Aluminum oxide (III)

2. For all oxides except hydrous aluminum oxide, a marked decrease in transmission was noted as the wave-length decreased, the transmission passing through a low minimum. All these strong minima, however, were well on the short wave-length side of the lower limit of ultra-violet light in sea-level sunlight.

3. Following is a list of the hydrous oxides in decreasing order of effective removal of U.V. light: Iron (III), Chromium(III), Titanium (IV), Nickel (II), Aluminum (III). It is known that from the point of view of enhancing film durability on outdoor exposure, hydrous iron oxide is excellent, whereas hydrous aluminum oxide and hydrous titanium oxide are poor. Hydrous nickel oxide is far better than hydrous titanium oxide or hydrous aluminum oxide. From the above list it would appear that although the difference between iron and aluminum might have a partial explanation in U.V. absorption, the unusually good behavior of hydrous nickel oxide is due to causes other than U.V. absorption.

EXPERIMENTAL DETAILS:

A. General

A Beckman Model D. V. spectrophotometer was used for all transmission measurements. Aqueous suspensions were placed in 1 centimeter lightpath quartz cells.

In most cases the dispersed hydrous oxides were obtained by rapid mixing of a dilute water solution of the metal chloride with a slight excess of dilute sodium hydroxide. Light transmission data were obtained immediately thereafter before the hydrous oxides had a chance to coagulate to the point where it seriously altered the light transmission value. In the case of hydrous nickel oxide, an aqueous suspension of a plant lot (A-2-P, lot 74910) was also run. In addition to this, a dried film prepared from this same lot was run. All three techniques gave essentially the same type of curve. There was enough difference between the curves however, to suggest that the degree of dispersion does alter the curve somewhat, which emphasizes the importance of attaching only a rough quantitative significance to the data. The curves are shown in Figure 1.

B. Hydrous Nickel Oxide

1. Preparation of dispersion for immediate examination.

A solution of $NiCl_2.6H_2O$ was prepared (0.5 gram/100 milliliters). The C.P. salt was assumed to be 100% $NiCl_2.6H_2O$.

A caustic solution was prepared by dissolving 0.516 grams sodium hydroxide in 100 milliliters of boiled distilled water. This was analyzed by titration with standard sulfuric acid whereupon the concentration was calculated as 0.498 grams sodium hydroxide per 100 milliliters.

A 10.2 milliliter portion of the nickel chloride solution was diluted to 100 milliliters and a 4.3 milliliter portion of the sodium hydroxide solution was diluted to 100 milliliters. The solutions were rapidly poured together into a third beaker with agitation. Transmission data were obtained immediately thereafter and the curve is shown in Figure 1.

The concentration of reagents was chosen so that the hydrous nickel oxide concentration, assuming a formula of $Ni(OH)_2$, was 0.01 gram/100 milliliters in a 25% excess of caustic. After coagulation of the hydrous nickel oxide, light transmission measurements were also obtained on the supernatant liquid to show that the observed decrease in transmission was due to the hydrous oxide and not to the dissolved salt. These measurements show considerably more light transmission and in no way resembles the curve of the hydrous nickel oxide. Transmission measurements were also obtained of a nickel chloride solution of concentration equivalent to the hydrous nickel oxide dispersion. The light transmission measurements of the solutions were all very close to 100%, all of which shows that the transmission curve obtained of the hydrous nickel oxide dispersed in the solution was due to the hydrous oxide and not due to unreacted nickel salt or anything else in solution.

2. Examination of aqueous plant pulp.

A plant batch of hydrous nickel oxide (A-2-P, lot 74910) was washed with water to the point where the presscake began to peptize. A portion of this peptized suspension analyzed 5.1% total

solids and was further diluted by dispersing a drop (approximately 0.05 milliliters) in approximately 35 milliliters of water. This gave a well dispersed suspension with very little tendency to settle and of the right concentration for transmission measurements. A light transmission curve was obtained and found to be similar to the curve obtained from the hydrous oxide directly formed. Figure 1 shows the curve after recalculation to a more comparable concentration basis for comparison with the curve of the directly formed hydrous oxide. To make this calculation it was assumed that the optical density (-log T) was proportional to concentration.

3. Examination of a dried film of a dispersed pulp.

The same peptized pulp of hydrous nickel oxide was used for this work as was used for the experiment described in the previous section. The original dispersion of approximately 5.1% solids was diluted with water (29.4 grams to 100 grams) to make a slurry of approximately 1.5% solids. A piece of clear flat quartz was dipped in and out of the slurry. One side was wiped clean and the film on the other side was allowed to air dry. A light transmission curve was obtained of the dried film adhering to the quartz slide. The curve was recalculated to a concentration basis comparable to the other hydrous nickel oxide curves for comparison purposes using the method described in section 2, and is illustrated in Figure 1.

It can be seen that all curves of hydrous nickel oxide are essentially the same, regardless of the technique of preparing the hydrous oxide or obtaining the curve. There are some differences, however, which may well have to do with the degree of dispersion of the oxide.

C. Hydrous Chromium Oxide

A stock solution of C.P. $CrCl_3.10\ H_2O$ (0.5 gram/100 milliliters) was prepared. The salt was assumed to be 100% $CrCl_3.10\ H_2O$. A 13.1 milliliter portion of the chromium solution was diluted to 100 milliliters. A 4.6 milliliter portion of the sodium hydroxide solution described in B-1 was diluted to 100 milliliters. The solutions were rapidly poured together with agitation into a third beaker and transmission data obtained as shortly thereafter as possible. This gave a chromium concentration of 0.01 gram/100 milliliters $Cr(OH)_3$. The light transmission curve is illustrated in Figure 2.

D. Hydrous Titanium Oxide

A stock solution of titanic chloride was prepared by adding 3 milliliters (5.2 grams) of anhydrous $TiCl_4$ to 12 grams crushed ice and 0.8 milliliters concentrated hydrochloric acid. The volume after the ice had melted was 15 milliliters. This solution was diluted in two steps. A 10 milliliters portion was diluted to 100 milliliters, giving a $TiCl_4$ concentration of 3.6 grams/100 milliliters. This solution was further diluted, 10 milliliters to 100 milliliters, to give

a final $TiCl_4$ concentration of 0.55 gram./100 milliliters. The solution remained clear during the time it was used but with overnight standing, it became cloudy. A 9.4 milliliter portion of the $TiCl_4$ solution was diluted to 100 milliliters. A 7.0 milliliter portion of the same sodium hydroxide solution described in B-1 was diluted to 100 milliliters. The solutions were rapidly poured together into a third beaker and transmission measurements were obtained immediately thereafter. The concentration of the solutions was so chosen that the final solution had a concentration of 0.01 gram/100 milliliter $Ti(OH)_4$. The light transmission curve is shown in Figure 2.

E. Hydrous Iron Oxide

A stock solution of ferric chloride was prepared by dissolving anhydrous $FeCl_3$ in water to give a concentration of 0.5 gram/100 milliliters. A 10.2 milliliter portion of the $FeCl_3$ solution was diluted to 200 milliliters and 4.5 milliliters of the same sodium hydroxide solution described in B-1 was diluted to 200 milliliters. The solutions were rapidly poured together into a third beaker and agitated. Transmission measurements were obtained immediately thereafter. The concentrations of the solutions were so chosen that the final solution had a concentration of 0.005 gram/100 milliliters $Fe(OH)_3$. This is only one-half as strong as previous concentrations because it was observed that at concentrations of 0.01 gram/100 milliliters, the hydrous ferric oxide flocculated too rapidly to permit the desired measurements. The light transmission curve is shown in Figure 2.

F. Hydrous Aluminum Oxide

A stock solution of aluminum chloride was prepared by dissolving anhydrous $AlCl_3$ in water to give a concentration of 0.46 gram/100 milliliters. A 7.4 milliliter portion of the $AlCl_3$ solution was diluted to 200 milliliters and a 7.8 milliliter portion of the same sodium hydroxide solution described in B-1 was diluted to 200 milliliters. Both solutions were rapidly poured together into a third beaker with agitation. Transmission measurements were obtained immediately thereafter. The final concentration was 0.005 gram/100 milliliters $Al(OH)_3$. A stronger concentration caused the hydrous oxide to flocculate too rapidly. The light transmission curve is shown in Figure 2.

DATA INTERPRETATION:

Admittedly the concentration of the dispersed hydroxide is only an approximate figure, hence the calculation of the absorption coefficient is only approximate, but it can be used as a rough measure of the effectiveness of ultra-violet removal by a paint film pigmented with the hydrous oxide. It is likewise true that it was not possible to tell through a measurement of transmitted light if the light was being removed by absorption or by scattering. It was assumed that the light was absorbed. If scattering features to a significant extent, the effectiveness of the hydrous oxide in removing ultra-violet light

is even less than the calculated figure, hence the calculated figure can be considered as a sort of limiting value, the true value being one making the oxide an even less efficient remover of ultra-violet light. It can be seen from Figure 3* that below 300 millimicrons there is no ultra-violet light in sea level sunlight. By referring to Figure 2, it can be seen that the region of strong absorption for the hydrous oxides is on the short wave length side of the point below which there is no ultra-violet light in sunlight. Above 300 millimicrons the intensity of ultra-violet light in sunlight increases rapidly and for the sake of making comparisons between the oxides studied, a wave length of 360 millimicrons was chosen as being sufficiently representative of the ultra-violet light in sunlight.

A typical dried pigmented paint film contains about 15% volume pigment solids. Using reasonable values for the specific gravity of the hydrous oxide, it becomes possible to calculate the film thickness required to cut the incident light intensity at 360 millimicrons wavelength to any predetermined value making use of the Beer-Lambert law. A table showing the film thickness required to cut the incident light intensity to 10% of its incident value will give some idea of how much protection the hydrous oxides studied will give from the photochemical effect of ultra-violet light. Following is a typical calculation showing the method used.

Calculation for Hydrous Nickel Oxide

The Beer-Lambert law is usually expressed by the following set of equations.

$$T = \frac{I}{I_o}$$

$$-\log \frac{I}{I_o} = D$$

$$D = ctk$$

T = Transmittance measurements obtained from the curve. It is % T ÷ 100.

I_o = Incident light intensity.

I = Transmitted light intensity.

D = Optical density defined by the equation $-\log \frac{I}{I_o} = D$.

c = Pigment concentration (grams/100 milliliters)

t = Optical light path (centimeters)

k = Proportionality constant usually called absorption coefficient; It is the optical density per unit concentration per unit light path.

*From W. E. Forsythe "Measurement of Radiation Energy", 1st ed., New York, McGraw-Hill Book Co. 1937.

From the spectrophotometric curve for hydrous nickel oxide (Figure 2), $T_{560m\mu} = 0.96$.

$$-\log T = D$$

$$-\log 0.96 = 0.0177 = D$$

$$k = \frac{D}{c \times t}$$

$$k = \frac{0.0177}{0.01 \times 1} = 1.77$$

If the light is to be reduced to 10% of its incident intensity in passing through the paint film, $I/I_0 = 10/100 = 0.1$

$-\log 0.1 = 1 = D$ (the required optical density)

Assume a specific gravity for hydrous nickel oxide of 4.1. Let the pigment concentration (g/100 ml) in a 15 volume % dried film = c.

$c = 15 \times 4.1 = 61.5$ g/100 ml.

Let t = film thickness required for an optical density of 1.

$$t = \frac{D}{ck} = \frac{1}{61.5 \times 1.77} = 0.01088 \text{ cm}$$

To convert to mils -

$0.01088 \text{ cm} \times 393.7 = 4.3$ mils

This distance represents the film thickness necessary to decrease the light intensity to 10% of its incident value.

The following table lists the calculated film thicknesses for the oxides studied.

Hydrous Oxide	Specific Gravity	Calculated Film Thickness (mils)
Iron (III)	3.46	0.05
Chromium (III)	3.2	0.8
Titanium (IV)	3.8	2.
Nickel (II)	4.1	4.
Aluminum (III)	-	v. much larger

Even though the film thickness values are admittedly only approximations the difference between the oxides is large enough to attach some quantitative significance to the data. It is seen that according to the table, the hydrous oxides of aluminum and nickel should be much worse in improving film stability than iron. It is

true that aluminum is much worse, and U.V. absorption may be, at least in part, responsible but the very good behavior of nickel as compared to titanium and aluminum leads one to believe that the unusually good behavior of hydrous nickel oxide is due to causes other than U.V. absorption.

This work is recorded in NB-1356-19.

ARH:lg

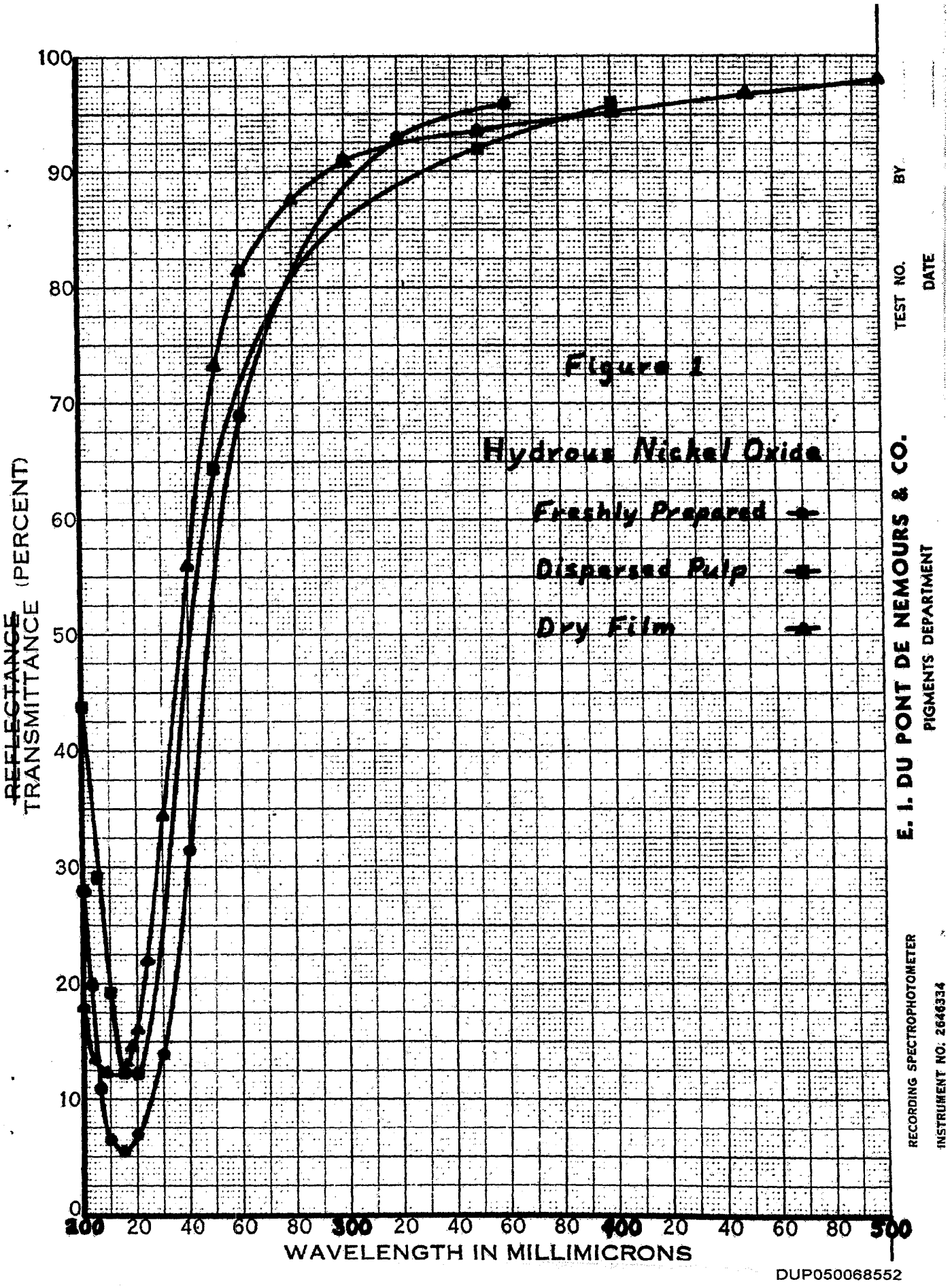
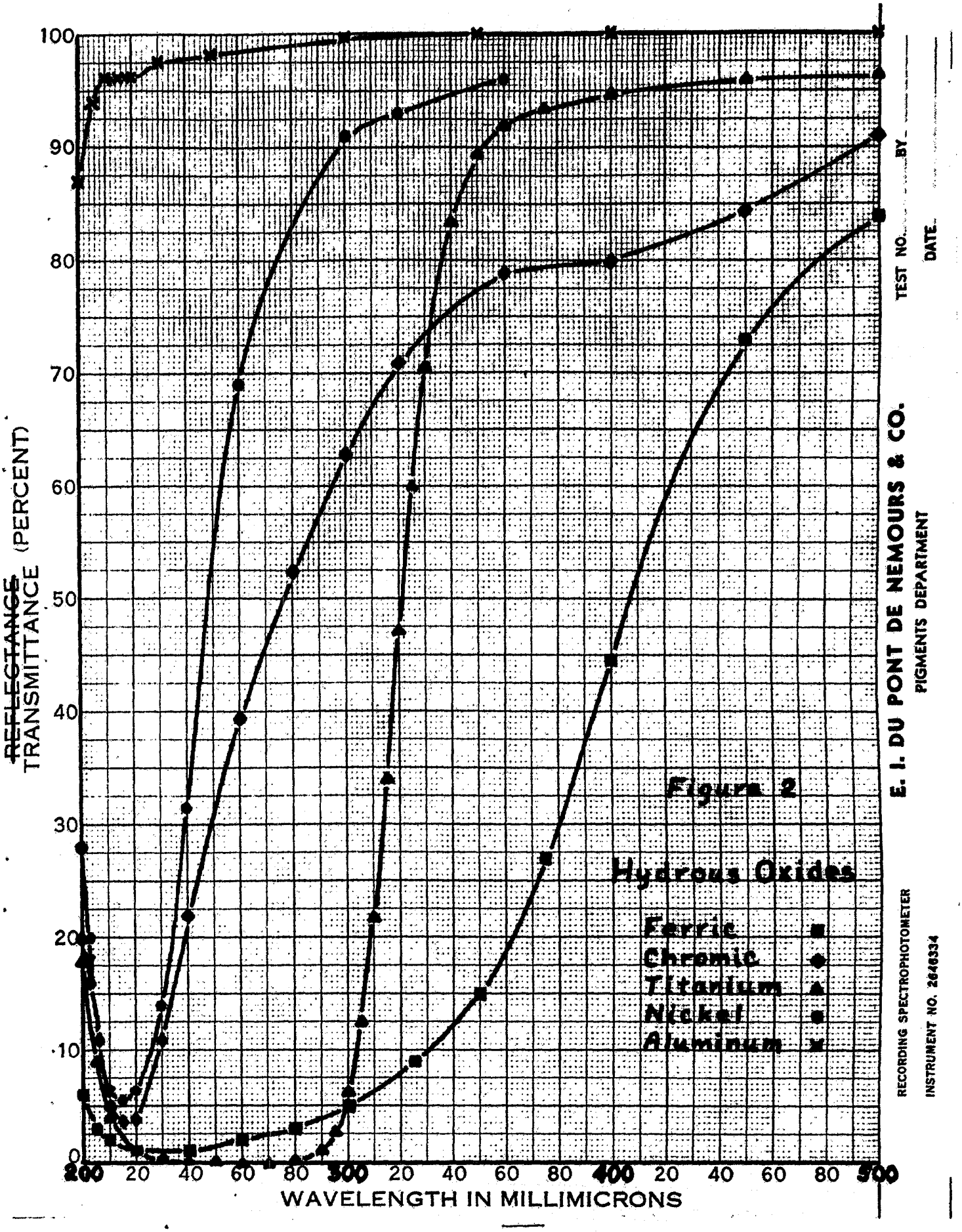
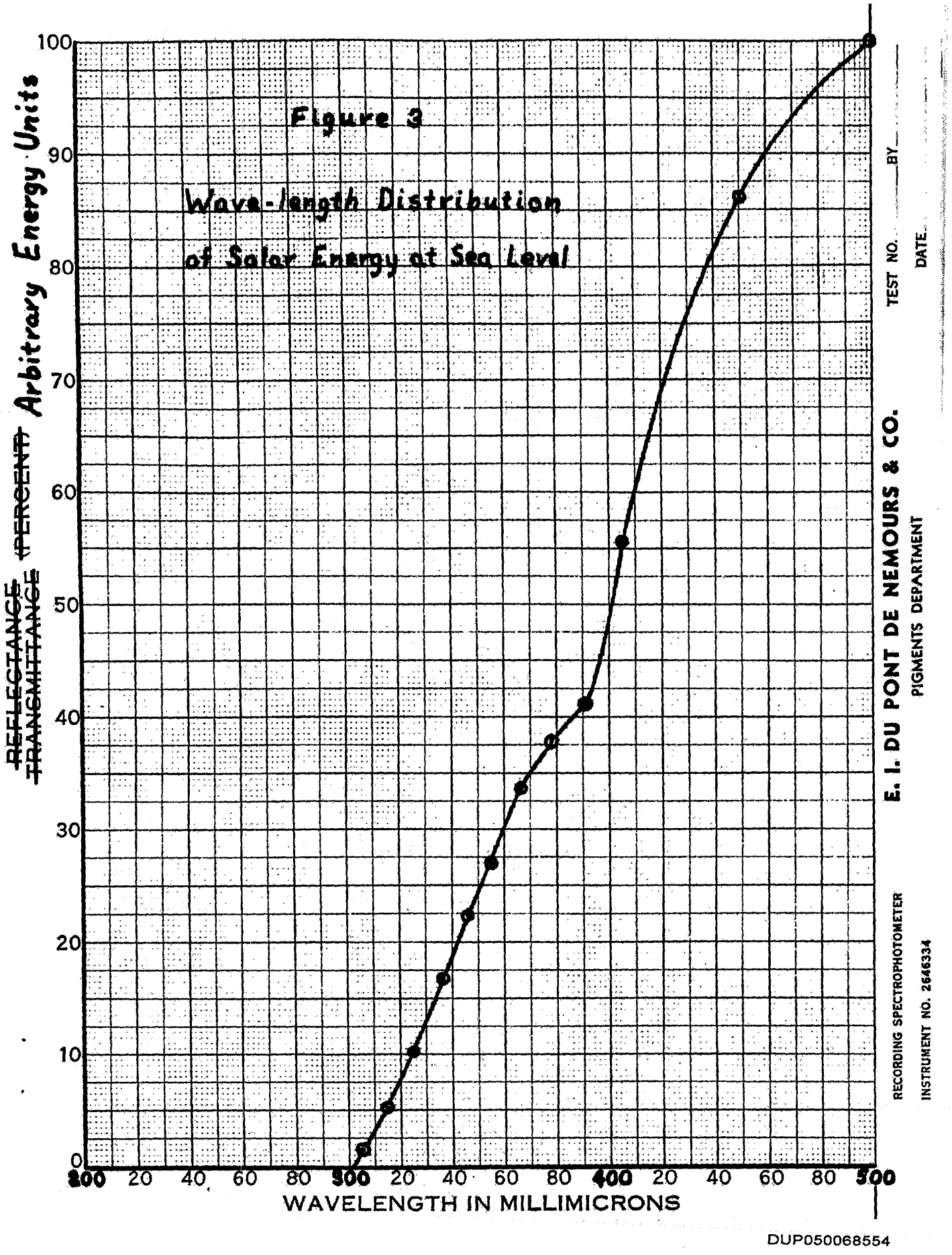


Figure 1
Hydrous Nickel Oxide
Freshly Prepared
Dispersed Pulp
Dry Film
REFLECTANCE
TRANSMITTANCE (PERCENT)
WAVELENGTH IN MILLIMICRONS
E. I. DU PONT DE NEMOURS & CO.
PIGMENTS DEPARTMENT
RECORDING SPECTROPHOTOMETER
INSTRUMENT NO. 2644334
TEST NO.
DATE
BY
DUP050068552



DUP050068553



DUP050068554