Studies on Copper Phthalocyanine and its Chlorinated Derivatives Based upon the X-ray Diffraction Patterns

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The molecular structure of copper phthalocyanine was first investigated by R. P. Linstead et al.[1] and later J. M. Robertson[2] studied its crystal structure by means of X-ray diffraction. He had only one form of copper phthalocyanine —namely, the α-form. This was prepared by sublimation as large needle crystal unsuited for pigment use. In order to reduce the particle size of copper phthalocyanine, the needle pigment is dissolved in concentrated sulfuric acid, and then is precipitated in fine particles by adding the acid solution to a large quantity of water with agitation. The first commercial pigment is the fine particles thus obtained. G. von Susich[3] showed that copper phthalocyanine conditioned in the above manner had a different X-ray diffraction pattern from that of the sublimed product studied by J. M. Robertson. Here the J. M. Robertson form is called α-form, because historically this crystal form was the first to be identified, and the first commercial pigment form is called β-form.

The copper phthalocyanine and lowly chlorinated copper phthalocyanines (containing chlorine atoms not more than six) are mostly used in blue pigments, while the highly chlorinated copper phthalocyanines (containing about 14 chlorine atoms) in green pigments. As to polymorphism of chlorinated copper phthalocyanines, D. N. Kendall[4], on the basis of infrared absorption measurement, reported that there were also two forms of crystal structures, α- and β-forms, in copper monochlorophthalocyanine (no mention is made of position of chlorine atom), whereas only one form of crystal structure was identified in highly chlorinated copper phthalocyanine green.

The author worked out X-ray diffraction patterns on twelve samples, six in needle forms and six in granular ones, of the following compounds; copper phthalocyanine, copper tetra-(3)-chlorophthalocyanine, copper tetra-(4)-chlorophthalocyanine, copper octa-(3, 6)-chlorophthalocyanine, copper octa-(4, 5)-chlorophthalocyanine and copper hexadecachlorophthalocyanine; the polymorphism was hereby investigated with copper phthalocyanine and its chlorinated derivatives.

Experimental

Materials.—Two forms of crystals, needle and granular forms, of copper phthalocyanine derivatives of different chlorine contents were synthesized as follows.

(1) *α-Form (I) and β-form (II) copper phthalocyanines.*—Synthesis of copper phthalocyanine was carried out following the method described in Ref. 5. From the product, then, α- and β-form crystals were obtained by the following procedure. First, copper phthalocyanine was put into a quartz glass tube, heated up to 550~580°C in an electric furnace, making the needle crystal of I sublime. α-Form crystal thus obtained was dissolved in 98% sulfuric acid of 20 times in weight at room temperature and allowed to stand 4 hr. Then, poured into ice water, granular II was formed, and separated through filtration. By chlorine analysis, it was found that there was just a trace of chlorine content, that is, 0.11%. Micro-Carius method was applied in all the following chlorine analyses.

Granular I of a size which seemed to be suitable for pigment was prepared by the method described in Ref. 6. Namely, 100 cc. of acetone, 1.2 kg. of steel shots of approximately 3 mm. in diameter and 5 g. of I in needle form which was obtained by sublimation were put into a porcelain pot of 500 cc. capacity and pulverized at 100 r. p. m. for 72 hr.; the product was granular I in brilliant greenish blue.

(2) *Copper tetra-(3)-chlorophthalocyanine (III) and copper tetra-(4)-chlorophthalocyanine (IV).*—

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[1] R. P. Linstead et al., *J. Chem. Soc.*, **1934**, 1036.

[2] J. M. Robertson, ibid., **1935**, 615; ibid., **1936**, 1195; ibid., **1937**, 219.

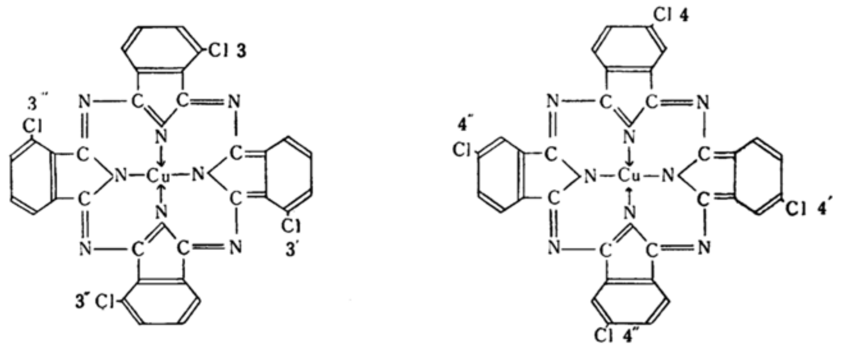
[3] G. von Susich, *Anal. Chem.*, **22**, 425 (1950).

[4] D. N. Kendall, ibid., **25**, 382 (1953).

[5] M. Shigemitsu, *J. Chem. Soc, Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 110 (1959) (presented at the 10th Annual Meeting of the Chemical Society of Japan held in April, 1957).

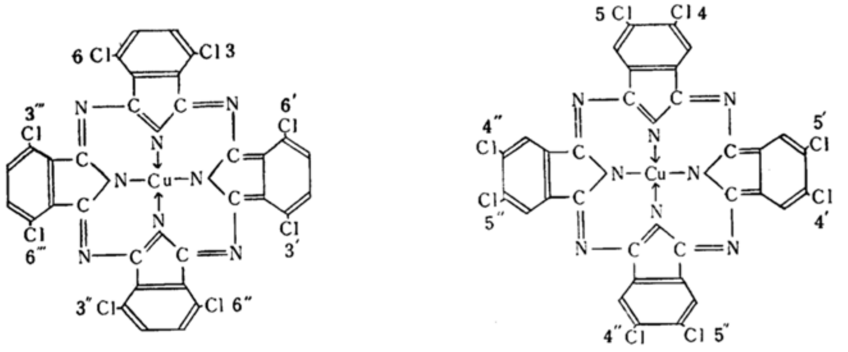
[6] U. S. Pat. 2,556,726 (1951); U. S. Pat. 2,556,727 (1951); U. S. Pat. 2,556,728 (1951); U. S. Pat. 2,556,730 (1951).

[7] M. Shigemitsu, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 112 (1959) (presented at the Autumnal Joint Meeting of Chemical Society of Japan with other Societies, Tokyo, 1957).



Copper tetra-(3)-chlorophthalocyanine Copper tetra-(4)-chlorophthalocyanine

Fig. 1



Copper octa-(3, 6)-chlorophthalocyanine Copper octa-(4, 5)-chlorophthalocyanine

Fig. 2

III and IV were prepared by condensing 3- and 4-monochlorophthalic anhydrides (see below) respectively with urea and copper in trichlorobenzene. From the mixture of monochlorophthalic anhydrides prepared following the method in Ref. 7, separated 3-monochlorophthalic anhydride, m. p. 121∼122°C (reported m. p. 122°C)[8] (*Anal.* Found: Cl, 19.40%) and 4-monochlorophthalic anhydride, m. p. 97∼98°C (reported m. p. 98°C°[8]) (*Anal.* Found: Cl, 19.44%) by repeating recrystallization with toluene-ethanol (1 : 1) solvent. The chlorine contents in III and IV derived from these 3- and 4-monochlorophthalic anhydrides were 19.72% and 19.80%, respectively.

Both of III and IV prepared in this way were of needle crystals. To convert them into granular forms, they were dissolved in 98% sulfuric acid of 20 times in weight at room temperature, allowed to stand for 4 hr. and poured into ice water.

Since chlorinated copper phthalocyanines do not sublime, it is impossible to obtain the needle crystals by sublimation, but they can be obtained by condensing various chlorophthalic anhydrides together with urea and copper in trichlorobenzene. Therefore, this method was adapted later in obtaining the needle crystals of various chlorinated copper phthalocyanines.

(3) *Copper octa-(3, 6)-chlorophthalocyanine (V) and copper octa-(4, 5)-chlorophthalocyanine (VI).* —V which was synthesized following the method described in Ref. 7 was taken up; it showed a chlorine content of 33.21% and was of needle crystal.

VI was synthesized by condensing 4, 5-dichloro phthalic anhydride (see below) together with urea and copper in trichlorobenzene; it showed a chlorine content of 33.23% and was of needle crystal. 4, 5-Dichlorophthalic anhydride, m. p. 185∼186.5°C (reported m. p. 185∼187°C)[8] (*Anal.* Found: Cl, 32.60%) was separated from the mixture of dichlorophthalic anhydrides[7] with toluene-ethanol (1:1) solvent.

To convert them into granular forms, they were dissolved in chlorosulfonic acid of 20 times in weight at room temperature, allowed to stand 4 hr. and poured into ice water.

(4) *Copper hexadecachlorophthalocyanine (VII).* —Needle-formed VII synthesized following the method described in Ref. 7, with chlorine content of 50.33%, was used. Granular VII was prepared by dissolving needle-formed VII in chlorosulfonic acid of 30 times in weight at room temperature, allowing it to stand for 4 hr. and then pouring it into ice water.

Methods.—(1) *Observation of pigment forms.* —Two types of samples were prepared as follows. One was made first by washing with water the

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[8] V. Villiger, *Ber.*, **42**, 3532 (1909).

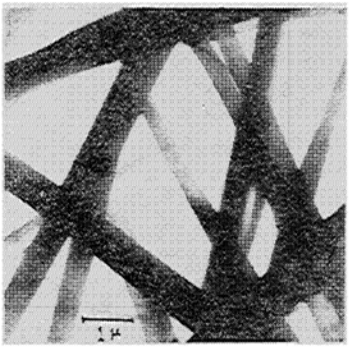

Fig. 3. α-Form copper phthalocyanine (I) (needle form)

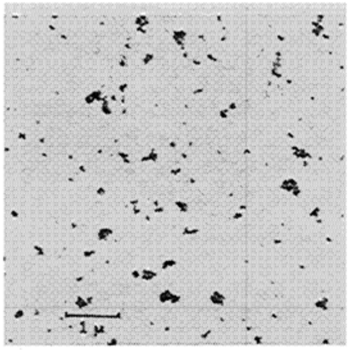

Fig. 4. β-Form copper phthalocyanine (II) (granular form)

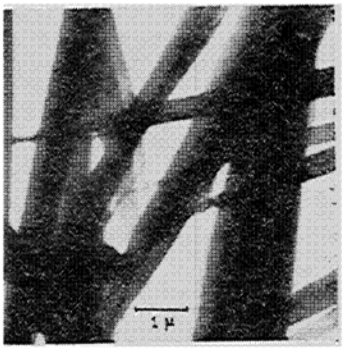

Fig. 5. Copper tetra-(3)-chlorophthalocyanine (III) (needle form)

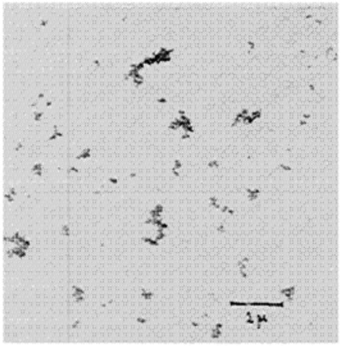

Fig. 6. Copper tetra-(3)-chlorophthalocyanine (III) (granular form)

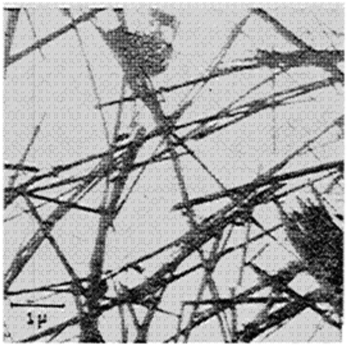

Fig. 7. Copper tetra-(3)-chlorophthalocyanine (III) (boiled for 10 hr. in trichlorobenzene)

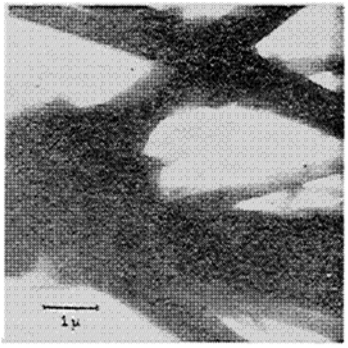

Fig. 8. Copper tetra-(4)-chlorophthalocyanine (IV) (needle form)

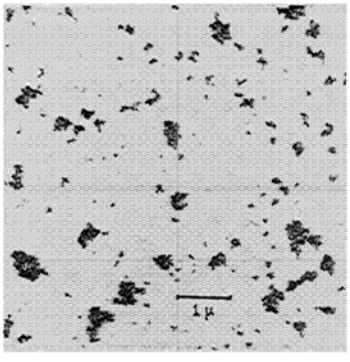

Fig. 9. Copper tetra-(4)-chlorophthalocyanine (IV) (granular form)

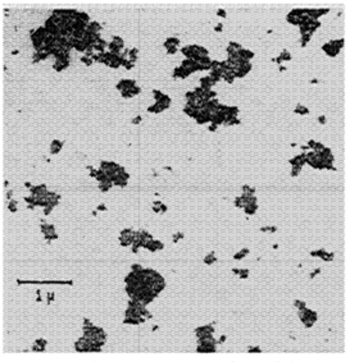

Fig. 10. Copper tetra-(4)-chlorophthalocyanine (IV) (boiled for 10 hr. in trichlorobenzene)

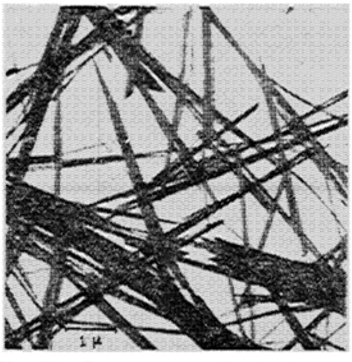

Fig. 11. Copper octa-(3, 6)-chlorophthalocyanine (V) (needle form)

granular pigments reprecipitated from the solution in 98% sulfuric acid of chlorosulfonic acid, and then placing and drying a drop of pigment suspension in water upon the collodion film of sample holder. The other was prepared first by drying the pigments obtained in any way other than by reprecipitation and then by sprinkling them over the collodion film of sample holder. The author photographed them with an electron microscope (Hitachi Works) at 2,000 direct magnification. The pictures were enlarged again by 10,000 times, and by means of these enlargements, their forms were closely examined.

(2) *Changes in pigment shade accompanied by being heated in trichlorobenzene.*—Granular pigments prepared by reprecipitation were heated in the boiling trichlorobenzene (b. p. 200~210°C) of 100 times in weight for 10 hr, and then filtered. After the sticking trichlorobenzene was eliminated by washing with ethanol, they were

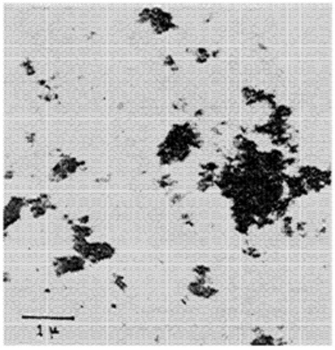

Fig. 12. Copper octa-(3,6)-chlorophthalocyanine (V) (granular form)

Fig. 13. Copper octa-(4,5)-chlorophthalocyanine (VI) (needle form)

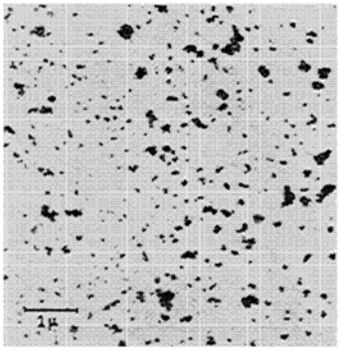

Fig. 14. Copper octa-(4,5)-chlorophthalocyanine (VI) (granular form)

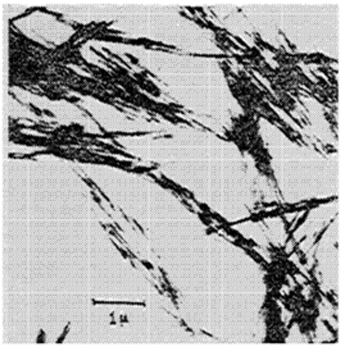

Fig. 15. Copper hexadecachlorophthalocyanine (VII) (needle form)

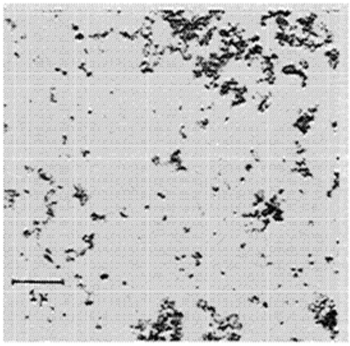

Fig. 16. Copper hexadecachlorophthalocyanine (VII) (granular form)

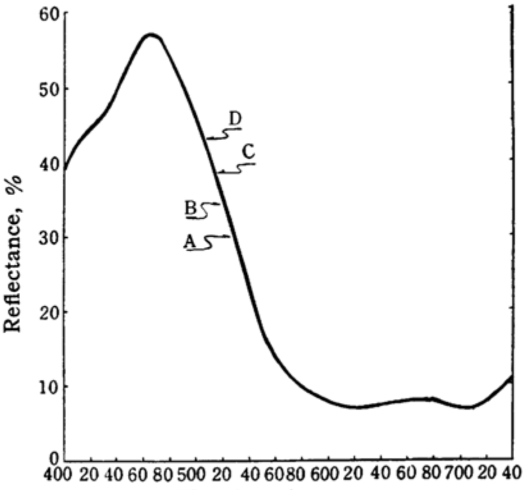

Fig. 17. α-Form copper phthalocyanine (I), (granular form):
A, untreated; B, stood for 5 days;
C, boiled for 1 hr.; D, boiled for 10 hr.

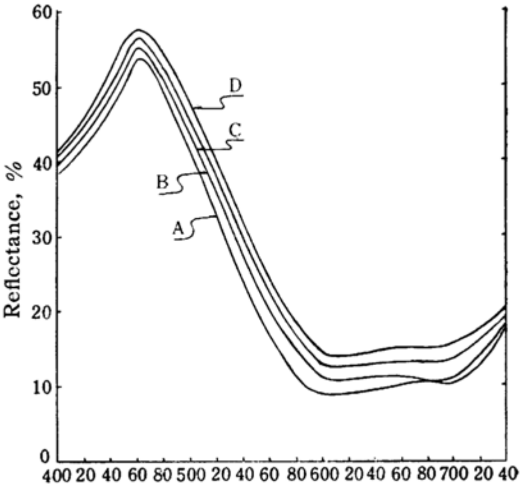

Fig. 18. β-Form copper phthalocyanine (II), (granular form):
A, untreated; B, stood for 5 days;
C, boiled for 1 hr.; D, boiled for 10 hr.

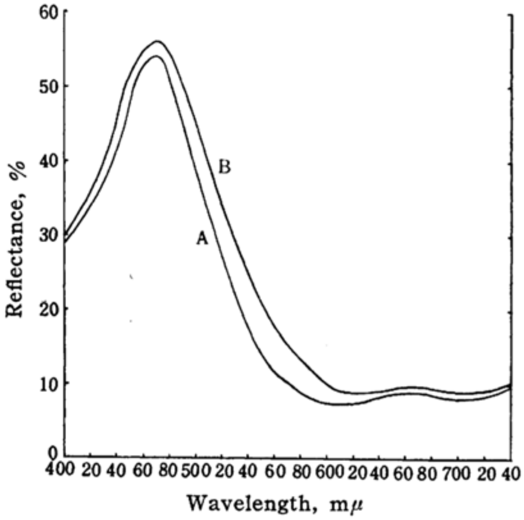

Fig. 19. Copper tetra-(3)-chlorophthalocyanine (III), (granular form):
A, untreated; B, boiled for 10 hr.

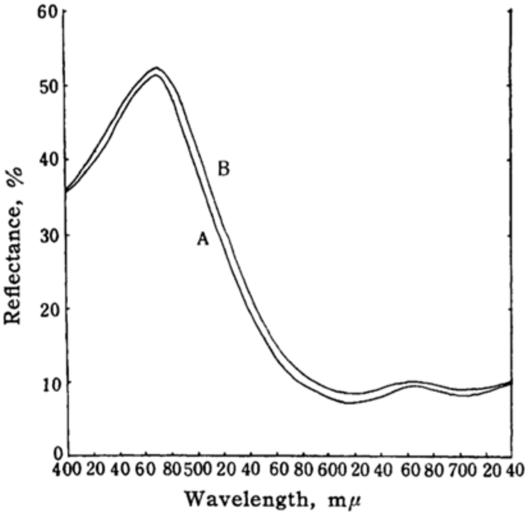

Fig. 20. Copper tetra-(4)-chlorophthalocyanine (IV), (graunlar form):
A, untreated; B, boiled for 10 hr.

dried at about 60°C. The pigments thus obtained and the original untreated ones were mixed respectively with polymerized linseed oil of 1.5 times in weight and were made into paste by grinding 400 rounds in a Hoover automatic muller. To 1 part of each paste was added 70 parts of zinc white paste (obtained by grinding 2 parts of zinc oxide with 1.5 parts of polymerized linseed oil), which was applied 0.5 mm. in thickness on a coated paper with a bladeoapplicator (Gardner Laboratory). These were dried at room temperature, their reflectance curves were obtained with a recording spectrophotometer (General Electric Co.), and calculation was thereby conducted.

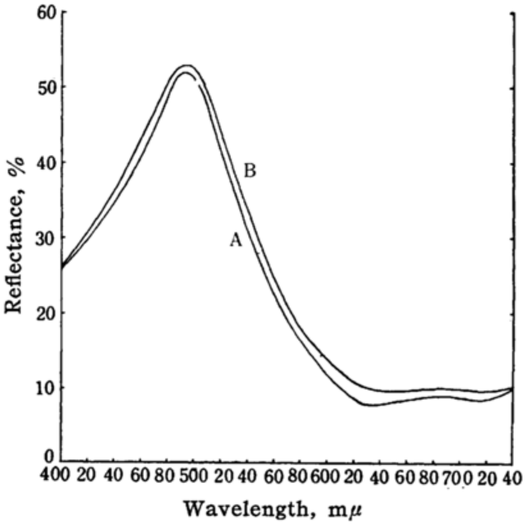

Fig. 21. Copper octa-(3, 6)-chlorophthalocyanine (V), (granular form):
A, untreated; B, boiled for 10 hr.

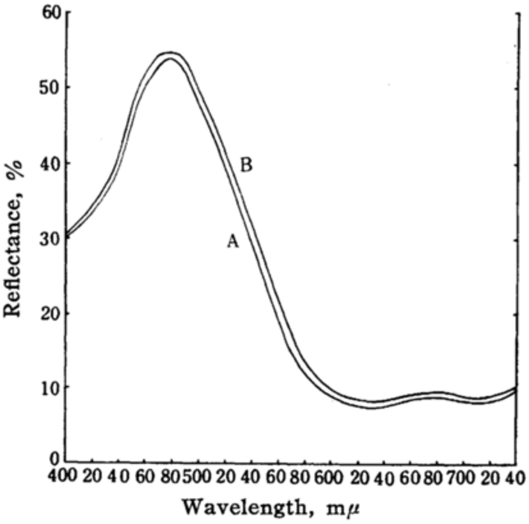

Fig. 22. Copper octa-(4, 5)-chlorophthalocyanine (VI), (granular form):
A, untreated; B, boiled for 10 hr.

(3) *Crystal structures of pigments.*—The X-ray diffraction patterns of each pigment were obtained with a recording X-ray diffraction apparatus (Philips Co.).

Results. — (1) *Forms of pigments.* — Photos taken with an electron microscope are shown (Fig. 3 to Fig. 16). Fig. 3 shows I obtained by sublimation, while Figs. 5, 8, 11, 13 and 15 show chlorinated copper phthalocyanines obtained by synthesis in trichlorobenzene; they are all in needle forms. Figs. 4, 6, 9, 12, 14 and 16 show II and chlorinated copper phthalocyanines, all in granular forms, obtained by dissolving the needle crystals in 98% sulfuric acid or chlorosulfonic

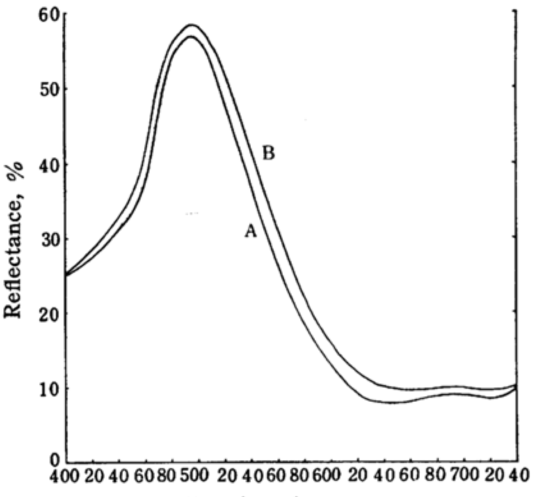

Fig. 23. Copper hexadecachlorophthalocyanine (VII), (granular form):
A, untreated; B, boiled for 10 hr.

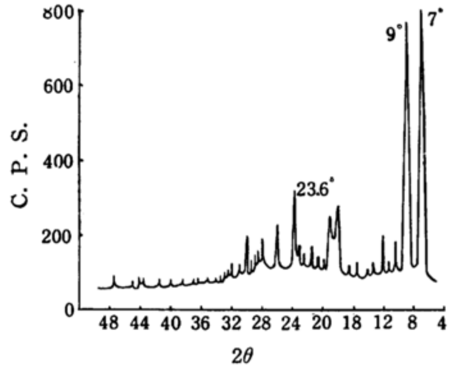

Fig. 24. α-Form copper phthalocyanine (I), (needle form)

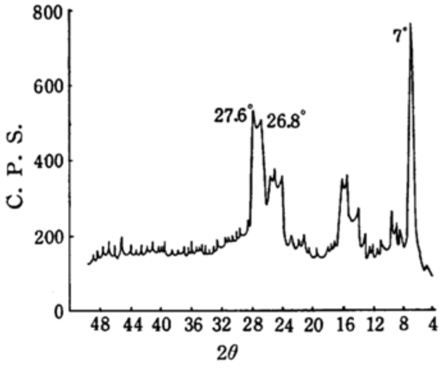

Fig. 25. β-Form copper phthalocyanine (II), (graunlar form)

acid and pouring them into ice water.

Fig. 7 shows the needle crystal prepared by boiling the granular III (Fig. 6) in trichlorobenzene for 10 hr. This change resembles the transformation of granular II into needle-formed I, which appears when the former is heated in organic solvents[9,10]. However, no change can be detected in case IV (Fig. 9) when it is heated in the boiling trichlorobenzene for 10 hr, as is manifested from Fig. 10.

It is known that, when a small amount of chlorine is introduced by the direct chlorination of copper phthalocyanine, a compound can be obtained which does not show any crystal growth in organic solvents[11]. In this case, chlorine is first substituted at the 4- or 5-position of phthalocyanine nucleus[7,12]. Meanwhile, according to Bansho et al.[13], no crystal growth takes place in the case of chlorinated copper phthalocyanine obtained from the direct chlorination or 4-monochlorophthalic anhydride. These facts are in good harmony with the results by the author.

As to copper octachlorophthalocyanines, on the other hand, no difference is formed any more in the crystal growth; independently of the positions which are occupied by chlorine atoms, 3,6- or 4,5-positions of phthalocyanine nucleus, no crystal growth takes place even in case copper octachlorophthalocyanines are boiled in trichlorobenzene for 10 hr. The case of granular VII is also quite the same.

(2) *Changes in pigment shade.* — Reflectance curves obtained with a recording spectrophotometer are shown (Fig. 17 to Fig. 23). Table I gives the data of these curves expressed in terms of C. I. E. Notation. In this table, *Y* denotes luminosity, *Pe* purity and λ_D dominant wavelength.

It is evident from Fig. 17, that granular I, even though boiled in trichlorobenzene for 10 hr.,

TABLE I. C. I. E. NOTATION

Sample	Reflectance curve	*Y* %	*Pe* %	λ_D mμ
A	Fig. 17	20.7	56.0	480.7
B		20.7	56.0	480.7
C		20.7	56.0	480.7
D		20.7	56.0	480.7
A	Fig. 18	19.1	55.0	475.8
B		23.4	52.0	478.8
C		24.2	51.0	479.7
D		25.2	49.6	479.8
A	Fig. 19	19.7	58.4	481.5
B		21.6	54.2	484.2
A	Fig. 20	18.4	56.1	478.3
B		18.5	56.0	478.7
A	Fig. 21	25.2	49.6	485.0
B		25.5	48.8	485.9
A	Fig. 22	21.6	55.8	482.5
B		21.9	55.6	482.7
A	Fig. 23	30.3	36.8	492.6
B		31.2	35.7	494.5

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[9] FIAT Report, No. 1313, **3**, 446 (1948).

[10] U. S. Pat. 2,486,351 (1949).

[11] U. S. Pat. 2,615,026 (1952); U. S. Pat. 2,618,642 (1952).

[12] R. P. Linstead et al., *J. Chem. Soc.*, **1939**, 1820.

[13] Y. Bansho et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **59**, 67 (1956).

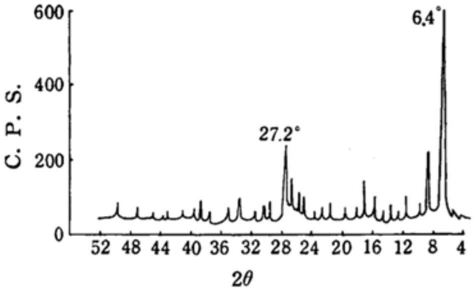

Fig. 26. Copper tetra-(3)-chlorophthalocyanine (III), (needle form)

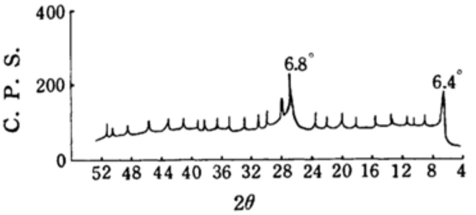

Fig. 27. Copper tetra-(3)-chlorophthalocyanine (III), (granular form)

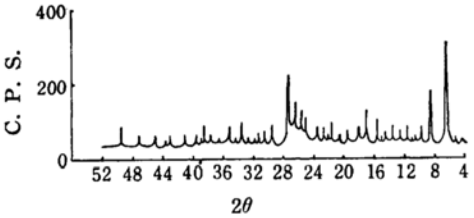

Fig. 28. Copper tetra-(3)-chlorophthalocyanine (III), (granular form); boiled for 10 hr.

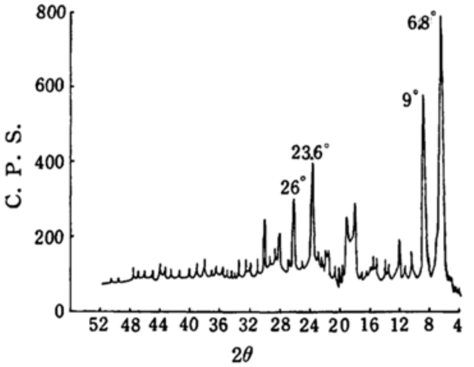

Fig. 29. Copper tetra-(4)-chlorophthalocyanine (IV), (needle form)

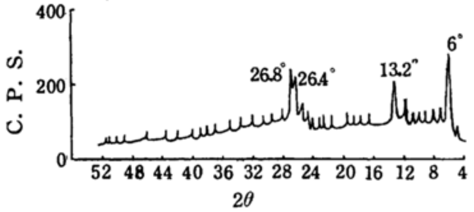

Fig. 30. Copper tetra-(4)-chlorophthalocyanine (IV), (granular form)

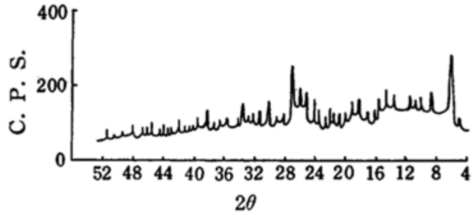

Fig. 31. Copper tetra-(4)-chlorophthalocyanine (IV), (granular form); boiled for 10 hr.

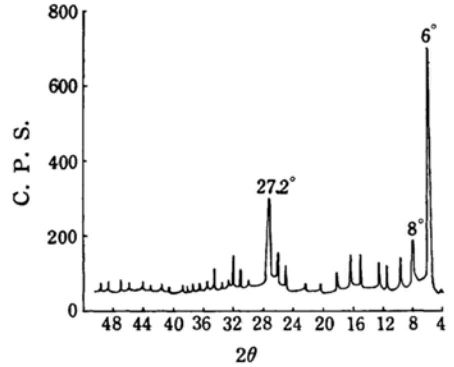

Fig. 32. Copper octa-(3,6)-chlorophthalocyanine (V), (needle form)

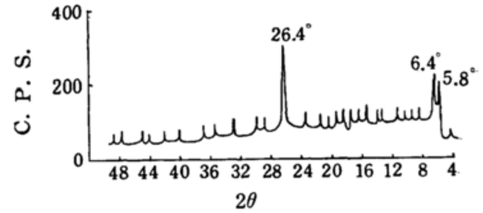

Fig. 33. Copper octa-(3,6)-chlorophthalocyanine (V), (granular form)

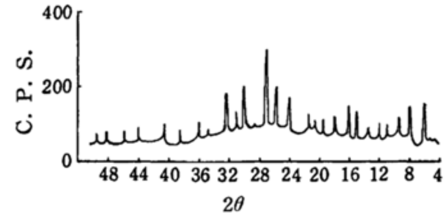

Fig. 34. Copper octa-(3,6)-chlorophthalocyanine (V), (granular form); boiled for 10 hr.

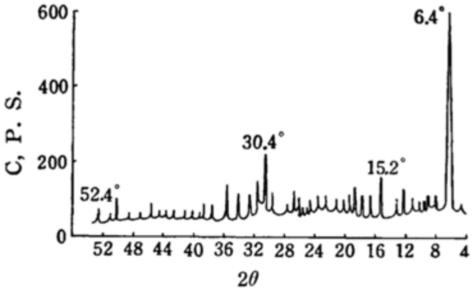

Fig. 35. Copper octa-(4,5)-chlorophthalocyanine (VI), (needle form)

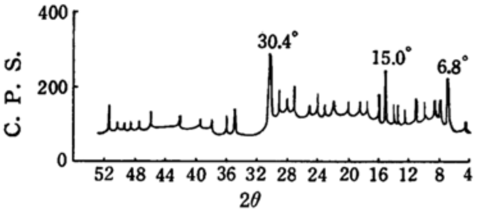

Fig. 36. Copper octa-(4,5)-chlorophthalocyanine (VI), (granular form)

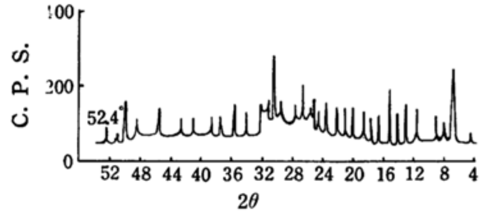

Fig. 37. Copper octa-(4,5)-chlorophthalocyanine (VI), (granular form); boiled for 10 hr.

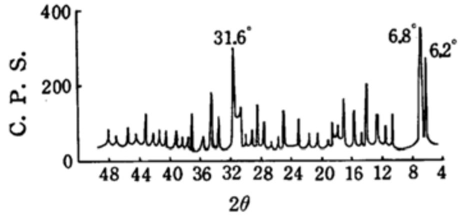

Fig. 38. Copper hexadecachlorophthalocyanine (VII), (needle form)

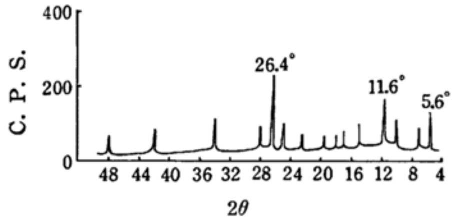

Fig. 39. Copper hexadecachlorophthalocyanine (VII), (granular form)

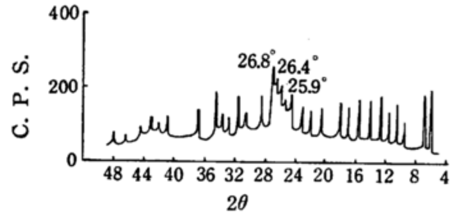

Fig. 40. Copper hexadecachlorophthalocyanine (VII), (granular form); boiled for 10 hr.

causes neither crystal growth nor color change, while in the case of granular II the crystal grows with remarkable change of shade, as shown in Fig. 18. As to the shade, its dominant wavelength shifts to the longer wavelength side by 4 mμ, that is, yellowishness increases.

Granular III grows into needle crystal and, as is clear from Fig. 19, changes in its shade. With a shift of its dominant wavelength by 2.7 mμ, it increases in yellowishness. On the contrary, its isomer, granular IV causes no crystal growth and scarcely changes at all in its shade, as shown in Fig. 20.

Though granular V causes no crystal growth, it changes in shade to some extent, its dominant wavelength making a shift to the longer wavelength side by 0.9 mμ just as illustrated in Fig. 21. On the contrary, its isomer, granular VI causes no crystal growth and scarcely changes in its shade at all, as shown in Fig. 22. It can be said that the effect of chlorine atoms at 3,6- or 4,5-positions on the color change is the same as far as tetrachloro- and octachloro-compounds are concerned.

Fig. 23 shows the color change of granular VII. As the degree of chlorination becomes higher, the color change caused by heating in trichlorobenzene tends to diminish, but even VII exhaustively chlorinated changes its shade to some extent and its dominant wavelength shifts to the longer wavelength side by 1.9 mμ with an increase in yellowishness. However, there is no such crystal growth here as is observed in the case of granular II and III.

Compared with the chlorine atoms of 4,5-positions, those of 3,6-positions have scarcely any power of checking the crystal growth in organic solvents, but they are very powerful in shifting their dominant wavelength to the longer wavelength side. The dominant wavelengths of granular III and its isomer, granular IV are 481.5 mμ and 478.3 mμ respectively, which show that chlorine atom of 3-position is more influential in making an increasing of yellowishness than that of 4-position. This is also the case with granular V and its isomer, granular VI. That is, the former has a dominant wavelength of 485.0 mμ while the latter one of 482.5 mμ.

(3) *X-ray diffraction patterns of pigments.*—X-ray diffraction patterns obtained with a recording X-ray apparatus are shown (Fig. 24 to Fig. 40).

Fig. 24 shows the needle-formed I prepared by sublimation and Fig. 25 shows the granular II prepared from the solution of I in 98% sulfuric acid through reprecipitation method. What is common to both of them is the line of 7°, but they have nothing in other respects. I has the second and third strongest lines at 9° and 23.6°, but II has them at 27.6° and 26.8°; this indicates that there is a great difference between the two forms.

Figs. 26 and 27 show respectively III in needle form as well as in granular form. Fig. 28 shows granular III boiled in trichlorobenzene for 10 hr. The line of 6.4° is the only point in common to Figs. 26 and 27. When the granular product is boiled in trichlorobenzene, its diffraction pattern changes as shown in Fig. 28, approaching that of the needle product (Fig. 26). This phenomenon perfectly coincides with the shade change exhibited by reflectance curves and the form change exhibited by electron microscopic photos.

Figs. 29 and 30 show respectively IV in needle form as well as in granular form. Fig. 31 shows the granular IV boiled in trichlorobenzene for 10 hr. What is common to Figs. 29 and 30 is the neighborhood of 6°. In the needle product, the second, third and fourth strongest lines are found at 9°, 23.6°, and 26°, but in the granular product they are at 26.8°, 26.4° and 13.2°, no similarity being found between the two forms. The granular product, if boiled in trichlorobenzene, changes to some extent and, judging from the diffraction pattern (Fig. 29), approaches the needle product, as shown in Fig. 31.

The X-ray diffraction pattern of needle-formed IV (Fig. 29) closely resembles that of needle-formed I (Fig. 24), but needle-formed III (Fig. 26) differs from needle-formed I. Granular IV (Fig. 30) and granular III (Fig. 27) show different patterns as is the case with the needle forms. Between III and IV, no similarity is found either in needle forms or in granular forms.

Figs. 32 and 33 show respectively V in needle form as well as in granular form. Fig. 34 shows the granular V boiled in trichlorobenzene for 10 hr. In Fig. 32 the strongest line is at 6° and the second and third strongest lines at 27.2° and 8° respectively. In Fig. 33 such lines are at 26.4°, 6.4° and 5.8° respectively, but no similarity is found between the two forms. When the granular product is boiled in trichlorobenzene, a diffraction pattern very similar to the needle form (Fig. 32) is obtained as shown in Fig. 34.

Figs. 35 and 36 show respectively VI in needle form as well as in granular form. Fig. 37 shows the granular VI boiled in trichlorobenzene for 10 hr. In Fig. 35 the strongest line is at 6.4° and the second and third strongest lines at 30.4° and 15.2°. In Fig. 36 such lines are at 30.4°, 15° and 6.8° respectively. Though there is no similarity between the two forms, their X-ray diffraction patterns are considerably closer to each other than those of I, II, III, IV and V. The granular product has no line at 52.4° which is in the case of the needle product. But, when it is boiled in trichlorobenzene, 52.4° line appears and the tendency of approaching the X-ray diffraction pattern of the needles product (Fig. 35) is also recongnized. On the other hand, no similarity is found between V and VI; this fact reminds us of the relation of III to IV. Thus, the influence of the position of chlorine upon the crystal structure is quite evident.

Figs. 38 and 39 show respectively VII in needle form as well as in granular form. Fig. 40 shows the granular VII boiled in trichlorobenzene for 10 hours. In Fig. 38 the strongest line at 6.8° and the second and third strongest lines at 31.6° and 6.2°. In Fig. 39 such lines are at 26.4°, 11.6° and 5.6° respectively. Thus there is no similarity between the two forms. When the granular product is boiled in trichlorobenzene, the strongest line is at 26.8° and the second and third strongest lines at 26.4° and 25.9°, showing a tendency of approaching the X-ray diffraction pattern of the needle product, just as in the case already described.

Discussion

(1) Polymorphism of Copper Phthalocyanine and its Chlorinated Derivatives.—It has been obvious that copper phthalocyanine and copper monochlorophthalocyanine have two forms of crystal structures. The author could make it clear that, chlorinated copper phthalocyanine have two form of crystal structures, no matter how large or small the chlorine contents may be.

This fact must be verified for copper phthalocyanines that their chlorine numbers ranges from naught to sixteen. These chlorinated copper phthalocyanines are to be obtained from mono-, di- and trichlorophthalic anhydrides with chlorine atoms at definite positions and tetrachlorophthalic anhydride. But it becomes difficult for chlorinated derivatives of phthalic anhydride to react as the chlorine contents grow larger. To cite an example of the experiments by the author, in the formation of phthalocyanine from tetrachlorophthalic anhydride, dechlorination reaction occurred and copper hexadecachlorophthalocyanine the author aimed at was not obtained. Meanwhile, phthalocyanine formation was run on the mixture of a given amount of chlorinated phthalic anhydrides, but it was not confirmed whether they reacted uniformly or singly. Consequently, this experiment was discontinued and examination was done with the six kinds of samples listed above. The aimed object was satisfactorily achieved by the results with them.

(2) Crystal Growth of Chlorinated Copper Phthalocyanines.—It is known that the introduction of chlorine atoms into copper phthalocyanine can prevent the crystal growth in organic solvents. Particularly, no crystal growth is recognizable in copper phthalocyanine green with a large chlorine content, but the position of chlorine atom plays an important role in crystal growth of lowly chlorinated compounds. Namely, chlorine atom at 4-position gives forth a very great action in suppressing the crystal growth but the one at 3-position gives hardly any effect.

When more than eight chlorine atoms are contained, crystal growth is not usually recognized. But, if boiled in such high boiling point organic solvent as trichlorobenzene, all the X-ray diffraction patterns of the products where no crystal growth is recognized tend to approach those of the needle products. This phenomenon is similar to the transformation of unstable β-form copper phthalocyanine into stable α-form by heating the former in organic solvents.

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