KN-50-16 BEHAVIOR OF COPPER PHTHALOCYANINE PIGMENTS IN PAINT SYSTEMS. I - APPLICATION OF ELECTRON MICROSCOPY AND X-RAY DIFFRACTION TO THE STUDY OF CRYSTAL GROWTH By: A. R. Hanke 1/49 - 8/50

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PIGMENT COLOR RESEARCH REPORT

Progress Report

Title: BEHAVIOR OF COPPER PHTHALOCYANINE PIGMENTS IN PAINT SYSTEMS. I APPLICATION OF ELECTRON MICROSCOPY AND X-RAY DIFFRACTION TO THE STUDY OF CRYSTAL GROWTH

Period Covered: JAN. 1949 TO AUG. 1950

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APPROVED BY: B.H. Perkins — DATE ISSUED: Oct. 4, 1950

Preface

This report is based on a paper prepared by A.R. Hanke and B.H. Perkins with the intent of publishing it in one of the scientific journals such as Ind. & Eng. Chem. Because of the critical patent situation surrounding the beta phase CPC pigment and the industrial importance of some of the finishing methods which are briefly referred to in the original draft, plans for publication were abandoned.

Table of Contents

I INTRODUCTION

The pigment copper phthalocyanine possesses certain outstanding characteristics, noteworthy of which are its great tinting strength, its excellent lightfastness, and its unusual chemical stability (1). Because of these excellent properties, copper phthalocyanine is extensively used in the pigment-consuming industries. Effective utilization of the full inherent qualities of this product in practical pigmented systems has presented certain problems, the one giving the most difficulty in paints being the tendency to change in tinting strength and hue on aging. These changes are well recognized by paint technologists and are generally attributed to changes in the size of the light scattering unit as a result of flocculation effect and/or crystal growth. Vesce (2) has demonstrated the occurrence of flocculation and crystal growth in systems pigmented with one type of copper phthalocyanine and has reported the influence of various solvents on the crystal growth of this sample, as revealed by examination with the light microscope following brief solvent exposure. No study of the crystal growth and flocculationbehavior of the several other available types of copper phthalocyanine pigments has been reported.

II TYPES OF COPPER PHTHALOCYANINE PIGMENTS:

Copper phthalocyanine pigments may be classified on the basis of their chlorine contents, which vary from approximately 0.3% to about 5.8% in the case of the commercially available types.[1] A second basis for classification is provided by crystal phase considerations. Two crystal phases of copper phthalocyanine have been recognized (3,4,5) the more stable phase being ordinarily designated as beta and the less stable phase as alpha. A classification of the usual commercial types of copper phthalocyanine pigments available in this country, on the basis of these considerations, is given in Table I. These pigment types are the ones examined with reference to crystal growth in typical paint systems or paint solvents. The designation "mono-chlor" refers to a product containing one chlorine atom per copper phthalocyanine molecule (6) while the "semi-chlor" type contains , on the average, one-half atom of chlorine per copper phthalocyanine molecule; a product containing about 4.4% chlorine is commercially available and has been designated in this report by the term "LB".

[1]The chlorinated blue pigment with chlorine content of 5.8% or less, which is the subject of this investigation, should not be confused with the highly chlorinated copper phthalocyanine green which contains up to about 50% chlorine. The chlorine content of the products under consideration is considerably lower; also the products are all blue and possess the same crystal structure as "chlorine-free" copper phthalocyanine. In contrast to this, the highly chlorinated pigment is green, and has an entirely different crystal structure.

Table I

Sample Designation	Sample Type	Crystal Phase	Approx. % Cl
MDD-1543, D-6623	Acid-Pasted, "Chlorine-Free"	Alpha	0.3
ABT-297-D Lot 349	Solvent-Ground, "Chlorine-Free"	Beta	0.3
BT-172-D Lot 433	Acid-Pasted, "Semi-Chlor"	Alpha	2.9
BT-284-D SD-38165	Solvent-Ground, "LB"	"	4.4
MD-1156-HT	Acid-Pasted, "LB"	"	4.4
MDD-1113	Acid-Pasted, "Mono-Chlor"	"	5.8

III EXPERIMENTAL:

Three sets of experiments were designed to observe the crystal growth behavior of the types of copper phthalocyanine listed in Table I.

A. Experiment No. 1 CRYSTAL GROWTH IN MINERAL SPIRITS

Some of each type of pigment was allowed to stand in mineral spirits at room temperature. "Varsol" No. 2, a mineral spirits purchased from Standard Oil Co. of New Jersey was used. From time to time, small amounts of pigment were withdrawn and observed by means of the electron microscope.

Mounts for the electron microscope were made by rubbing a few drops of the slurry with a spatula and thinning with more mineral spirits until a uniform dispersion was obtained. A drop of this thinner dispersion was then placed on a mounted preformed "Formvar" film.

In those cases where a change was observed to have resulted from the exposure, x-ray spectrometer records were obtained after filtering off the mineral spirits and air drying the residue. This was done to observe any change in crystal phase that might have occurred during the crystallization.

B. Experiment No. 2 CRYSTAL GROWTH IN A LACQUER VEHICLE

By ball mill grinding, typical lacquer enamels were prepared from the pigments listed in Table I with the exception of the "mono-chlor" and the acid-pasted "LB" types. The lacquer vehicle is designated as KV-36 and its composition is outlined below.

Lacquer Vehicle KV-36

Grinding Vehicle		T-3601	
*GE-2570	-53.3%	Butyl Acetate	-37.0%
Di butyl phthalate	- 5.3%	Toluol	-35.0%
Blown Castor Oil (Baker's #15)	- 2.7%	Ethyl Acetate	-12.5%
T-3601	-38.7%	Butyl Alcohol	-12.0%
		Ethyl Alcohol (23A)	- 3.5%

* A glyceryl phthalate resin modified with a non drying oil. See General Electric's catalogue on Glyptal Alkyd Resins for more detailed specifications.

Preparation of Blue Lacquer

Pigment	- 68 grams
Grinding Vehicle	-362 grams
Thinning Vehicle	-170 grams
Ball mill for	- 72 hours
Add Thinning Vehicle	-331 grams

Thinning Vehicle

1/4 sec. nitrocellulose (70% solids)	- 14.9%
1/2 sec. nitrocellulose (70% solids)	- 14.9%
T-3601	- 70.2%

This blue lacquer was placed in a can with a tightly fitting cover and stored in an oven at 50°C (122°F). From time to time portions were withdrawn and electron micrographs were obtained. The mounts were prepared by the following technique: a few drops of the lacquer were thinned with a few drops of T-3601 and the mixture was worked with a spatula on a suede finished "Carrara" glass plate until a uniform dispersion was obtained. A drop of this dispersion was then placed on a glass microscope slide and smeared out with another slide; the dried lacquer film so produced was floated on water and picked up by a mounting screen. In those cases where appreciable crystal growth took place, some of the pigment was extracted from the enamel and x-ray spectrometer records were obtained to observe any crystal phase change that might have occurred. The pigment was removed from the vehicle by thinning with the "thinner" designated T-3601 and centrifuging until most of the pigment was thrown down. After decantation the pigment was reslurried with more thinner and again centrifuged. The pigment was then vacuum dried at room temperature. Using this technique, some of the finer particles remained suspended, but since the primary purpose was to ascertain if crystallization was accompanied by a phase change, interest was centered mainly on the large crystallites and the loss of some of the fine particles was in reality an advantage.

C. Experiment No. 3 CRYSTAL GROWTH IN AN ALKYD VEHICLE

By ball mill grinding, a typical alkyd enamel was prepared of the same pigments used for Experiment No. 2. The alkyd resin used was a drying oil modified glyceryl phthalate, designated as Glyptal 2458. The enamel has the following composition:

Blue Alkyd Enamel

Pigment	- 84 grams
"Glyptal" 2458	-529 grams
Mineral Spirits (Varsol #2)	-251 grams
Grind	- 72 hours
Reduce with GE-2458	-314 grams

From time to time portions of the alkyd enamel were removed and electron micrographs were obtained. The dispersion was thinned for mounting by mixing a few drops of the enamel with a few drops of xylol. The thinned mixture was uniformly dispersed by working with a spatula on a suede finished "Carrara" glass plate. A drop of the thinned enamel was then placed on mounted preformed "Formvar" film.

In those cases when pigment was extracted from the vehicle for x-ray diffraction records, the extraction was made by centrifuging the slurry twice with mineral spirits, followed by a centrifuging with a mixture of equal parts of acetic acid, ethyl alcohol, and butyl acetate. The separation was difficult and never complete, but sufficiently good to obtain meaningful x-ray diffraction records.

D. Details Concerning Experiment 2 & 3

For about the first month of aging of the lacquer and alkyd enamels, the cans were removed from the oven every third day and were shaken for 10 minutes on a paint "rejuvenator" (manufactured by the Miracle Paint Rejuvenator Co.), and then replaced in the oven. This was done to make sure no settling to a hard cake occurred. It was subsequently observed, however, that no hard cake was formed even when the enamels were not shaken, so this practice was discontinued. Before any enamel was withdrawn for testing, the can was placed on the "rejuvenator" and was shaken for 10 minutes. The contents were then inspected with the aid of a spatula to be assured of good uniformity. Towards the latter part of the time series, when a tendency to skinning become evident, any skin present was removed by straining. Good dispersion before sampling was desirable because these masstone enamels were also extended with TiO_2 and examined spectrophotometrically. A critical discussion of these spectrophotometric curves will be given in the second report of this series.

For experiments number 2 & 3 the total aging time was one year. For the alkyd series, this total aging time was at a temperature of 50°C. For the lacquer series, the "semi-chlor" and the "LB" types were maintained at 50°C for 11 weeks and then at room temperature for up to one year. For the "Cl-free" alpha, and beta phase types, the lacquers were maintained at 50°C for 7 weeks and thereafter at room temperature up to a total time of one year.

After 7 weeks aging, the oven temperature was inadvertently raised for a short but unknown length of time and the lacquer cans blew their tops losing varying amounts of thinner. The loss in thinner was adjusted by adding T-3601 in sufficient quantity to bring the total solids back to the original value of 37%.

IV CRYSTAL GROWTH CHARACTERISTICS OF COPPER PHTHALOCYANINE:

Fig. 1 illustrates the extreme crystal growth experienced by the acid-pasted "chlorine-free" type copper phthalocyanine. From a material for which no crystals can be seen initially at a magnification of 35,000 diameters, the material takes on a completely crystalline appearance in three days in mineral spirits. A similar crystallization takes place in the lacquer and alkyd systems although the rate is slower in these media. The longest time interval shown for the figure is 9 weeks but the crystalline appearance is the same after one year aging.

This crystallization is accompanied by a crystallographic phase change. Fig. 2 shows x-ray spectrometer records of the pigment used in the lacquer system. The change in the diffraction pattern, particularly at 2θ values of 9.1° and 15.8° is evidence that a phase change has occurred.

Fig. 3 shows an alpha phase copper phthalocyanine pigment containing 2.9% chlorine. It is an acid-pasted product and is referred to as "semi-chlor" copper phthalocyanine. It grows crystals in all three media but to a lesser extent than does the comparable "chlorine-free" material. It should be particularly noted that the crystal habit is different in the lacquer than in the alkyd system. In the lacquer the crystals are of a feathery nature and tend to aggregate into sheaf-like bundles. In the alkyd system the crystals are more block-like in habit although there still is a tendency towards the acicular. Since the alkyd enamel contains considerable mineral spirits, it is not surprising to observe that the crystal habit in mineral spirits is about the same as in the alkyd enamel. A further observation to make from Fig. 3 is that in the case of the lacquer there is very little, if any, additional crystal growth after 5 weeks. In the case of the enamel, there is some evidence of continued crystal growth after 5 months. It appears that crystallization is more rapid in the lacquer system and is complete in a shorter length of time than in the alkyd system.

Crystal growth of the "semi-chlor" type is also associated with a phase change but the phase change is far from complete. Fig. 4 shows definite evidence of some conversion to the beta phase after aging for one year. The transformation is more pronounced in the lacquer system than in the alkyd system. It is most evident in straight mineral spirits, but in no case has it approached the completeness of the transformation characteristics of the alpha phase "chlorine-free" pigment.

ELECTRON MICROGRAPHS

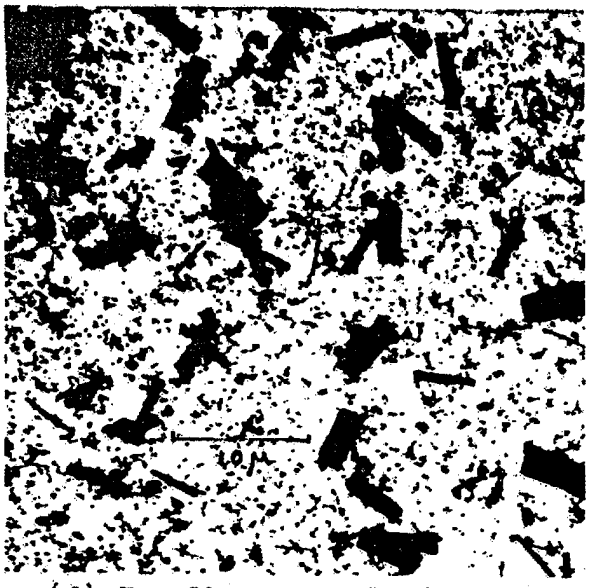
Figure 1

[illegible]-ATED CHLORINE FREE COPPER PHTHALOCYANINE

(a) Untreated

(b) In Mineral Spirits 3 Days

(c) In Lacquer [illegible]



(d) In Alkyd Enamel, 9 weeks

Figure 2
X-RAY SPECTROMETER RECORDS ILLUSTRATING PHASE CONVERSION
OF "CHLORINE-FREE" COPPER PHTHALOCYANINE

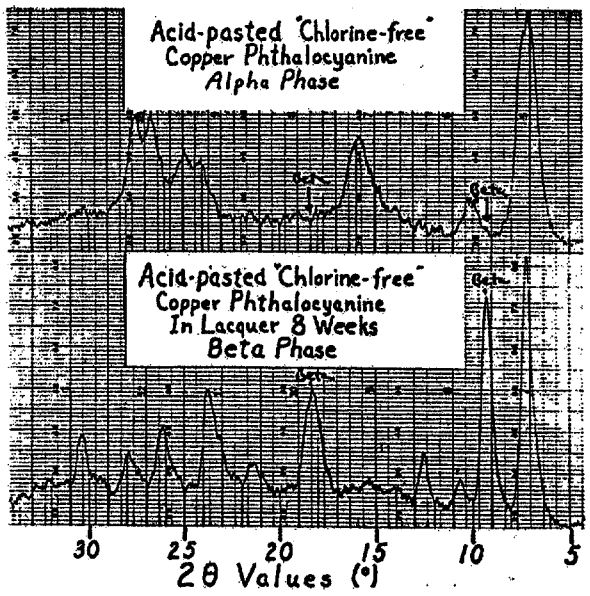
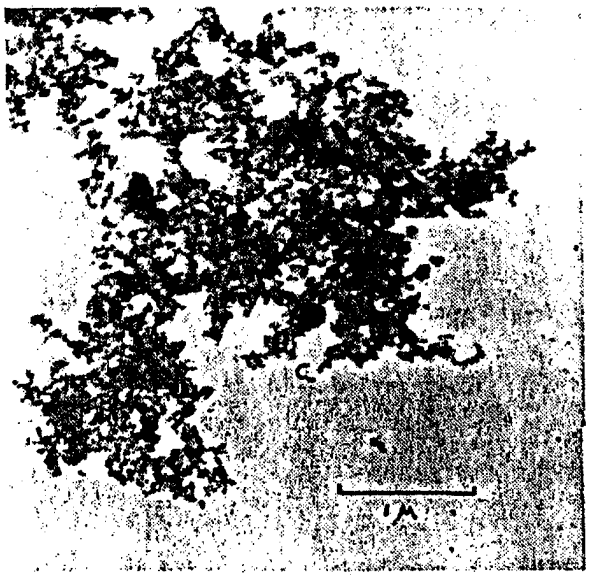
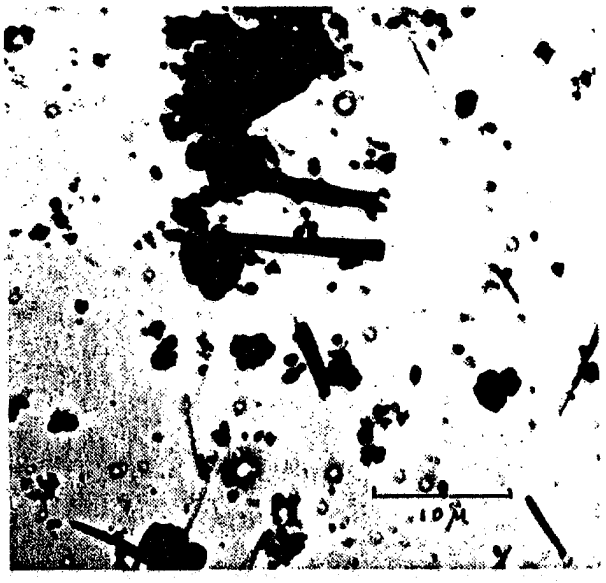


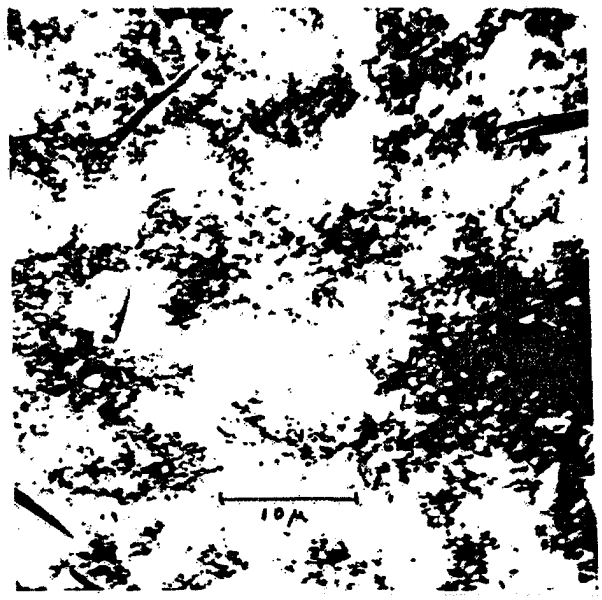
Figure 3
ELECTRON MICROGRAPHS OF ACID-PASTED "SEMI-CHLOR" (2.9% CHLORINE) COPPER PHTHALOCYANINE



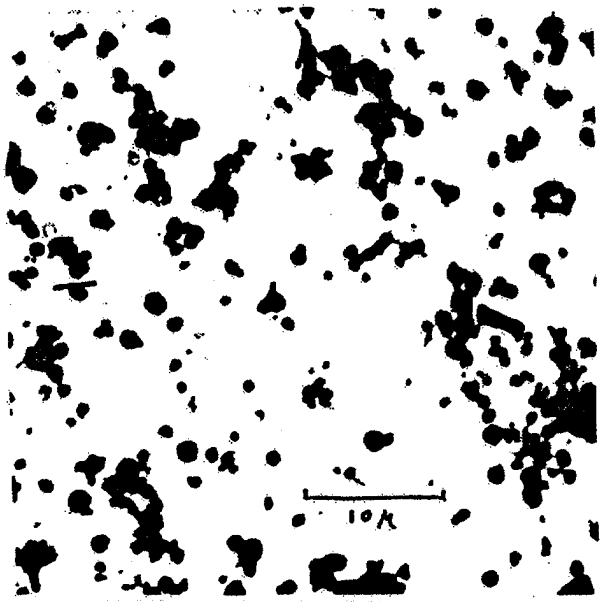
(a) Untreated



(b) In Mineral Spirits 5 Weeks



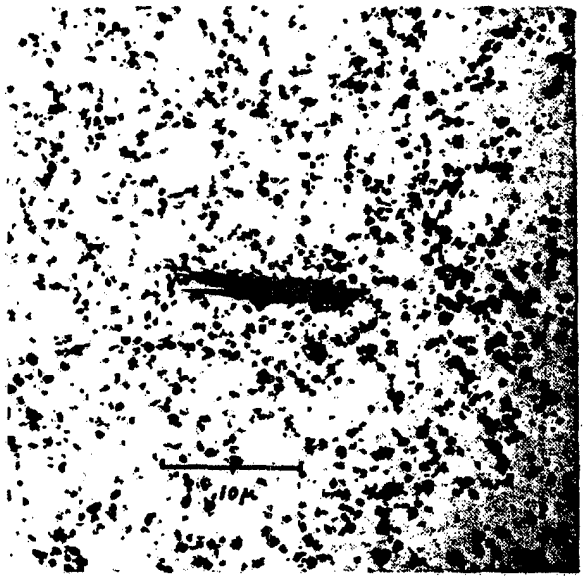
(c) In Lacquer 5 Weeks



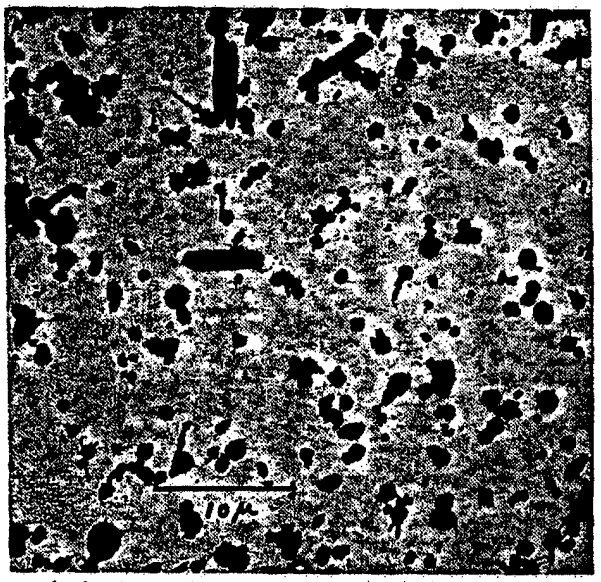
(d) In Alkyd Enamel, 5 Months

Figure 3 Cont'd

ELECTRON MICROGRAPHS OF ACID-PASTED "SEMI-CHLOR" (2.9% CHLORINE) COPPER PHTHALOCYANINE



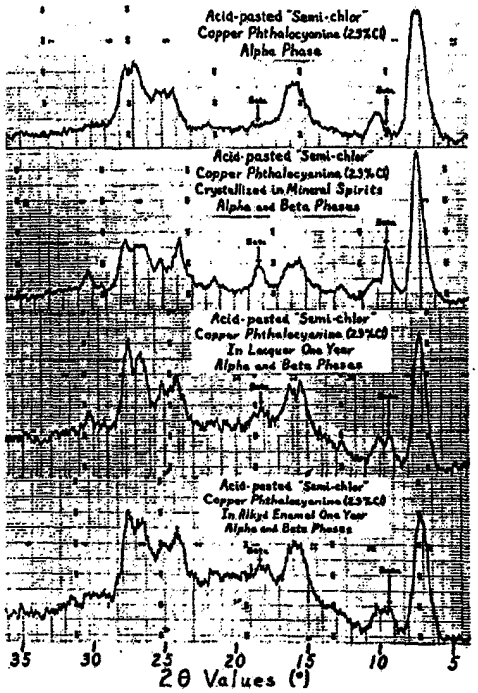
(e) In Lacquer 1 Year



(f) In Alkyd Enamel 1 Year

Figure 4

X-RAY SPECTROMETER RECORDS ILLUSTRATING PARTIAL PHASE CONVERSION OF "SEMI-CHLOR" (2.9%)Cl) COPPER PHTHALOCYANINE



In the case of the "LB" type pigments (chlorine content 4.4% and alpha phase). It was observed that if the pigment was finished by acid-pasting, far more crystal growth occurred than if the pigment was finished by solvent grinding. Fig. 5 shows this crystal growing property of an acid-pasted product containing 4.4% chlorine. No lacquer or alkyd enamel of this type of "LB" pigment was studied. That the crystal growth in mineral spirits is associated with a partial phase transformation is shown in Fig. 6 where the peak characteristics of the beta phase at the 20 value of 9.2° is clearly evident for the solvent exposed sample.

The solvent-ground type of "LB" pigment is also in the alpha phase. This pigment was observed in mineral spirits, a lacquer system, and an alkyd system. Fig. 7 shows that very little, if any, crystal growth occurs even after aging for one year. An occasional crystal does make its appearance but a typical non-crystalline field is shown. No evidence of any conversion to the beta phase is shown by the x-ray spectrometer records. Fig. 8 shows records of enamels aged one year and there is no evidence of any beta phase.

The alpha phase "mono-chlor" type is an acid-pasted CPC with a chlorine level of 5.8% and is the highest chlorine content pigment studied. This pigment tends to grow a lacy type of crystal in mineral spirits, as shown in Fig. 9. At this chlorine level, no phase change could be detected. Fig. 10 shows x-ray spectrometer records illustrating this point.

We now leave the alpha phase products and consider a beta phase copper phthalocyanine pigment. Fig. 11 shows a "chlorine-free" pigment, which differs from that of Fig. 1 in that it is in the beat phase wheras the "chlorine-free" pigment previously described was in the alpha phase. The crystals of this beta phase product show no evidence of crystal growth in any of the systems during the period of study which covered 5 months for the mineral spirits and one year for the lacquer and alkyd enamel. The pigment initially is shown to be crystalline in nature but these crystals, or more likely crystal fragments, do not show any measurable growth. The attempt failed to get a good dispersion for an electron micrograph of the alkyd enamel after aging one year but the dispersion is good enough to observe that the individual crystallites are still of about the same size. Far better dispersion was obtained with the lacquer and here it was easy to see that no growth has occurred.

V CAUSE OF CRYSTAL GROWTH:

The crystal growth which is observed with certain types of copper phthalocyanine under the aforementioned conditions is apparently associated with the following factors:

e 5

"LB" (4.4%Cl) COPPER PHTHALOCYANINE

(b) In Mineral Spirits 2 Weeks

re 6

TRATING PARTIAL PHASE CONVERSION

R PHTHALOCYANINE (4.4%Cl)

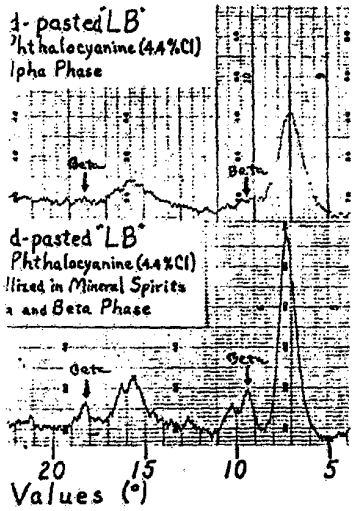
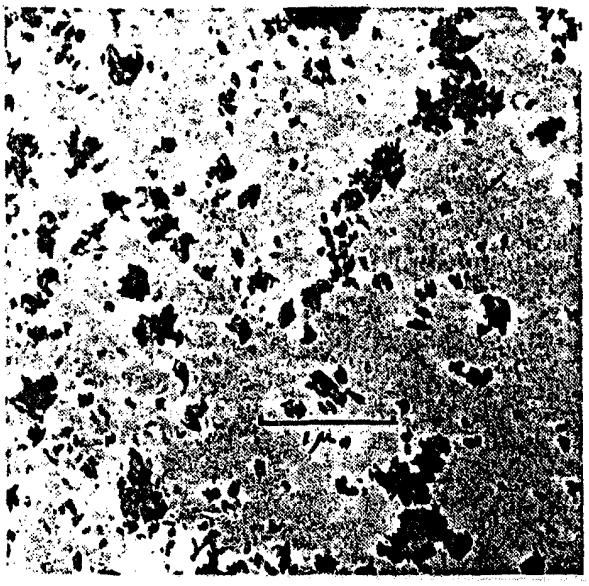
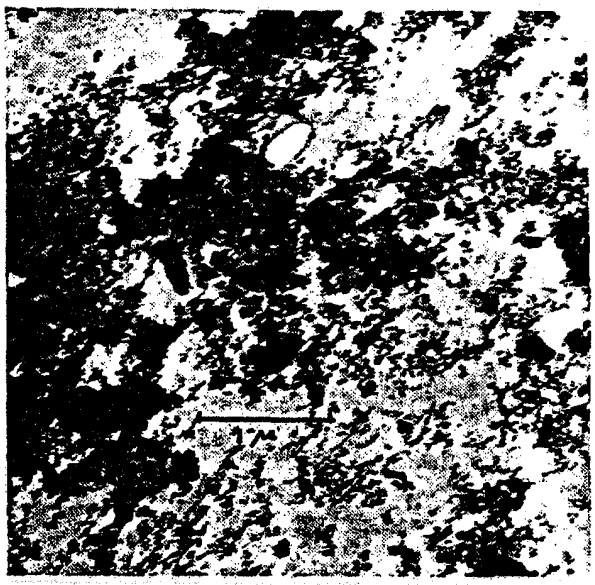


Figure 7

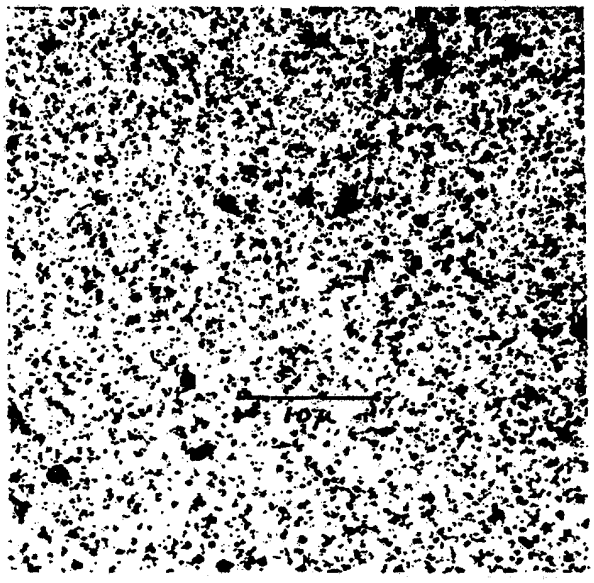
ELECTRON MICROGRAPHS OF SOLVENT-GROUND "LB" COPPER PHTHALOCYANINE (4.4%Cl)



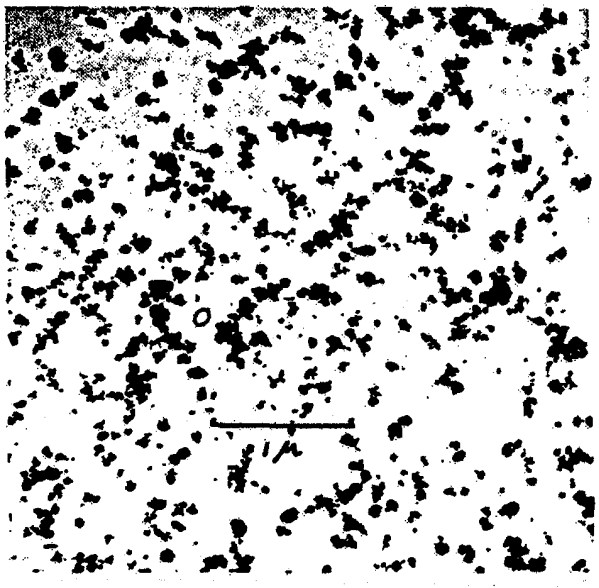
(a) Untreated



(b) In Mineral Spirits 5 Months



(c) In Lacquer 1 Year



(d) In Alkyd Enamel 1 Year

Figure 8

X-RAY SPECTROMETER RECORDS ILLUSTRATING STABILITY OF SOLVENT-GROUND "LB" COPPER PHTHALOCYANINE (4.4%Cl)

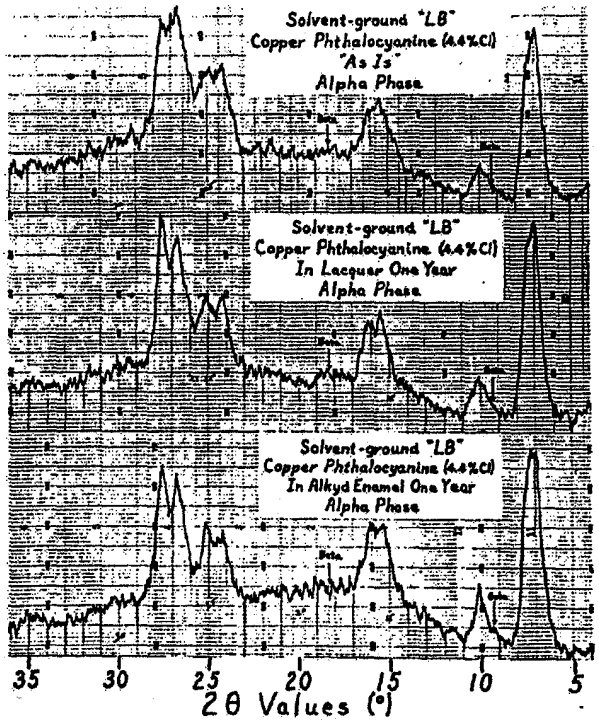
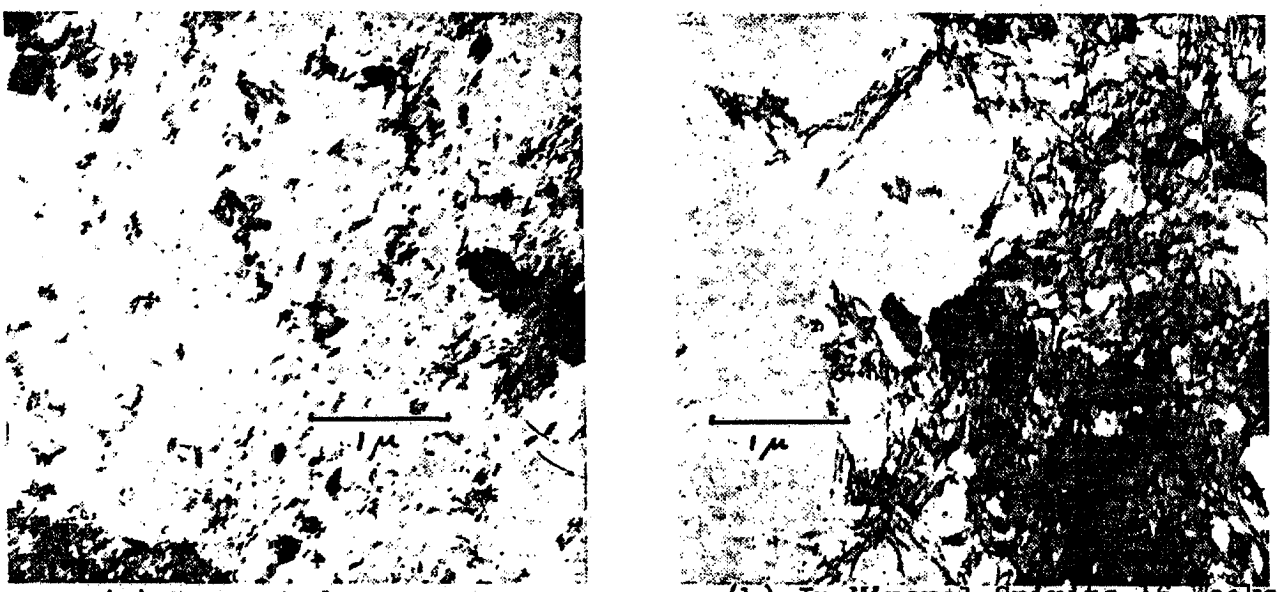


Figure 9

ELECTRON MICROGRAPHS OFACID-PASTED "MONO-CHLOR" COPPER PHTHALOCYANINE (5.9%Cl)



(a) Untreated (b) In Mineral Spirits 16 Weeks

Figure 10

X-RAY SPECTROMETER RECORDS ILLUSTRATING STABILITY OF ACID-PASTED "MONO-CHLOR" COPPER PHTHALOCYANINE (5.9%Cl)

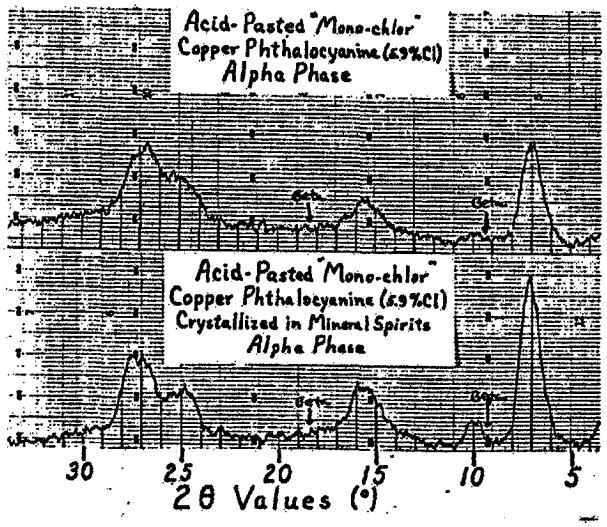
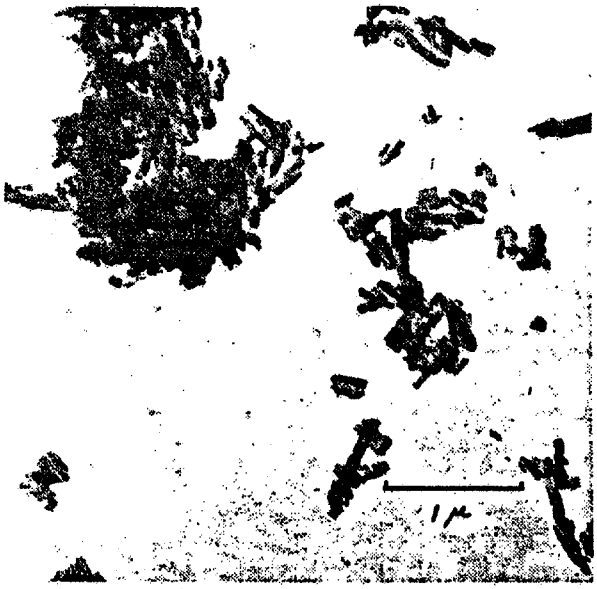
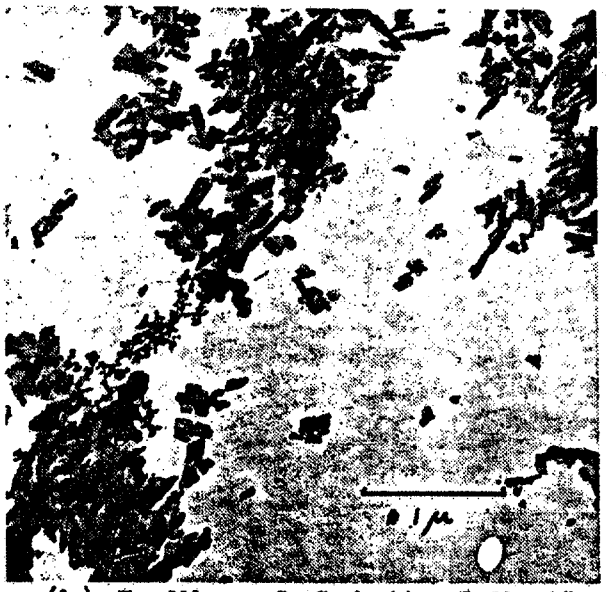


Figure 11

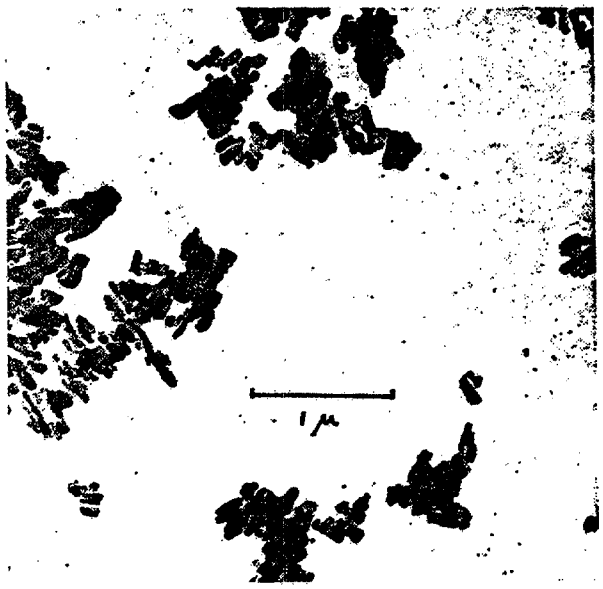
ELECTRON MICROGRAPHS OF SOLVENT-GROUND "CHLORINE FREE" COPPER PHTHALOCYANINE



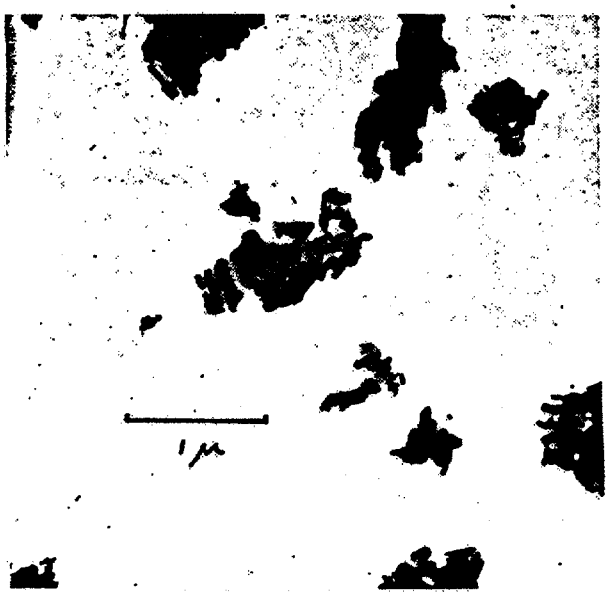
(a) Untreated



(b) In Mineral Spirits 5 Months



(c) In Lacquer 1 Year



(d) In Alkyd Enamel 1 Year

A. CHANGE OF PHASE

A transformation from the alpha phase to the more stable beta phase apparently brings about crystal growth; a growth in particle size has accompanied the phase transformation in all the investigated cases. This effect is most pronounced with acid-pasted "chlorine-free" copper phthalocyanine. With increasing chlorine content there is apparently a decreased tendency for transformation to the beta phase. In the case of products containing up to 4.4% chlorine, the existence of the beta phase can still be established, but we have been unable to establish the existence of the beta phase in samples of chlorine content as great as 5.8%. The decrease in crystal growth tendency on increasing the chlorine content from 0.3% to 5.8% or more is believed to be due to the stabilizing effect of the chlorine on the alpha phase. Obviously, if the material is initially in the beta phase - as in the case of the sample cited previously - the force promoting such phase transformation is lost.

B. CRYSTAL STRAIN

The hypothesis that crystal strain also contributes to the tendency towards crystal growth is suggested by the fact that "LB" type CPC does not grow crystals if solvent-ground (Fig. 7), but does grow crystals if acid-pasted (Fig. 5). It is reasonable to suppose that crystallites formed suddenly through the rapid flooding of a sulfuric acid solution would exist in a state of greater [illegible] strain than a product solvent-ground from crude CPC. As previously mentioned, the higher the chlorine content, the less tendency there is to grow crystals, but even with the "mono-chlor" type, which is the highest percent chlorine type studied, the acid-pasted product still grew a very lacy type of crystal (Fig. 9). Here again this tendency towards crystal growth is believed to be associated with the fact that the product is acid-pasted and the crystallites are in a condition of strain. The relief of this strain through recrystallization can account for some of the crystal growth observed among some CPC pigments. This mechanism of crystal growth has long been recognized in the metallurgical field but has received little attention in the field of organic chemistry.

The crystal strain hypothesis stated above is not to be confused with the well recognized tendency of large crystals to grow at the expense of the small ones owing to the larger surface energy of the latter. In the case of the particular systems under examination this factor does not appear to be very important. For example, in the case of the stable "LB" type pigment in which the particles are of size comparable to the smallest which have been observed with copper phthalocyanine pigments, and with which this influence would be expected to be operative, no appreciable crystal growth is observed over a period of the year.

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VI CRYSTAL GROWTH ASSOCIATED WITH LOSS IN TINTING STRENGTH:

One of the tinctorial changes that can be expected with crystal growth is a loss in tinting strength. We have found that the tinting strength of copper phthalocyanine pigments increases with decreasing particle size down to the smallest particle size which we have been able to obtain. The particle size estimates were obtained through nitrogen adsorption measurements made according to the method of Brunauer, Emmett, and Teller (7). This loss in tinting strength as the average particle size increases is illustrated in Table II. These data were derived from a grinding study where the different particle sizes were obtained by different degrees of grinding. This work was reported by B. H. Perkins in KM48-5.

That an increase in particle size due to crystal growth causes a loss in tinting strength is very evident in the case of the "chlorine-free", alpha phase type of CPC, which grows crystals very vigorously (see Fig. 1). This strength loss will be illustrated in the second report which will deal with the spectrophotometric interpretation of the changes occurring in these enamel systems. For this report it will suffice to say that the strength loss in this instance is sufficient to reduce materially the value of this type of pigment for application in paint systems.

It is worthy of note that strength loss due to crystal growth of copper phthalocyanine is also observed in pigmented systems apart from the paint industry. For example, it is very noticable in the coloring of transparent vinyl plastics where crystal growth can be easily demonstrated in a common plasticiser such as dioctyl phthalate. This ester is one that Vesce (2) would classify as a "safe" i.e., non crystal growing solvent.

Flocculation or agglomeration of the pigment particles plays an important role in determining pigment strength; an increase in flocculation causes a decrease in pigment strength. In the case of the pigments under examination, flocculation seemed to occur to a lesser degree for the "strain free" solvent milled pigment than for their "strained" acid-pasted counterparts. In the two paint systems studied, the degree of flocculation appeared to be a complicated function of the age of the enamel so that this effect tended to obscure the crystal growth effects. the changes in flocculation will be discussed in detail in the second report.

Table II

Surface Area Sq. Meters per gram	*Avg. Particle Size (Side of square cross-section in microns)	Relative Tinting Strength
98.1	0.029	100
81.1	0.035	92
62.5	0.046	81
22.8	0.125	50

*Calculated from the specific surface data assuming crystallites of square cross-section parallelepipeds, a Sp. Gr. of 1.54, and a ratio of length to width of 5. The equation is given below:

Equation

$$W = \frac{1}{pA} \times \frac{2 + 4R}{R}$$

W = Side of square cross-section in microns

p = Specific gravity

A = Specific surface in square meters per gram

R = Ratio of length to width

SUMMARY:

1. The evidence suggests that the tendency of copper phthalocyanine to grow crystals in paint media is a consequence of the tendency of the system to reach a lower energy level through crystal phase transformation, and by relief of crystal strain through recrystallization.

2. Crystal growth can be minimized in any of the following ways:

   A. Increase the stability of the alpha phase through the introduction of chlorine into the molecule.

   B. In the case of "chlorine-free" copper phthalocyanine, prepare the pigment in the form of the more stable beta phase.

   C. Reduce the crystal strain by allowing a recrystallization during pigment finishing.

3. Copper phthalocyanine pigments which have been finished in a "strain-free" condition through solvent milling, and in

which the phase stability has been increased thru the introduction of 4.4% chlorine into the molecule do not show crystal growth in typical paint systems. These conditions are realized in our BT-284-D type pigment.

4. Beta phase "chlorine-free" copper phthalocyanine pigments (e.g. BT-297-D) are crystal stable.

5. Crystal growth is associated with a loss in pigment strength and a change in hue (the larger the particle size, the redder the hue) but because of changes in degree of flocculation associated with many paint systems, one cannot attribute all strength changes to crystal growth. As flocculation comes under better control, crystal growth effects will assume more importance as a cause for loss in pigment strength.

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