Serial No.

Copy No. KN-48-3

#1 - Numerical File

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

KN-48-3

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

FINAL REPORT

TITLE: COPPER PETHALOCYANINE PIGMENTS. PHYSICAL STUDIES I. PARTICLE SIZE AND DIMORPHISM

Period Covered: APRIL 1946 - DECEMBER 1947

FILE: 223.4

DATE: 3/29/48

223.4

N42152

Serial No. KN-48-3

Copy No. 1

Copy to:

#1 - Numerical File
2 - Research Office (223.4)
3 - Library File
4 - Imperial Chemical Industries, Ltd.
5 - " " " "
6 - " " " "
7 - W. F. Spengeman
8 - Jackson Laboratory - Orchem
9 - Extra
10 - Extra
11 - Extra
12 - Extra

NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

FINAL REPORT

TITLE: COPPER PHTHALOCYANINE PIGMENTS. PHYSICAL STUDIES I. PARTICLE SIZE AND DIMORPHISM

PERIOD COVERED: APRIL 1946 - DECEMBER 1947.

CHARGE: A-II-C (229)

SUBMITTED BY: B. H. Perkins 3/26/48 DATE SUBMITTED: 2/6/48

APPROVED BY: A. Siegel. 3/29/48 DATE ISSUED: 3/29/48
2/13/48

I N D E X

TABLES:

FIGURES:

INTRODUCTION:

The studies reported here were undertaken by the Newark Physics Laboratory to provide information for use in the general investigation of conditioning crude copper phthalocyanine for use as a pigment. The Physics Laboratory program was an outgrowth of attempts to obtain a satisfactory explanation for the differences in behavior, on ball milling in kerosene, of "chlorine-free" copper phthalocyanine and copper phthalocyanine containing an appreciable proportion of chlorine. The major portion of the work discussed herein has accordingly been concerned with investigation of the effect of ball mill grinding in solvent on the physical properties of the pigment.

This report covers the period April, 1946 - thru December, 1947; the greater portion of the work was carried out by Dr. Karush during August-December, 1946. As Dr. Karush has left the employ of the Company, the work is being reported by the writer, under whose general supervision most of it was carried out.

SUMMARY AND CONCLUSIONS:

Chlorine-free copper phthalocyanine is polymorphous, two crystalline phases having been identified by x-ray methods. Crude chlorine-free copper phthalocyanine (CPC), chlorine-free CPC which has been exposed to aromatic hydrocarbon solvents, or chlorine-free material which has been heated to high temperatures (e.g. 300°C) exist in what is designated as the beta structure. On the other hand, all very small particle size copper phthalocyanine (i.e. material of strength greater than that of BT-172-D standard), regardless of chlorine content, exists in a second structure which is designated as alpha.* Salt-milled or acid-pasted CPC, whether chlorine-free, LB type (see Glossary), or monochlor CPC, exists in this alpha form. In the case of chlorine-free material, heating, or exposure to aromatic hydrocarbon solvents, of the alpha phase pigment results in its conversion to the beta structure, which latter phase appears to be the more stable for such chlorine-free material.

Both crude and finished LB type copper phthalocyanine which contains as much as 4.4% chlorine exist in the alpha structure, regardless of the method of finishing or of exposure to solvents. The beta structure is not observed with such material. Similarly, only the beta form is found in the case of monochlor CPC (5.8% Cl).

- -

*The nomenclature originally adopted by the Newark group differed from that indicated, the phase designated here as beta being called alpha in accordance with conventional practice of so designating the form which is the more stable at room temperature. Subsequently, information was obtained which showed that Pigments Department practice differed from that used by other groups. Accordingly, to avoid confusion, the nomenclature indicated in this report was adopted.

The information obtained in the course of this investigation supports previous findings to the effect that, in the particle size range investigated, the strength of the pigment increases with decreasing particle size (Ref. 1 and 2). To obtain the strength of standard copper phthalocyanine toner BT-172-D, it appears that the pigment must have a surface area of the order of 50-60 square meters per gram.

Determination of specific surface of the pigment appears to provide an adequate measure of its particle size. Useful estimates of particle size, which in general indicate the same relative size order as do specific surface data, can be obtained from line breadth measurements of the x-ray patterns of the pigment samples. No completely satisfactory electron micrographs have been obtained of CPC samples of particle size of 0.1 micron or less, owing to inability to disperse the small particles to the desired degree. However, qualitative confirmation of the particle size estimated from specific surface has been obtained in certain cases by means of electron micrographs.

FUTURE WORK:

The formal Physics Laboratory program of phthalocyanine investigations was discontinued at the end of 1946 owing to the changed personnel situation in that laboratory. Since that time, a limited amount of work has been carried on for the phthalocyanine research group on a service basis. It is planned to continue this arrangement until current problems associated with "start-up" of the new plant have been disposed of, at which time a long range investigation program will be formulated.

DISCUSSION:

Polymorphism of Copper Phthalocyanine

Study of the crystal structure of copper phthalocyanine was undertaken in 1946 to provide information for use in the study of conditioning methods for copper phthalocyanine pigments being carried on by the Newark research group. The initial investigations by the Physics group were concerned with attempts to provide an explanation for the observation that although a pigment of strength comparable to that of BT-172-D standard could not be prepared by ball-milling crude chlorine-free CPC in kerosene, no difficulty was encountered in obtaining samples of strength superior to that of the current standard by grinding chlorine-containing CPC, such as the monochlor or LB type, under comparable conditions (Refs. 3, 4).

Information available in the literature regarding crystal structure and phase composition of CPC (Ref. 5) suggested that the difficulty of obtaining satisfactory size reduction in the case mentioned might be associated with the polymorphism of CPC. Unfortunately, the data were inadequate to permit satisfactory conclusions regarding this point. Accordingly, study of the significance of the phase relationships of CPC and of their relation to the problems under consideration was inaugurated.

It has been found as a result of this study that the investigated copper phthalocyanine pigments can be classified (Table I) into two general groups. Those samples giving an x-ray spectrometer record like that shown in Figure I have been classified as having the alpha structure, while those giving a record like that of Figure II are said to have the beta structure. A given type pattern is most easily distinguished from the other one by the presence in the beta pattern of marked diffraction maxima at 2θ values of 18.2° and 9.2° which are absent in the alpha pattern. (The 2θ = 9.7° "peak" in the alpha pattern is significantly displaced from the position of the aforementioned peak at 2θ = 9.2°).

TABLE I

CLASSIFICATION OF COPPER PHTHALOCYANINE PIGMENTS ACCORDING TO STRUCTURE

GROUP 1 Alpha Structure Only	GROUP 2 Beta Structure
Salt-milled CPC*	Crude Chlorine-free CPC
Acid-pasted CPC*	Chlorine-free CPC after exposure to hydrocarbon solvents**
Monochlor CPC, either crude or finished.	
LB type CPC (4.4% Cl), either crude or finished	Chlorine-free CPC after heating at 300°C for 3 hrs.**
Acid-pasted or salt-milled chlorine-free CPC ball-milled in alcohol or acetone.	Crude semi-chlor CPC***
	Semi-chlor CPC (crude, acid-pasted or salt-milled) after severe exposure to ± hydrocarbon solvents.***
	Crude chlorine-free CPC ball-milled in solvents.
	Crude semi-chlor CPC ball-milled in solvents.***

*Applies to all samples, regardless of chlorine content, in the investigated range 0.1 - 6% Cl, which have been finished by acid-pasting or salt-milling to yield products of standard strength and have not subsequently been exposed to solvents or heated.

**Holds for samples finished by any of the investigated methods: acid-pasting, salt-milling, solvent-milling.

***Both phases present.

The following generalizations are supported by the experimental results:

(1) All samples of properly acid-pasted or salt-milled CPC, as indicated by strength greater than that of standard BT-172-D, exhibit the alpha structure, regardless of chlorine content.

(2) All samples of monochlor (5.8% Cl) CPC, or of LB type CPC containing as much as 4.4% chlorine, exhibit the alpha structure only. The beta structure has not been observed with any samples of this type examined thus far.

(3) The beta structure has been observed only with relatively large particle size pigments; despite repeated attempts, no beta phase sample of strength greater than that of BT-172-D has been prepared. Conversion of the alpha phase to the beta has resulted in crystal growth in all cases observed thus far. The largest surface area observed thus far with beta structure CPC is approximately 50 square meters per gram.

(4) No alpha structure sample of very small specific surface (i.e. large particle size) has been found thus far. The minimum surface area observed with alpha structure CPC, is approximately 20 square meters per gram. This value is less than the surface area found with some beta phase samples, indicating that the size range of alpha and beta structure materials overlap.

(5) LB type CPC containing only 3.5% chlorine, (as well as some - but not all - samples containing 4.0% Cl), and semi-chlor CPC (3.0% Cl) are dimorphic. The crude pigment or the solvent-milled sample in these cases is apparently a mixture of the alpha and beta phases; the acid-pasted or salt-milled pigment is in the alpha phase.

(6) The two phases can coexist in the same sample.

Certain of these generalizations will be discussed at greater length in the sections which follow.

Determination of Relative Proportion of Beta Structure Material in Mixtures with the Alpha Phase.

The presence of a small proportion of the beta phase in mixture with the alpha phase can be most easily detected by means of the diffraction maximum at $2\theta = 9.1\text{-}9.2^{\circ}$ which is given by the beta phase. The effect of mechanically mixing 10% and 30% (on basis of the mixture) of beta phase CPC with the alpha phase (acid-pasted CPC) is clearly evident on comparison of Figures III and IV with Figure II. It is apparent that the presence of as little as 10% of the beta phase is recognizable in this case.

It should be noted, however, that crude, very large particle size beta phase CPC was used in making the mixture containing only 10% of the beta phase, whereas relatively small size solvent-milled chlorine-free material was used in making the mixture on which Figure IV is based. A comparison of a mixture (70% alpha, 30% beta), made with use of crude chlorine-free CPC, with the aforementioned one, reveals that the solvent-milled chlorine-free CPC produces less of a change in the x-ray diffraction pattern than does the crude (large particle size) CPC; accordingly, it appears desirable to repeat the study using solvent-milled CPC. The difference between the effect of the crude CPC and that of the solvent-milled CPC does not appear to be sufficient to alter the conclusions presented here, however.

Tinctorial Effect of Beta Phase

All the commercial CPC pigments examined thus far have been in the alpha phase and this phase appears to be tinctorially more desirable than the other one. Samples which contain an appreciable proportion of beta structure CPC are greener and less intense (duller) than the corresponding pigment in the alpha form. It is suspected that at least some of the apparent dullness of beta phase pigment is a consequence of the fact that all such samples are of relatively large particle size as experience has shown that in the case of CPC pigments, tinctorial intensity increases as particle size decreases. In any event, the beta phase is objectionable from the tinctorial standpoint, in CPC for pigment use.

Effect of Chlorine Content on Structure

It is evident from the information presented in Table I that the beta structure is apparently the more stable one in the case of "chlorine-free" CPC, and that alpha phase chlorine-free CPC tends to be converted into the beta phase by exposure to suitable liquids or by heating. The examined samples of Monochlor (5.8% Cl), or Newark LB type of chlorine content of 4.4% or greater, were found to exist only in the alpha structure, regardless of method of finishing, heating or exposure. Crude semi-chlor CPC (3% Cl) exists largely in the beta form while crude LB type CPC containing only 3.5% chlorine contains some beta phase.

In the case of the compounds of relatively great chlorine content (>4.4% Cl) prolonged exposure to hydrocarbon solvents do effect some slight change in structure, although even after such treatment there is no definite evidence for the presence of the beta form.

There appears to be a general increase in stability of the alpha structure with increasing chlorine content up to a chlorine content in the range 4-5%, beyond which changes in chlorine content are apparently productive of no marked effects. As previously noted, crude chlorine-free CPC (.1 - .3% Cl) exists in the beta structure, as does also crude semi-chlor CPC (3% Cl) to a large extent, and acid-pasted or salt-milled portions of such pigments revert to the beta structure on exposure to suitable solvents (e.g. xylene or trichlorbenzene). Acid-pasted or salt-milled LB type CPC made by the Newark process similarly undergoes a phase change on exposure of this type when the chlorine content is only 3.5%; when the chlorine content of the LB pigment is 4.4%, no major change results on such exposure. It appears that the stability of the alpha phase in the case of the aforementioned LB type pigment undergoes relatively abrupt increase with increase in chlorine content from 3.5 to 4.4%; it is worthy of note also that the presence of beta structure material in crude LB CPC was evident when the chlorine content was only 3.5% but was not observed with a sample containing 4.4% chlorine. Present indications are that there may be a "critical" chlorine content for stability of this type pigment in the range 4-4.5% Cl but data bearing on this point are not conclusive and additional study is necessary.

It is obvious that a considerable quantity of chlorine-free CPC must be present in LB type CPC which contains only 4.4% chlorine, as the chlorine content is 5.8% when only chlorine containing CPC is present. It appears that in the case of LB type pigment, the chlorine-containing portion tends to stabilize the chlorine-free material, as the change resultant from exposure to aromatic hydrocarbon solvents of LB (4.4) CPC is very much less than would have been expected from its necessary content of chlorine-free pigment.

Effect of Chlorine Distribution on Phase Stability

It appears that the crystal stability of alpha structure CPC of a given chlorine content is promoted by distribution of the chlorine in such a way that no molecule contains more than one chlorine atom. This is suggested by the fact that, for the same chlorine content, LB type CPC samples prepared with use of a sample of chlorphthalic anhydride (ex Niagara Alkali Co.) known to contain a considerable proportion of dichlor phthalic anhydride are appreciably less stable than samples made with Newark process chlorphthalic acid which contains less of the dichlor materials. Indications have been obtained that a more stable product results when LB type CPC is prepared with good agitation, assuring uniform mixing of the reactants, than when poor agitation is used. With poor agitation, the possibility of non-uniform distribution of the available chlorine is increased (Ref. 6).

Methods of Effecting Phase Changes:

Salt milling and acid-pasting by the techniques used for the production of small particle size pigments yield largely - if not entirely - the alpha structure, regardless of chlorine content of the CPC, in the investigated range, 0.1% - 6% Cl. " "Finishing" of pigment by ball-milling in solvents may or may not result in phase change, depending on pigment type and nature of solvent. In general, it may be said that the possibility of effecting anything approaching quantitative conversion from beta phase to alpha phase by this technique (solvent grinding) can be excluded, but a change from the alpha structure to beta structure can be brought about by grinding alpha type chlorine-free CPC in suitable solvents such as hydrocarbons or trichlorbenzene. For example, ball milling of previously acid-pasted or salt-milled (i.e. "alpha" material) chlorine-free CPC in kerosene results in marked loss in pigment strength and in change to the beta phase; no such change occurs, however, on treatment of LB or monochlor CPC in this way. On the other hand, no phase change results if the milling of chlorine-free pigment takes place in acetone or isopropyl alcohol.

The minimum chlorine content of crude CPC necessary to insure adequate phase stability so that particle size reduction can be effected by the ball-milling technique cannot be specified with great precision at present. Semi-chlor CPC (3% Cl) appears to represent approximately the minimum chlorine content of crude CPC for satisfactory grinding results in kerosene insofar as pigment strength is concerned. It should be noted that the chlorine content for satisfactory grinding is not necessarily the same as the chlorine content necessary to insure complete absence of the beta phase). The solvent-milled product in this case is approximately equal in strength to BT-172-D, but is greener in hue, and contains a large proportion of "beta" material.

Crude chlorine-free CPC is improved slightly in strength by ballmilling in kerosene, but it has not been possible to achieve strength more than 85% of that of BT-172-D in this way; when ground in alcohol it is possible to attain pigment strength only slightly less than that of current standard commercial pigment (BT-172-D), which is considerably less strength than can be realized if the pigment is converted to the alpha phase (e.g. by acid pasting) before grinding in alcohol. When the crude pigment is ground in alcohol, the finished material is greener than the standard product; the pigment in this case is largely - if not entirely - in the beta structure. If the crude material is converted to the alpha phase (e.g. by acid pasting) it retains that structure of subsequently ground in alcohol; if ground in kerosene, it reverts to the beta phase with loss in strength.

Transformation of alpha phase material into the beta phase also can be brought about in the case of chlorine-free CPC by means of heating. Heating salt-milled (alpha structure) chlorine-free CPC in vacuo at 300°C for 3 hours results in substantially complete conversion to the beta form and effects marked growth in particle size. Heating for 2 hours at 205°C (open air) resulted in only slight phase change.

Effect of "Sulfation" on Crystal Structure

At one time it was believed that a considerable part of the tinctorial improvement resultant from "sulfation" of LB/CPC (i.e. formation of CPC sulfate by addition of concentrated sulfuric acid to the condensation slurry, followed by reconversion to CPC by hydrolysis) was a consequence of conversion of any of the tinctorially undesirable (green) beta phase CPC present to the alpha structure. The evidence now indicates that such conversion is of minor importance in the case of chlorine-containing CPC of the type to be manufactured by the Pigments Department (4.4% chlorine). In this case the absence of any detectable amount of beta phase in the crude pigment before sulfation has been definitely established and no phase change is evident as the result of the treatment. This should not be interpreted, however, as meaning that a change could not be brought about were the pigment in the beta structure before sulfation, as it appears possible that such change could be effected. We have not investigated this point, however, in any detail.

Preparation of Beta Structure CPC of Good Pigment Strength

Attempts were made to prepare samples of beta structure CPC of tinctorial strength comparable to that of commercial phthalocyanine pigments, all of which examined to date have been alpha structure material. It was considered not inconceivable that such small particle size CPC, even though chlorine-free, would be resistant to crystal growth.

Attempts to transform small particle size alpha structure pigment into beta phase material of approximately the same size particles were unsuccessful; in all cases in which such phase transformation took place, pronounced particle size growth also resulted, so that the product was of poor strength. This was true when the transformation resulted from heating, as well as when it was brought about by solvent exposure. Only by ball-milling in selected non-hydrocarbon solvents (e.g. alcohol) has it been possible to obtain beta phase pigment of strength approximating that of the commercial standard, and even in this case such strength is barely achieved and then only with difficulty. The maximum surface area observed with such material is 47 square meters per gram as compared to values of 95 found with solvent-milled LB type pigment.

Beta structure solvent milled pigment was found not to be completely resistant to crystal growth on exposure to aromatic hydrocarbon solvents, and was also poor in tinctorial qualities, being green and dull compared to the corresponding acid-pasted sample. As the result of these findings, the interest in preparing strong beta-structure pigment has decreased considerably.

The difficulties encountered in the aforementioned attempts at preparing strong pigments by ball-milling chlorine-free CPC in hydrocarbon solvents is readily explicable on the basis of the findings discussed in the foregoing sections.

Programs involving study of conceivable means for direct preparation of pigment of small particle size, investigation of the effect of pressure on phase stability, and study of the mechanism of phase transformation by means of salt milling, were formulated, but were discontinued owing to lack of staff following the change in personnel of the Physics Laboratory.

Determination of Particle Size From Specific Surface.

Determinations of specific surface of copper phthalocyanine pigments by the Brunauer-Emmett-Teller technique involving nitrogen adsorption (Ref. 12) have, in general, provided data from which useful estimates of particle size can be made. However, in certain cases the method apparently leads to serious error. For example, extraction of the soft texture treating agent (naphthenic acid) which was present in one sample to the extent of approximately 10%, apparently increased the surface area from 16.3 to 77.0 square meters per gram.* The method also yields obviously erroneous values for the specific surface of acid-pasted samples which have been dried without special treatment. For example, in the case of one dried sample of acid pasted material, a surface area of only 0.4 square meters per gram was found, which corresponds to particles which should be visible microscopically. The misleading results in these cases are apparently a consequence of cementation during drying.

Particle size data for representative samples are shown in Table II.

- -

Footnote:

*This matter was reviewed with Prof. Emmett by Prof. Seitz at our request. No satisfactory explanation for the change was achieved. It is conceivable that naphthenic acid can "cement" the particles together.

TABLE II

PARTICLE SIZE OF CPC SAMPLES (REF.10)

SAMPLE	X-RAY[3] (dia)	SURFACE AREA					
		Meters²/gr.	Spheres[2] (dia)	Prisms[x] W	Prisms[x] 1	Electron Micrographs[xx] W	Electron Micrographs[xx] 1
LB Type, Crude CPC	(0.022)μ	22.8	0.17μ	0.13μ	0.51μ	-	- μ
LB Type, Acid-pasted	0.014	56.2	0.069	0.050	0.21	0.04	0.12-.14
LB Type, Solvent grd.	0.017	85.9	0.045	0.035	0.14	0.02-.04	0.09-.14
LB Type, Solvent grd.[1]	-	94.9	0.041	0.031	0.12	-	-
LB Type, Salt-milled	0.013	88.8	0.044	0.033	0.13	0.03-.04	0.08-.14
Semi-chlor, acid-pasted	0.015	98.1	0.040	0.030	0.12	-	-
Cl-Free, Crude CPC	-	4.1	0.95	0.70	3.5	0.5-1	2-4
Cl-Free, Acid-pasted	0.015	50.0	0.078	0.057	0.29	-	-
Cl-Free, Solvent grd.	0.036	47.3	0.082	0.060	0.30	-	-
Cl-Free, Salt-milled	0.015	77.6	0.050	0.037	0.19	-	-

x Particles assumed to be rectangular parallelepiped with length/width = 4. See Reference 8.

xx No completely satisfactory micrographs have been obtained. Data given are order of magnitude only, and represent results of visual estimates without attempt at detailed statistical analyses of data.

1. Strong type solvent-ground pigment.

2. Calculated from equation.

$$\text{diameter (microns)} = \frac{3.90}{\text{Area in meters}^2 \text{ per gram.}}$$

3. See appendix. Also ref.11.

X-Ray Methods

Estimation of particle size from x-ray line broadening has also provided useful data. The relative sizes obtained by the x-ray method are in general agreement with those calculated from specific surface data (Table II). The size data obtained from x-ray methods indicate a smaller particle size than that calculated from specific surface. This has been interpreted to mean that the "coherent domain" is appreciably smaller than the size of the particle.

Details of the calculation of particle size from x-ray data are given in the appendix.

Electron Microscopy

No great difficulty has been encountered in obtaining satisfactory electron micrographs of weak, relatively large particle size CPC such as, for example, crude (beta structure) chlorine-free CPC. However, it has not been possible in general to secure satisfactory micrographs with small particle size pigment such as solvent ground, acid pasted, or salt milled samples of strengths equal to or greater than that of BT-172-D standard. The difficulty apparently is a consequence of inability to obtain satisfactory dispersion of the pigment particles in preparation of the mounts for use in the microscope. Various mounting techniques have been investigated: the use of dispersion agents such as "Blancol", ammonium naphthenate, PBSS (poly benzyl sodium sulfate), dioctyl phthalate, or sulfonated CPC, to facilitate dispersion of the pigment on mixing in a high speed mixer with water, did not lead to satisfactory mounts. In all cases large aggregates were evident in the electron micrograph obtained from mounts prepared in this way. Similarly, ball mill grinding of the samples in water in the presence of various dispersing agents did not yield satisfactory dispersion. The best results obtained to date have resulted when the mounts were made by a dispersion technique involving preparation of an ink by grinding the pigment samples with oleic or naphthenic acid on a "Hoover" muller, adding a portion of the resulting ink to hot ammonium hydroxide solution, and placing a drop of the resulting water dispersion on a preformed nitrocellulose film. While it has not been definitely established that the dispersion technique does not affect particle size of the pigment, it is believed that this is the case with pigments of small particle size, since there is no evidence of particle size reduction on preparation of conventional inks by use of the Hoover muller, as judged from strength comparison of the inks prepared in the muller with the inks prepared by flushing (no grinding). There is, however, serious doubt as to whether the method is applicable to pigment of relatively large particle size, i.e., pigment of size range between that of crude CPC and BT-172-D. Also, there is considerable question as to whether the method would be satisfactory as a means for determining particle size changes on ball milling of crude CPC, for example. It is planned to investigate these matters further.

In the case of strong samples of CPC, no improvement in the quality of the electron micrographs has resulted from the use of the metal shadowing technique. In fact, there is some evidence which indicates that the metal used for "shadow casting" can bridge the gaps between adjacent very small particles of CPC to make such aggregates appear as one large particle. Only in the case of salt milled CPC has it been possible to obtain apparently satisfactory micrographs from shadowed mounts. In this case the micrographs from the shadowed mount indicate the presence of roughly spherical particles, whereas micrographs from a comparable non-shadowed mount (different sample of salt milled CPC) indicate the presence of very small needle-like particles. This matter is being investigated further.

The best micrographs obtained thus far indicate that solvent ground and acid-pasted (low turbulence drowned) CPC possess approximately the same particle size, and the particles appear to possess the same shape in the two cases. Salt milled samples, on the other hand, appear to be appreciably smaller than the solvent ground or acid pasted material, but - at least in the case of the non-shadowed mounts - the particle shapes appear to be approximately the same as that for the material processed in the aforementioned other two ways. These results relative to particle size obtained from the electron micrographs are in harmony with the data from specific surface measurements.

The effect of heating on the particle size and shape of salt milled (beta structure) chlorine-free CPC is clearly indicated by electron micrographs. The effect on exposure of such salt milled material to solvent is also clearly evident in this case. Of interest is the observation that water grinding of crude CPC results in appreciable particle size reduction, with the production of a considerable proportion of very small particle size material, but without, however, the complete elimination of the large particles.

Electron micrographs of ball milled (kerosene) crude chlorine-free CPC (beta phase) and acid-pasted (semi-chlor) CPC (alpha phase) are shown in Figures V and VI, respectively.

- -

Foot note: Of interest is the recently reported observation (F. A. Hamm, "Polymorphism of Organic Pigments", an as yet unpublished paper delivered at the December, 1947 meeting of the Electron Microscope Society of America) that bombardment of CPC(presumably chlorine-free) with 65 KV electrons in an electron microscope results in a phase change. It was not possible to duplicate this reported finding in this laboratory with use of the low energy (30 KV) electrons available.

It is considered worthy of note that, with the samples examined thus far by means of the electron microscope, the differences between the appearance of the alpha and beta types has been such as to permit classification of the samples according to crystal structure on the basis of electron micrographs alone. The difference in the appearance of the two types is readily evident on comparison of Figures V and VI. However, only relatively large particle size beta structure CPC has been examined in this fashion; it appears that difficulty might be encountered in making classifications in this way if a small particle size beta structure sample were involved.

Effect of Finishing Method on Particle Size

Particle size data for pigment finished by acid pasting, salt milling, and solvent milling are shown in Table II. It has been found that the variation between samples finished by a given method are greater than the differences which can be attributed to the method itself. Present indications are that at the present state of the art, particles can be obtained by ball milling techniques which are within the same range of particle size as is obtained by acid pasting and drowning by the high turbulence technique currently used commercially to yield small particle size products. While the maximum specific surface we have found thus far for salt-milled samples is slightly less than the maximum indicated for acid-pasted material, this is not considered indicative of inherent superiority of acid-pasting methods in this respect, inasmuch as only a limited amount of information is available in the Newark laboratories on the salt-milling process, and it is our opinion that improvement would be effected by further study. The indicated acid-pasted sample (Table II) having a surface of 98 meters^2 per gram was supplied to us by Jackson Laboratory. It represents acid-pasted chlorine-free CPC drowned by a high turbulence technique and stabilized with 4% of salt-milled tin phthalocyanine and "soft-texture" treated with trichlorbenzene. Apparently, because of the soft texture treatment, the sample did not exhibit the previously mentioned spurious low apparent specific surface characteristic of acid-pasted material which has been dried without treatment. Also, since only traces of the treating agent remained in the dry pigment, the results should not have been influenced by the presence of treating agent. This sample represents the (dry) acid pasted material of greatest strength and specific surface examined in the Newark laboratories.

Relationship Between Particle Size and Tinctorial Strength

In general, we have found, in accordance with previous observations (Ref. 1, 2), that the tinctorial strength of copper phthalocyanine pigments increases with decreasing particle size in the investigated range. The exceptions to this generalization have been found in cases of very hard samples where there is good reason to believe that the full tinctorial value could not be

realized owing to cementation of the pigment particles, or in cases in which no satisfactory particle size data could be obtained owing to the presence of naphthenic acid or other contaminants which cause erroneous results by the nitrogen adsorption method. In such cases the strength realized by flushing procedures, in which the pigment is evaluated without allowing opportunity for cementation during drying, has been much greater than that obtained by test of the dried pigment. It is worthy of note that such strength discrepancies are confined to acid-pasted samples; in the case of the investigated salt-milled and solvent-ground samples, the same strength has been realized by test of the dry pigment as with flushing procedures.

Some idea of the strength-size relationship can be gained from the data presented in Table III.

For fuller discussion of particle size-strength relationships the reader is referred to a report by the Jackson Laboratory Physical Chemistry group (Ref. 7).

TABLE III

Relationship Between Strength and Surface Area
for CPC Pigments Finished by Ball-Milling in Alcohol

SAMPLE	SURFACE AREA (meters^2 per gram)	STRENGTH BY TF-132-11 (% of BT-172-D)
Crude LB (unground)	22.8	60-70
Ground with 1/2" balls	62.5	105%
Ground with 5/32" balls	81.1	120
Ground with 5/32" balls	85.3	120
Ground with 5/32" balls (S.W.)	94.9	125-130
(MD-1255*)	98.1	130-135

*Acid pasted sample supplied by Jackson Laboratory.

Polychlor CPC

The x-ray spectrometer records obtained with crude polychlor CPC, acid-pasted polychlor CPC, and solvent-ground polychlor CPC, are shown in Figures VII, VIII and IX, respectively. The differences in the patterns appear to be due to the effects of changes in particle size rather than to polymorphism.

It has been found that polychlor CPC changes from a green to a blue on ball-milling in an aqueous medium in contact with iron, in the absence of a suitable inhibitor (Ref. 4). When chemical analysis failed to provide an explanation for the change in hue, a brief x-ray investigation was inaugurated in the hope that this would provide a possible solution of the question. However, the patterns of the material before and after the aforementioned change were quite similar and no difference in the two records was evident which was considered indicative of a significant structural difference.

An explanation was also sought thru x-ray studies for the fact that samples of polychlor CPC of a given chlorine content differ significantly in hue; for example, occasional samples of chlorine content in the range 45-46% are reported to be as yellow in hue as conventional samples containing approximately 47.5% chlorine. The x-ray studies failed to indicate a cause for the abnormality.

Values for the specific surfaces of polychlor CPC samples are shown in Table IV. (The results of duplicate determinations are indicated in two cases to give an idea of the reproducibility of results). It is to be noted that because of the greater density of polychlor CPC as compared to CPC, for a given value of specific surface the particle diameter calculated for polychlor CPC is only 1.54/2.09 of that of the size for CPC. Hence, it appears that the particle size of the stronger polychlor CPC samples is approximately the same as that of the stronger CPC samples.

Future Studies of Polychlor CPC

An extensive program of x-ray studies of polychlor CPC is outlined in another report (Ref. 9) in which are also presented the results of a preliminary survey of the problem. A more specific program will be drawn up following acknowledgement completion of plant start-up.

Acknowledgement

The x-ray patterns and specific surface data referred to herein were obtained by the Experimental Station Physics Group on samples supplied by the Newark Research Department. Suggestions were received from the Experimental Station group as well as from Professor Seitz (Carnegie Institute of Technology) who assisted in a consulting capacity in much of the work reported here.

TABLE IV

SPECIFIC SURFACE OF POLYCHLOR CPC SAMPLES

SAMPLE	SURFACE AREA (meters^2 per gram)	PARTICLE DIAMETER* microns.
Crude polychlor CPC[1]	14.0	0.21
Crude polychlor CPC[2]	3.43 3.58	-
Acid-pasted Standard (GT-486-D, SD-48421)	69.7	0.042
Solvent-milled pigment[1]	78.4 77.9	0.039

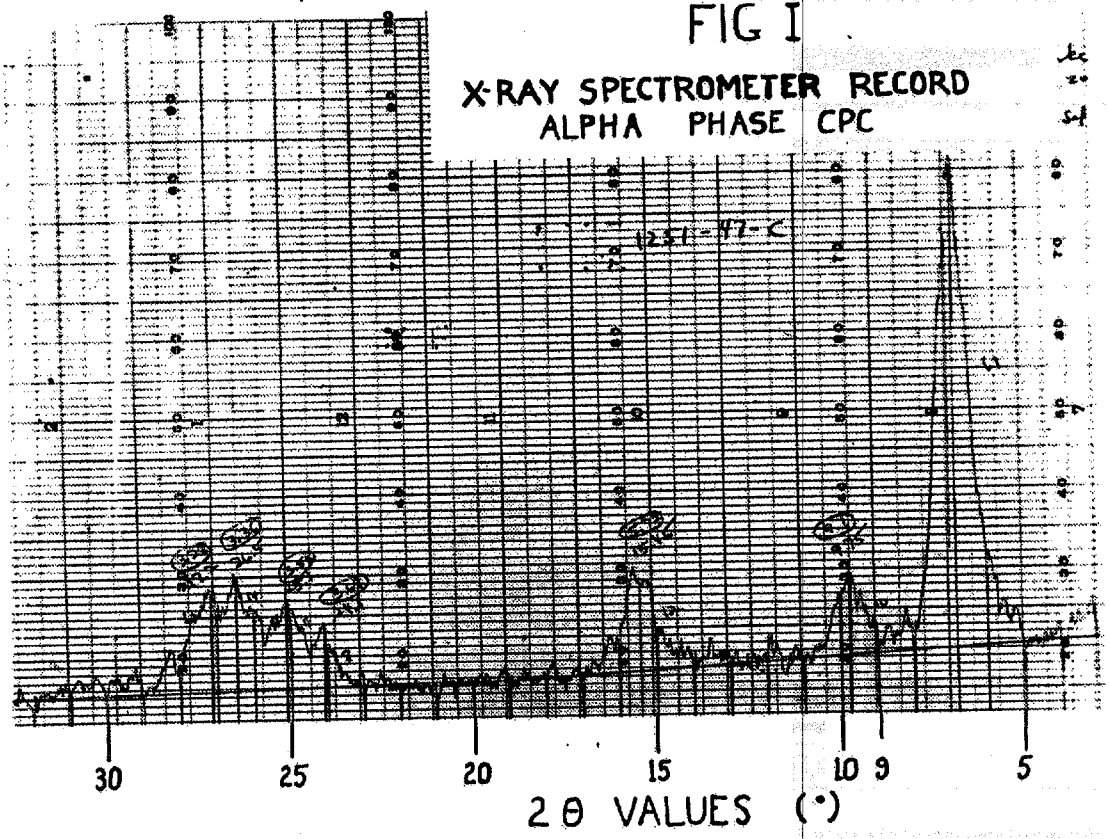
*Diameter calculated from equation:

$$\text{Diameter (microns)} = \frac{2.82}{\text{Surface Area in meters}^2 \text{ per gram}}$$

1. Chlorinated by aluminum chloride-sodium chloride eutectic process. Sample supplied by Jackson Lab.

2. Chlorinated by "dry chlorination method". Sample supplied by Jackson Lab.

FIG I



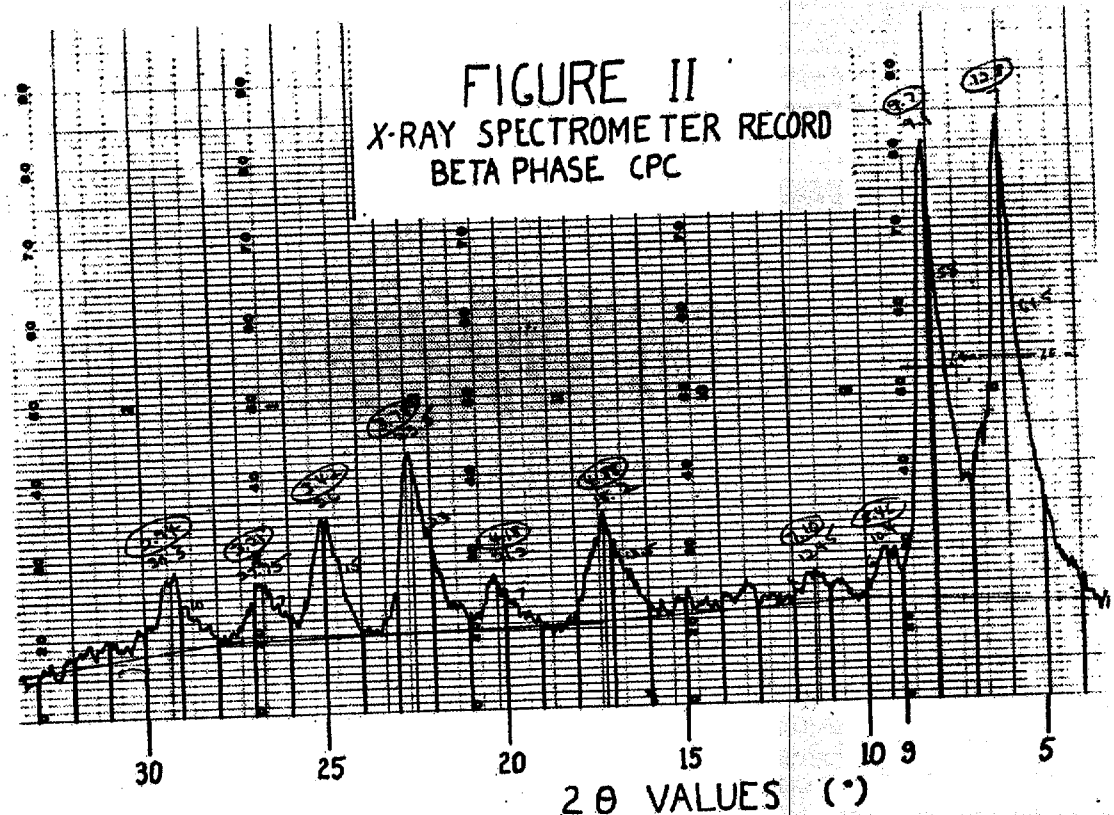


FIGURE III

X-RAY SPECTROMETER RECORD

MIXTURE: 10% BETA PHASE, 90% ALPHA

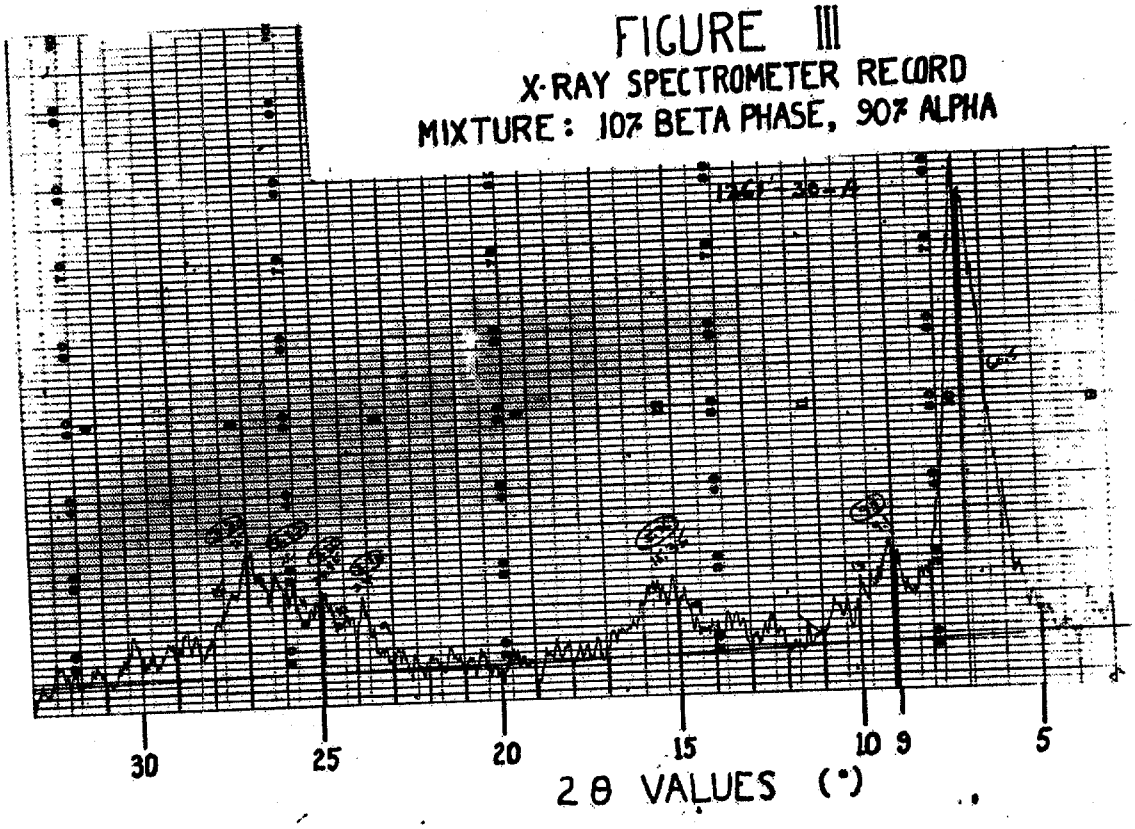


FIGURE IV

X-RAY SPECTROMETER RECORD

MIXTURE: 30% BETA PHASE, 70% ALPHA PHASE

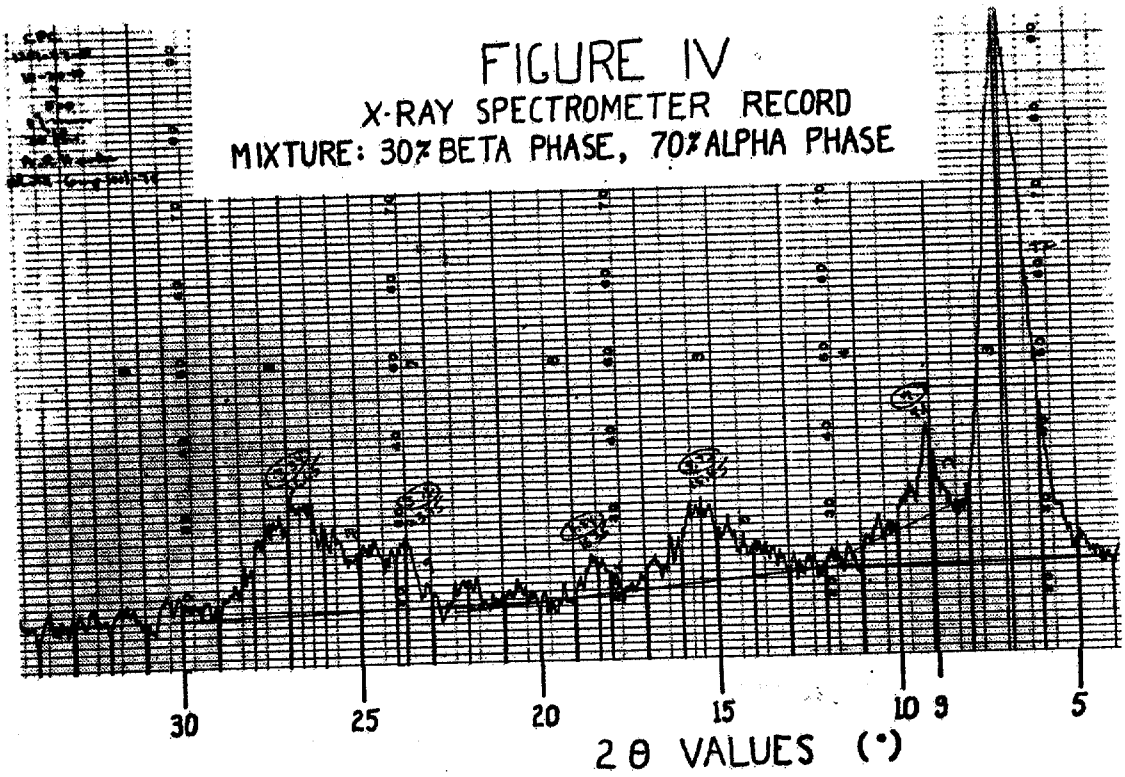


FIGURE V

ELECTRON MICROGRAPH OF SAMPLE OF CHLORINE-FREE CPC
AFTER MILLING IN KEROSENE.

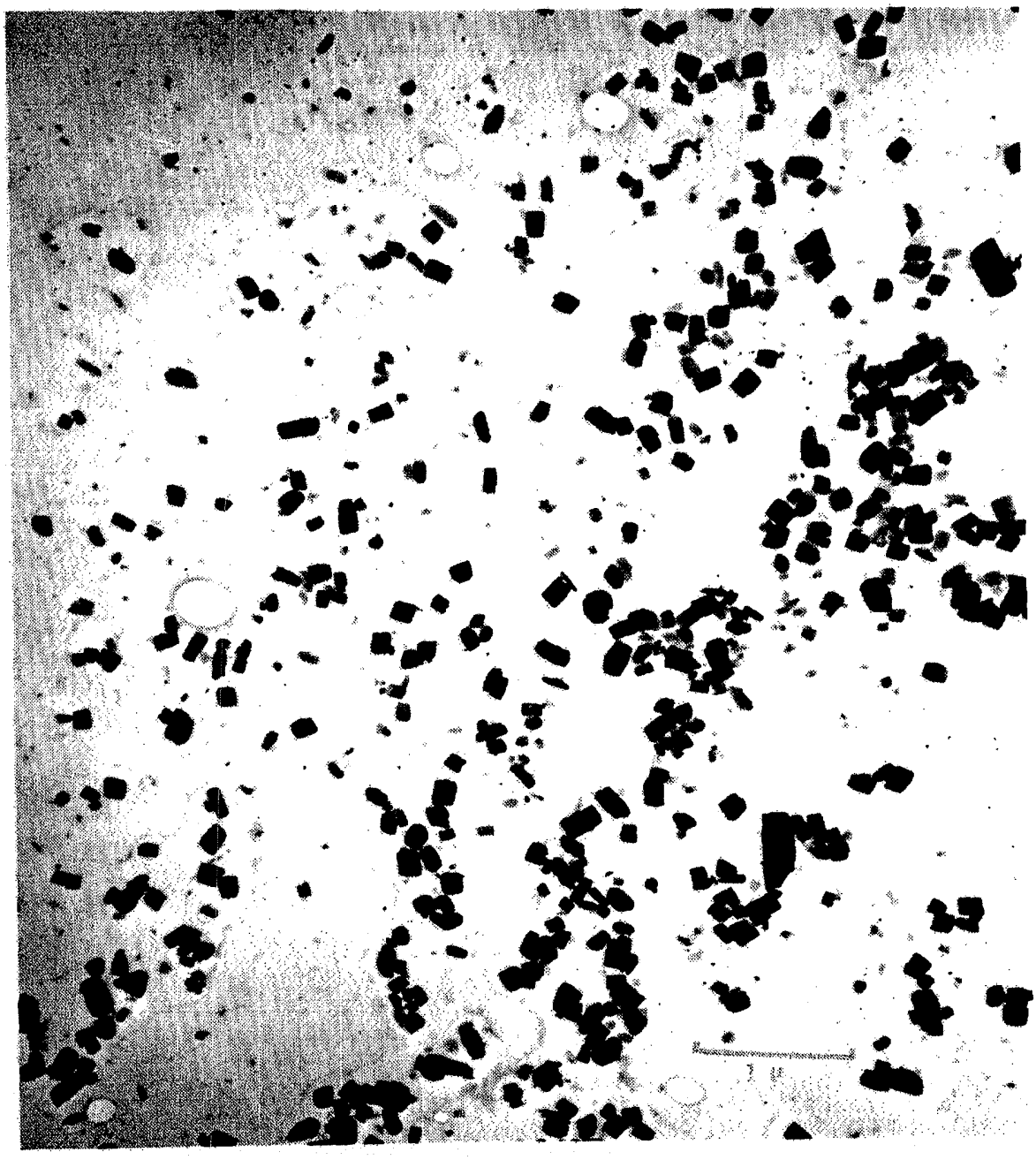


FIGURE VI

ELECTRON MICROGRAPH OF ACID-PASTED CPC

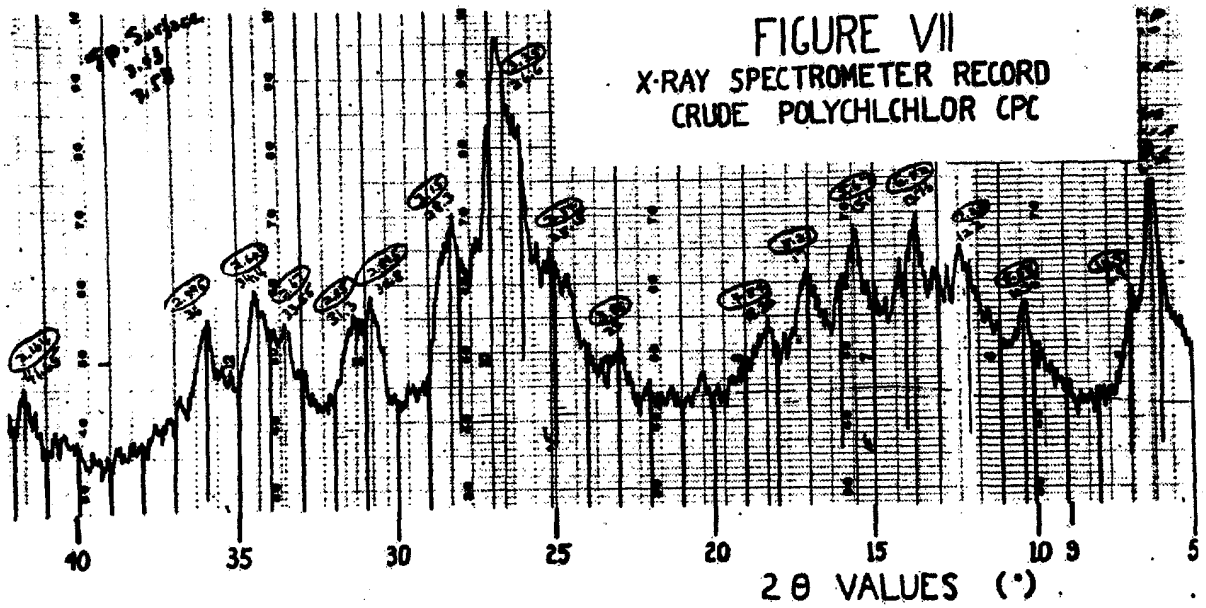


FIGURE VII
X-RAY SPECTROMETER RECORD
CRUDE POLYCHLCHLOR CPC

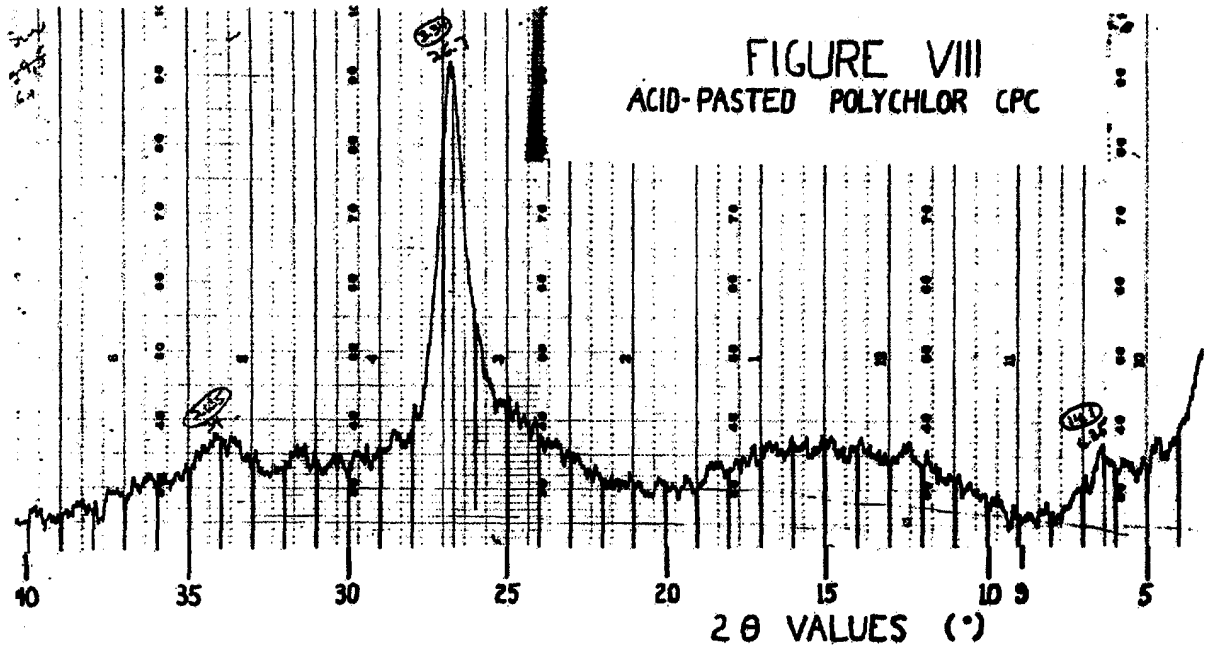


FIGURE VIII
ACID-PASTED POLYCHLOR CPC

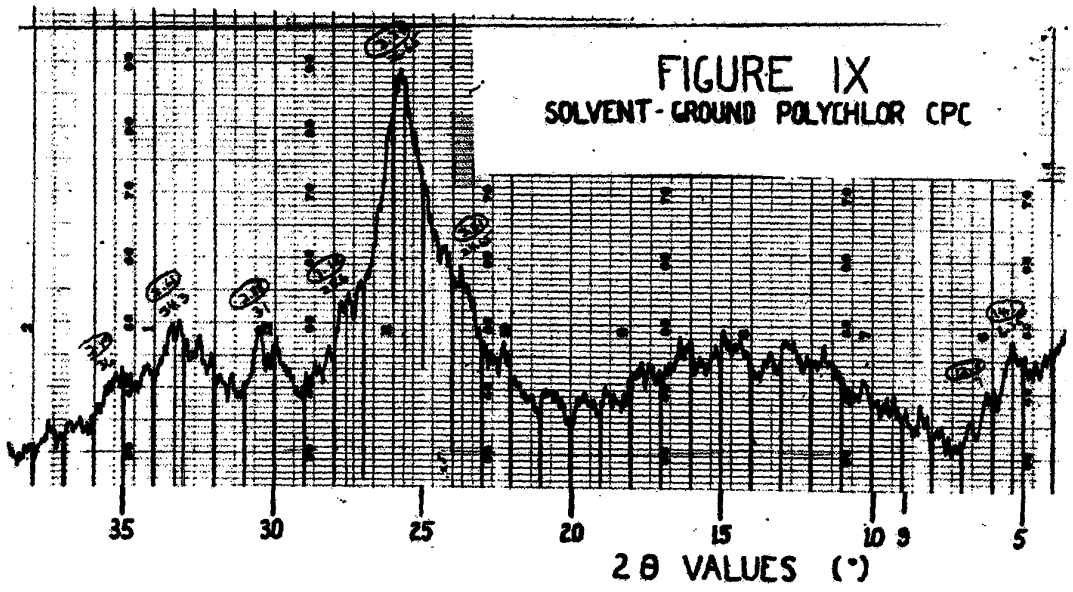


FIGURE IX
SOLVENT-GROUND POLYCHLOR CPC

REFERENCES:

1. ESP-37-201. "Particle Size and Tinctorial Strength of CPC" E. D. Bailey. 1937.

2. KN-37-631. "Particle Size and Tinctorial Strength of Copper Phthalocyanine". A. Siegel. November, 1937. Newark File 223.4

3. KN-46-19. "The Finishing of Phthalocyanine Pigments I: Wet Grinding Study". F.W.Lane. June 3, 1946. Newark File: 223.4

4. KN-46-55. "Progress Report. The Finishing of Phthalocyanine Pigments II. Wet Grinding Study". A.J.Stratton. August 12, 1946. Newark File: 223.4

5. I.C.I. Report H-2757. "Monastral" Fast Blue B. Substitution of Acid Pasting Process by Milling Methods". F.R.Cropper. April, 1937.
Also see British Patent application No. 5721-1944. American Cyanamid Company.

6. KN-47-51. "Monastral Fast Blue LB: Process Development". F. F. Ehrich. February, 1948. Newark File: 223.4

7. JLR-28-34. Serial No. 19784. "Optical Properties of Colored Solids I. Theoretical Study of Dilute Suspensions" by F. C. Chromey and M. J. Schuler, April, 1947.

8. Letter, C. G. Wortz to A. R. Hanke, March 24, 1947. "Specific Surface of Pigments. Calculation of the Dimensions of Rod-shaped Particles from Surface Area Measurements".

9. DED X-47-12. "Monastral" Green Process Development. Crystallographic Studies. MX-1074". J. R. Caddell. July, 1947.

10. Letter, B. H. Perkins to D. Graham, "Phthalocyanine Pigments: Determination of Particle Size from x-ray Line Broadening". April 23, 1947. Newark File: 223.4.

11. L.S. Birks and H. Friedman, "Particle Size Determination from x-ray Line Broadening". J. Applied Physics 17, 687 (1946).

12. Brunauer, Emmett, Teller, "Adsorption of Gases in Multimolecular Layers", JACS, 60, 309 (1938).

EXPERIMENTAL DETAILS:

Notebook 1228

X-ray Spectrometer records are filed in the group leader's office in #23 building.

APPENDIX I:

DETERMINATION OF PARTICLE SIZE FROM X-RAY LINE BROADENING

Particle size data relative to copper phthalocyanine samples were calculated from x-ray data according to the method described by Birks and Friedman, J. Applied Physics, 17, 687 (1946). The equation used is -

$$D = \frac{K\lambda}{B \cos \theta}$$

where $B^2 = B'^2 - b'^2$

and D = particle diameter, in radians

B = line broadening (in radians)

B'= line width at half-maximum (in radians)

λ = is the wave length of the x-radiation used (Cu, K_α in our case)

θ = is the Bragg angle (radians)

b'= "instrument width" (in radians)

K = is a constant which we have taken equal to 1.

The value of b' was taken as the line width at half-maximum obtained with samples of large particle size CPC (crude Cl free). In the case of spectrometer records obtained with use of the Experimental Station Geiger counter spectrometer with slit widths 10-20-10, b' has the value of 0.00447 radians. (The value of b' is approximately 0.00618 radians with slit widths of 20-40-20 which have been used occasionally in the x-ray work). The "half-width" of the peak corresponding to a θ value of 3.4 - 3.5° has been used in the calculations of particle size.

GLOSSARY:

"Chlorine-free" CPC. Pigment prepared by the phthalic anhydride-urea-kerosene route. Contains less than 0.5% chlorine.

LB Type CPC. Pigment prepared by the phthalic anhydride-urea-kerosene route with the use of sufficient chlorphthalic acid (or derivatives) to obtain a product containing approximately 4% chlorine.

BT-172-D. Current DuPont commercial standard acid-pasted semi-chlor CPC. Contains approximately 10% of a soft-texture treating agent consisting of triethanolamine-lauric acid ester-salt.

Strength, as referred to herein, is measured by the quantity of pigment (in the form of an ink) which must be mixed with a given quantity of a white pigment paste to match a given mixture of the standard pigment with the white pigment paste (see TF-132-11). A pigment is said to be 20% strong, for example, if 100 parts of it match the aforementioned mixture obtained with use of 120 parts of the standard CPC.

Salt-milling. A method of reducing the particle size of pigment involving ball milling it (dry) in the presence of 4-10 times its weight of salt in a ball mill with pebbles or metal bars or rods.

Solvent milling. Ball milling pigment with balls in a conventional ball mill in the presence of a solvent.