Serial No. KN-50-11

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

KN-50-11

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

A NEW PHASE "NAPHTHANIL" PIGMENT FROM PCONA → NOL (RT-566-D)

Period Covered: 1945 - 1950

FILE: 221

DATE: 8/4/50

NJ6278

Serial No. KN-50-11

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

Title: A NEW PHASE "NAPETHANIL" PIGMENT FROM POONA → NOL (RT-566-D)

Period Covered: 1945 - 1950

Charge: 1101-11-40

SUBMITTED BY: A. R. HANKE A R Hanke 8/3/50 DATE SUBMITTED: July 18, 1950

APPROVED BY: E. H. PERKINS E H Perkins 8/3/50 DATE ISSUED: 8/4/50

INTRODUCTION

In 1945 it was observed by the writer that if PCONA → NOL was refluxed in chloroform, a rather sudden and marked color change resulted. In 1947, during an attempt to measure the chloroform solubility of a series of "Naphthanil" pigments, it was observed that the solubility of certain "Naphthanil" pigments, particularly 5-nitro-2-amino-anisole → NASD and PCONA → NOL, varied in an erratic sort of manner. That this erratic solubility was associated with a crystallographic phase change was established by crystal seeding experiments and by X-ray diffraction records.

Since the Sales Division exhibited interest in the yellow hue of the new phase PCONA-NOL, attention was directed to the development of a practical method for making this new product. This report describes that development. The new phase will be called the beta phase and the conventional phase will be referred to as the alpha phase.

PATENT SITUATION

Competitive Patents

None.

Pertinent Literature References

1. FIAT REPORT 1313 Vol. 3, page 183 - Polymorphism in "Naphthanil" pigments. Page 393-401 - Identification of "Naphthol" mixtures by X-ray diagrams. Page 414-15 - General polymorphism. Page 434-438 - Polymorphism of organic dyes.

2. George Susich, "Identification of Organic Dyestuffs by X-ray Powder Diffraction". Analytical Chemistry 22, 424 (1950). Polymorphism of organic pigments is mentioned. Three phases of metal-free phthalocyanine are cited as an example.

Present Protection

It is believed that the new phase product is patentable as a new composition of matter. The process for preparing it is also believed patentable.

A patent memorandum on what to base a patent application is being prepared.

SUMMARY & CONCLUSIONS

1. A new phase [illegible] of [illegible] (PCONA → NOL (beta phase) with much yellower masstone and tint than the conventional phase material (alpha phase) can be prepared by refluxing the alpha phase with chloroform and then salt milling the dried refluxed material.

2. In order to have the solvent alone effect a transformation, it is necessary to maintain a sufficiently high ratio of solvent to pigment. A ratio of 50 ml chloroform per 0.25 grams or greater will allow a rapid phase conversion. A ratio of 50 ml chloroform per 0.40 grams will not allow conversion.

3. The two steps of solvent treatment and salt milling may be combined in a single operation wherein the pigment is dispersion milled. A satisfactory mill charge consists of 380 grams sodium chloride, 35 grams pigment, and 7 grams chloroform. The action of the milling operation contributes to the phase transformation since much less solvent is required in dispersion milling than if the solvent treatment is given first, followed with salt milling.

4. Straight salt milling also effects some phase conversion.

5. Chlorinated solvents with some exceptions effect a phase transformation.

6. The estimated mill costs starting with finished RT-566-D using a dispersion milling method described later is $3.80/lb. This is covered in a memorandum by B. H. Perkins 6/24/50 File 221.

7. The beta phase pigment has the necessary transparency to yield attractive metallized finishes. When compared to the alpha phase, i.e. RT-566-D, it is far yellower in masstone. In Dulux, and in a melamine modified alkyd enamel, it is slightly on the defensive in durability by weatherometer exposure tests, and slightly on the defensive in reactivity by viscosity measurements.

EXPERIMENTAL

A. Evidence for the Existence of a New Phase

If RT-566-D (PCONA → NOL) is allowed to reflux in chloroform for a few minutes and if the ratio of chloroform to pigment is high enough, a marked yellowing of the pigment is observed. It is important in effecting this phase transformation by solvent action that the ratio of solvent to pigment be sufficiently high. There appears to be a limiting value of this ratio below which the transformation is uncertain. For example, 50 ml of chloroform for 0.85 grams pigment will allow a rapid transformation during reflux whereas 50 ml of chloroform for 0.40 grams of pigment will show no apparent change during reflux.

Solvents other than chloroform also cause a phase transformation. An exhaustive list of solvents has not been obtained but it appears that with a few exceptions chlorinated solvents work best. Table I gives what information is known so far on the ability of a solvent to cause the transformation.

TABLE I

EFFECT OF SOLVENT ON RT-566-D

	Phase Changes
Chloroform	"
Trichlorethylene (Trielene)	"
Ethylene dichloride	"
Monochlorbenzene	"
Trichlorbenzene	"
Carbon tetrachloride	No Change
Tetrachlorethylene (Perclene)	"
Acetic Acid	Slow-doubtful
Acetone	No Change

Figure 1, p.4 shows X-ray spectrometer comparisons of the alpha and beta phases. For Figure 1A, phase transformation was achieved by refluxing 1.3 grams RT-866-D in 250 mm chloroform for 10 minutes. The transformed pigment was filtered and dried. It is believed that very nearly complete phase transformation has been achieved. Figure 1B, is the conventional alpha phase PCONA-NOL. The difference in crystal structure between the new and old phase is quite obvious. Of particular note is the strong peak at a 2θ value of 27.2° for the beta phase as against a strong peak at a 2θ value of 26.1° for the alpha phase. Also, two prominent peaks at 2θ values of 13.2° and 15.6°, for the alpha phase are absent in the beta phase and the beta phase shows two new peaks at 2θ values of 14.4°, and 18.7°.

Table II lists the 2θ values and interplanar spacings of the diffraction maxima for each phase. The precision of the 2θ measurements is around 0.2°. An arbitrary intensity factor is also given ranging from 0 to 100 to better illustrate the intensity differences. Not too much reliance should be placed on the relative intensities, however, because it is difficult to measure them and the results are somewhat dependent on the mounting technique employed for the sample preparatory to obtaining a curve. This is due to crystal orientation which is very difficult to avoid. Diffraction maxima with a relative intensity of less than 5 are not listed.

TABLE II

X-RAY DIFFRACTION COMPARISON OF THE TWO PHASES OF PCONA-NOL

ALPHA PHASE			BETA PHASE		
2θ	Interplanar Spacing (A°)	Relative Intensity	2θ	Interplanar Spacing(A°)	Relative Intensity
26.1	3.42	61	27.2	3.28	59
21.5	4.13	7	21.9	4.06	7
20.6	4.31	7	20.5	4.33	11
19.7	4.50	9	19.9	4.46	11
15.8	5.60	12	14.4	6.14	20
13.2	6.70	29	18.7	6.96	15
10.2	8.66	10	10.4	8.50	15
7.2	12.27	15			

B. Preparation of New Phase Material on Semi-Works Scale by Solvent Treatment

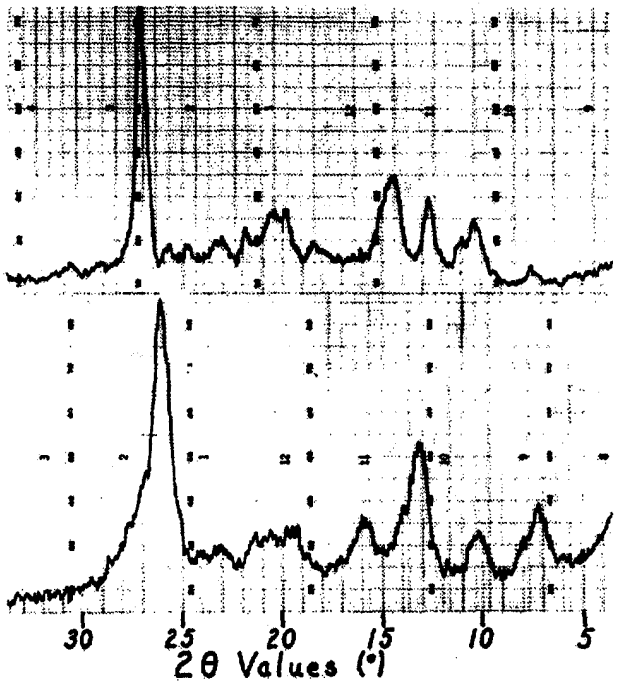
The high ratio of solvent/pigment necessary to effect a phase transformation makes the process extremely unwieldy for large scale production. It was observed, however, that a lower solvent to pigment ratio could be tolerated if the pigment was added stepwise to a large volume of chloroform. The first increment would be completely transformed and these new phase crystals would then apparently act as seed to aid in the subsequent phase conversion. The semi-works

FIGURE 1

X-RAY DIFFRACTION RECORDS OF ALPHA AND BETA PHASE PCONA→NOL

A. Beta Phase

B. Alpha Phase



batches were, therefore, made by the stepwise addition of pigment to chloroform. Appendix 1 gives the method used for the solvent treatment on a semi-works scale.

This solvent treated material is not suitable as a pigment without further processing, because considerable crystal growth occurs during solvent exposure, making the product opaque and entirely unsuitable for use in metallics. It is, therefore, necessary to reduce the particle size to something comparable to that of the original pigment to obtain the desired properties.

C. Preparation of Solvent Treated RT-566-D of Small Particle Size

To effect a particle size reduction of this new phase material wet grinding with a 50/50 mixture by volume of methyl alcohol and water was tried first. This did not give sufficient particle size reduction, hence salt milling was tried. Salt milling gave sufficient particle reduction and metallics with the proper "flash" were obtained. Appendix 2 gives the grinding details used to yield an acceptable product with a specific surface of 53.7 sq. meters per gram, as compared to 32.5 sq. meters per gram for the original untreated RT-566-D.

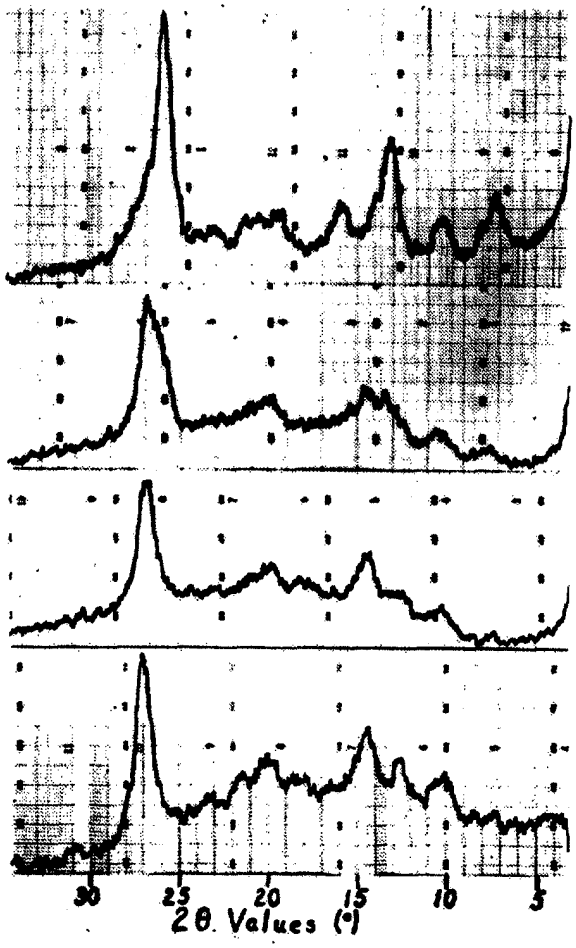
It was found possible to combine the phase conversion step through solvent action with the particle size reduction step of salt milling in a single operation of dispersion milling. It was further observed that some phase conversion occurred with just simple salt milling, which partially explains why phase conversion occurs during dispersion milling at ratios of solvent to pigment far lower than would cause phase conversion during solvent reflux alone. The grinding details for dispersion milling given in Appendix 3 are those used for laboratory scale products.

In the laboratory dispersion milling experiments, particle size was not reduced to the same extent as with straight salt milling using the 25 gal. semi-works mill, but the pigments were sufficiently transparent to be satisfactory in metallics. It is also believed that using a regular mill instead of a gallon can, as used for the laboratory samples, will result in more efficient grinding and hence a better reduction in particle size. It was generally observed that the smaller the particle size, the more transparent the pigment hence it is rather important that the milling operation yield a particle whose size is as small as possible if one requires maximum transparency. Figure 2 p.6 shows X-ray diffraction records indicating a phase change and also shows the specific surface measurements of the ground products. Figure 2A shows the alpha phase "as is" RT-566-D. Figure 2B shows the "as is" RT-566-D salt milled, i.e. no solvent added. Note that some phase conversion has occurred. It is difficult to estimate the extent of conversion because the converted material will have a larger crystallite size and yield a stronger diffraction peak, and also considerable interference of the diffraction maxima of the two phases exists.

FIGURE 2

X-RAY DIFFRACTION RECORDS OF MILLED RT-566-D

	Specific Surface Square Meters/gram
A. "As Is"	32.3
B. Salt Milled	14.9
C. Dispersion Milled with Chloroform	22.4
D. Dispersion Milled with "Triclene"	21.1



Even so, it appears that considerable conversion has taken place. Figure 2C shows the result of dispersion milling with chloroform as the solvent and Figure 2D shows the result with Triclene. In all cases phase conversion has occurred, altho it is difficult to say if the conversion is complete. It is also of interest to note that the specific surface of the milled product is actually less than the original pigment but they are still acceptable in metallics and more efficient grinding should increase the specific surface to something more nearly comparable to the original pigment. That salt milling is capable of reducing the particle size is apparent from the results already mentioned where salt milling the beta phase material yielded a specific surface of 53.7 sq. meters/gram. This is a substantial increase over the figure of 38.3 sq. meters/gram for the original alpha phase RT-566-D.

The estimated mill costs starting with finished alpha phase RT-566-D using dispersion milling in a mill 6' diameter x 6' long and containing 131 lbs. of pigment per charge is $3.50 per lb. This is covered in detail in a memorandum by B. H. Perkins 5/24/50 File 221.

PIGMENT PROPERTIES

The beta phase product is far yellower in masstone than the alpha phase product. In baked overstripe bleed in Dulux or Syntex 20/melamine, it is superior to the alpha phase but it still must be classed as a bleeding color. Weatherometer exposure causes it to become somewhat lighter and duller to a slightly greater extent than the alpha phase material. In reactivity the beta phase is slightly worse than the alpha phase as can be seen from Table III.

TABLE III

REACTIVITY COMPARISON

		Cup Readings in Seconds				
"SYNTEX"-MELAMINE MODIFIED ALKYD	Adjusted Initial Reading Ford Cup	3 Days Ford Cup	7 Days Ford Cup	7 Days Parlin Cup	1 Month Parlin Cup	Degree of Thixotropy
Alpha Phase PCONA-NOL (RT-566-D)	26	32	34	62	54	sl. thix.
Beta Phase PCONA-NOL	25	45	50	100	60	v. "
RT-551-D	22	23	27	190	296	v. "
"DULUX"					1 Month Ford Cup	
Alpha Phase PCONA-NOL (RT-566-D)	21	49	58		79	sl. thix.
Beta Phase PCONA-NOL	20	20	21		129	no "
RT-551-D	19	22	24		25	no "

All initial viscosities were too high for Ford Cup readings so the viscosities were pre-adjusted to about the same value by adding thinner. It is not valid, therefore, to compare initial readings. The results appear somewhat inconsistent, which serves to illustrate that the true differences are not great and the actual differences will depend to a considerable extent on the vehicle, and for some conditions the new phase may be better in reactivity than the old phase. The Parlin cup was used for the "Syntex" at one month because insufficient enamel remained to make a Ford cup reading but it is valid to compare this one month reading with the 7 day Parlin cup reading.

No outdoor exposure results are available as yet but an outdoor exposure series is under way and the results will be given in a later report. Samples have also been sent to F. & F. at Parlin and Philadelphia for evaluation.

SUGGESTIONS FOR FURTHER WORK

No detailed study has been made to establish the optimum conditions for the dispersion milling method. During the 16 hr. grind, very nearly complete phase conversion occurred. Further work may show that less grinding effects just as complete a conversion.

No study was made of the solvent requirement in dispersion milling. Further work may show that less solvent than 7 grams for 35 grams of RT-566-D will give just as complete phase conversion. Further work may show that the particle size reduction may be more effectively achieved by milling in two steps. The first step in the presence of a solvent will cause the phase conversion, and the second step will be milling after evaporation of the solvent which will allow a rapid reduction in particle size. Perhaps a balance of pigment/solvent can be achieved which will allow both rapid phase conversion and sufficiently rapid reduction in particle size to occur in a single step.

For this work, finished standard RT-566-D was used. In actual practice RT-566-D dried presscake should be suitable. There should be no need to pulverize this, altho this point was not studied. It may be possible to eliminate any special treatment given RT-566-D to make it suitable as a finished pigment. It may be possible to simplify the formula for making RT-566-D, if it is to be converted to the new phase. This point was not studied.

Since the new phase pigment will present a lower energy level for the crystal lattice, it is at least thermodynamically sound to suppose that the new phase crystals can be formed directly in the coupling procedure. No work of this sort was done. Crystal seeding and/or the use of solvent present during coupling may allow the direct formation of the new phase crystal.

Appendix 1 - Procedure for Phase Conversion of Alpha Phase PCONA-WOL Through Solvent Treatment

Charge the 75 gallon glass lined Pfandler reactor with 175 lbs. technical grade chloroform. Add 1/2 lb. RT-566-D. Heat to reflux with agitation. This will require about 1-3/4 hours. Add a second 1/2 lb. portion of pigment and after a time interval of 3/4 of an hour add a third increment of 1/2 lb. pigment. After an additional hour add a fourth increment of 1/2 lb., making a total of 2 lbs. pigment. Continue refluxing for 4 hours. Distill off 125 lbs. chloroform. Turn off heat and discharge slurry into pans. Evaporate remaining chloroform at room temperature (ventilated hood) until almost dry. Transfer to the vacuum dryer (8" - 10" vacuum without heat) for overnight drying. Pigment is dry and needs no further treatment other than particle size reduction.

Appendix 2 - Procedure for Grinding and Finishing Solvent Treated Beta Phase PCONA-WOL

Charge the 25 gal. #14 Bldg. ball mill with 380 lbs. of standard mixture of steel balls and rivets. Add 22-1/2 lbs. oven dried hot sodium chloride. Grind briefly to warm up mill. Add 2-1/2 lbs. pigment (solvent treated RT-566-D). Grind 72 hours.

Empty the mill in the conventional manner. Emptying time approximately 2 hours. Remove salt and iron using a 50 gal. wooden barrel equipped with a non corrosive steam line and mixer. For the solvent, dissolve 12 lbs. concentrated CP hydrochloric acid in about 25 gals. water contained in the barrel. Add "mill powder", agitate and heat with steam to 200°F. Maintain temperature for about 1 hour. Press using No. 206 press (2 frames). Press wash with cold water until chloride free (18 hrs.). Dry at 140°F. for 22 hours. It dries to a soft powder.

Appendix 3 - Procedure for Dispersion Milling and Finishing Alpha Phase PCONA-WOL TO Produce Beta Phase Pigment Quality PCONA-WOL

Charge a one gallon paint can with 3850 grams of steel balls (a mixture of 3/8" and 1/2"), 1000 grams rivets, 360 grams hot dry sodium chloride, 35 grams RT-566-D, and 7 grams solvent. Note: only two solvents have been tried so far, chloroform and Trichlene. Mill for 16 hours. Screen off the balls and rivets. Place the mill powder in a four liter beaker and extract the salt and iron by boiling with a hydrochloric acid solution made by adding 50 ml concentrated hydrochloric acid to 1 liter of water. After boiling 1 hour filter and wash with warm water until chloride-free. Dry at 140°F. for 16 hours. It dries to a soft powder.

NOTE-BOOK REFERENCES

Early Evidence of Existence of New Phase PCONA→NOL..NB 1132-48 p.154, 159

Chloroform Solubility of "Naphthanil Pigments".....NB 1232-35 p.176

Crystal Seeding Experiments.....NB 1268 p. 51

First Experiment to Prepare and Examine New Phase PCONA→NOL.....NB 1285 p. 97

Methyl Alcohol/H_2O Milling of New Phase Material....NB 1285 p. 144

Methyl Alcohol/H_2O Milling of New Phase Material....NB 1356-1 p. 26

First S.W. Trial of $CHCl_3$ Treatment of PCONA→NOL....NB 1285 p. 154

Second S.W. Trial of $CHCl_3$ Treatment of PCONA→NOL...NB 1285 p. 160

Determining Ratio of $CHCl_3$ to Pigment Necessary for Conversion.....NB 1285 p. 155

Acetone Treatment of PCONA→NOL.....NB 1356-3 p. 36

First Laboratory Salt Milling Experiment.....NB 1356-8 p. 82

Second Laboratory Salt Milling Experiment.....NB 1356-16 p. 134

S.W. Salt Milling Experiment.....NB 1356-12 p. 102

Seeking Solvents that Cause Phase Conversion.....NB 1356-11 p. 100

First Dispersion Milling of PCONA→NOL.....NB 1356-18 p. 140

Complete Conversion to Beta Phase for Purpose of X-ray Diffraction Characterization.....NB 1356-20 p. 155

Evaluation Study of New Phase Pigment.....NB 1356-17 p. 136