

## Reduction of Copper Hexadecachlorophthalocyanine

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It was manifest by the previous study<sup>1)</sup> that the darkening of chlorinated copper phthalocyanine green by reducing agents was caused, not by variation in forms, but by variation in its crystal structure or in its chemical composition. The degree of discoloration corresponded, though very little, to that of decrease in chlorine content, from which it was inferred that hydrogen atoms had been introduced into phthalocyanine nucleus. If phthalocyanine nucleus is to be reduced, either C=C or C=N bond is considered to be the position of reduction. Whether the position attacked is C=C or C=N is made clear by using the exhaustively chlorinated compound (copper hexadecachlorophthalocyanine, I). Hence the author used I as a sample and studied the mechanism of reduction.

### Experimental

**Materials.**—Copper hexadecachlorophthalocyanine (I).—The compound which was synthesized according to the method previously reported<sup>2)</sup>, was used as chlorinated copper phthalocyanine green. Reducing agent was made to act upon it, which was then oxidized, reprecipitated and heated as follows.

**Pulverization.**—I was dissolved in chlorosulfonic acid, poured into ice water, and deposited as fine particles. The chlorine content was 50.33% (Calcd. 50.34%) as previously indicated<sup>2)</sup>.

**Reduction.**—One gram of I and 30 cc. of 20% aqueous solution of rongalit (addition compound of formalin and sodium hydrosulfite) were placed in a stainless steel autoclave of 50 cc. capacity and heated at 150~155°C for 20 min. The product was filtered off, washed with water and dried. It was dark green particles.

**Oxidation of the reduced product.**—One gram of the reduced product was added to 80 cc. of 2% sulfuric acid containing 0.2 g. of ceric sulfate and heated at 70~80°C for 1 hr.

**Reprecipitation of the reduced product.**—One gram of the reduced product was dissolved in 30 g. of chlorosulfonic acid at room temperature and poured into ice water. The precipitate thus

obtained was filtered and washed with water.

**Heating of the reduced product.**—The reduced product was heated at 250~255°C for 3 hr. in a stream of nitrogen.

**Methods.**—Variation in color observed in the case of reduction of I and of oxidation, reprecipitation and heating of the reduced product was studied by measuring the reflectance curves with a recording spectrophotometer (General Electric Co.). Samples for reflectance-curve measurement were made in the same procedure as previously reported<sup>1)</sup>. X-ray diffraction patterns of I and its reduced product were obtained with a recording X-ray diffraction apparatus (Philips Co.) and variation in crystal structure was studied.

Then, elementary analysis of I and its reduced product was conducted. Also, infrared spectra (Nujol) were taken of I, its reduced product, the reoxidized reduced product and the reprecipitated reduced product, using a Perkin Elmer 12B instrument.

### Results

**Reflectance Curves.**—Fig. 1 shows the reflectance curves of I, its reduced product

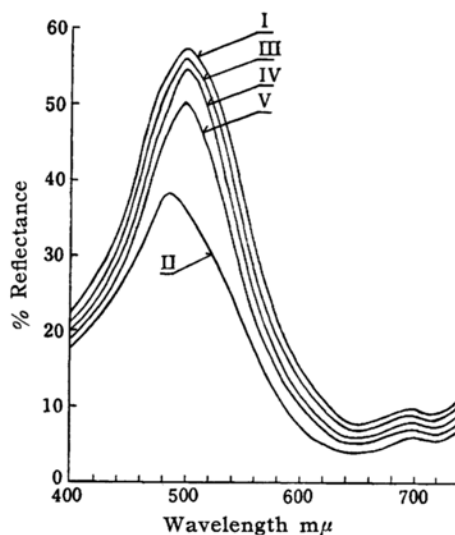


Fig. 1. Reflectance curves of copper hexadecachlorophthalocyanine (I), its reduced product(II), reoxidized reduced product(III), reprecipitated reduced product(IV) and heated reduced product(V).

1) M. Shigemitsu, This Bulletin, 32, 502 (1959).

2) M. Shigemitsu, J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi), 62, 112 (1959) (presented at the Autumnal Meeting of Chemical Society of Japan, Tokyo, 1957).

(II), the reoxidized reduced product(III), the reprecipitated reduced product(IV) and the heated reduced product(V). Table I gives their C.I.E. Notations. In this table,  $Y$  denotes luminosity,  $P_e$  purity and  $\lambda_D$  dominant wavelength.

TABLE I. C.I.E. NOTATIONS

Sample	$Y$ %	$P_e$ %	$\lambda_D$ m $\mu$
I	30.34	36.8	492.6
II	22.18	39.1	488.9
III	29.96	37.2	490.8
IV	29.58	37.5	490.2
V	28.41	38.1	489.7

When a reducing agent acted upon I, its luminosity lowered from 30.34 to 22.18% and it darkened in color. When this darkened pigment was heated at 250~255°C for 3 hr. in nitrogen stream, its luminosity increased to 28.41% approaching that of untreated pigment; when being oxidized and reprecipitated, the pigment increased its luminosity to 29.96 and 29.58%, respectively, recovering color of luminosity approaching that of untreated material. Thus the variation in color is of a reversible trend.

**X-ray Diffraction Patterns.**—Figs. 2 and 3 show the X-ray diffraction patterns of I and its reduced product.

It was made clear by the previous study that the darkening by the action of re-

ducing agent was not due to the change in the form of pigment particles. Now, with the aid of X-ray diffraction method, no change was observed in the crystal structure either. Thus the color change is supposed to be due to the difference in the chemical composition of the compounds in question.

**Elementary Analysis.**—Results of analysis of I and II are given in Table II.

TABLE II. RESULTS OF ELEMENTARY ANALYSIS

Sample	C %	H %	N %	Cl %	Cu %
I Found	34.10	0.09	9.90	50.33	5.64
I Calcd.	34.09	—	9.94	50.34	5.63
II Found	33.60	1.26	9.80	49.75	5.59
III*	33.67	1.23	9.82	49.71	5.57

\*III, Calculated value when fourteen hydrogen atoms were added to I.

I contains no hydrogen, but, on reduction, its hydrogen content increased to 1.26% indicating the addition of fourteen hydrogen atoms.

**Infrared Spectra.**—Figs. 4, 5, 6 and 7 show infrared spectra of I, II, III and IV. Fig. 8 shows that of copper phthalocyanine containing no chlorine, which was measured by Tyler et al.<sup>3)</sup> The lower curve in Fig. 8 denotes the use of Nujol and the upper curve, shown partly, denotes the use of hexachlorobutadiene.

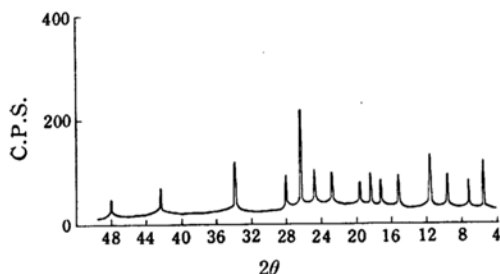


Fig. 2. X-ray diffraction pattern of copper hexadecachlorophthalocyanine (leaflet, fine particle).

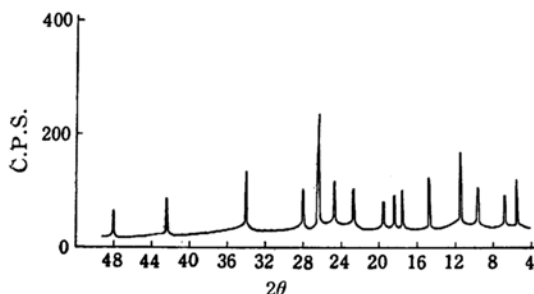


Fig. 3. X-ray diffraction pattern of reduced product of copper hexadecachlorophthalocyanine (leaflet, fine particle).

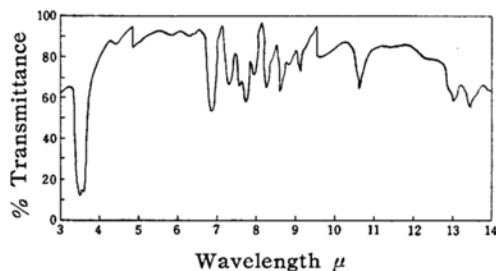


Fig. 4. Infrared spectrum of copper hexadecachlorophthalocyanine.

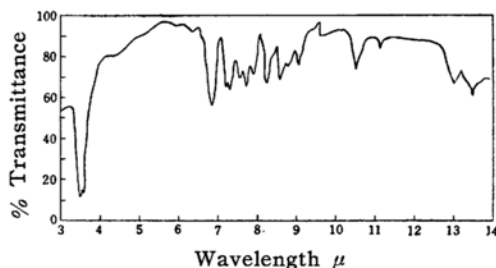


Fig. 5. Infrared spectrum of reduced product of copper hexadecachlorophthalocyanine.

3) J. E. Tyler et al., *Anal. Chem.*, 25, 393 (1953).

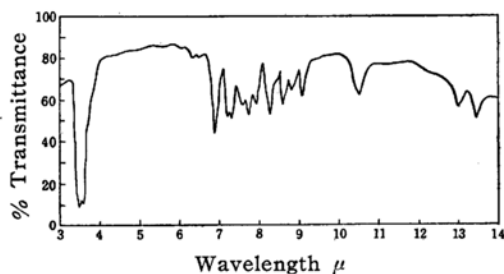


Fig. 6. Infrared spectrum of reoxidized reduced product of copper hexadecachlorophthalocyanine.

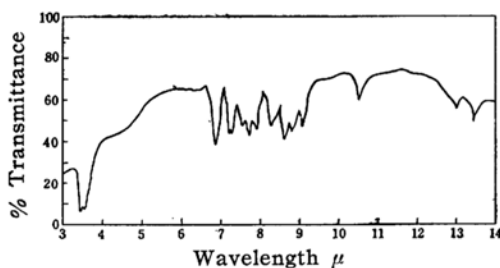


Fig. 7. Infrared spectrum of reprecipitated reduced product of copper hexadecachlorophthalocyanine.

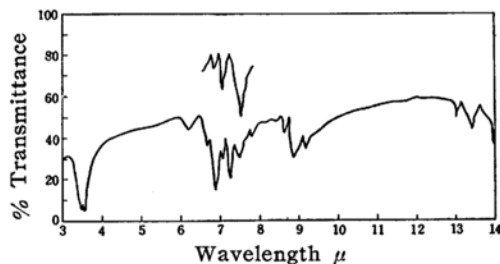


Fig. 8. Infrared spectrum of copper phthalocyanine.

When sixteen hydrogen atoms of copper phthalocyanine were chlorinated to give I, absorption bands at  $720\text{ cm}^{-1}$ ,  $1090\text{ cm}^{-1}$ ,  $1125\text{ cm}^{-1}$ ,  $1290\text{ cm}^{-1}$  and  $1415\text{ cm}^{-1}$  of copper phthalocyanine disappeared and those at  $947\text{ cm}^{-1}$ ,  $1095\text{ cm}^{-1}$ ,  $1210\text{ cm}^{-1}$ ,  $1273\text{ cm}^{-1}$  and  $1305\text{ cm}^{-1}$  were exhibited. The absorption band at  $1415\text{ cm}^{-1}$  of copper phthalocyanine became even more conspicuous when hexachlorobutadiene was used instead of Nujol.

### Discussion

Copper phthalocyanine, I and II are compared (Fig. 9). The absorption band at  $1415\text{ cm}^{-1}$  of copper phthalocyanine disappears in I but, when being reduced, the compound shows again the absorption band at  $1412\text{ cm}^{-1}$ . Therefore, this absorption band is due to the vibration of

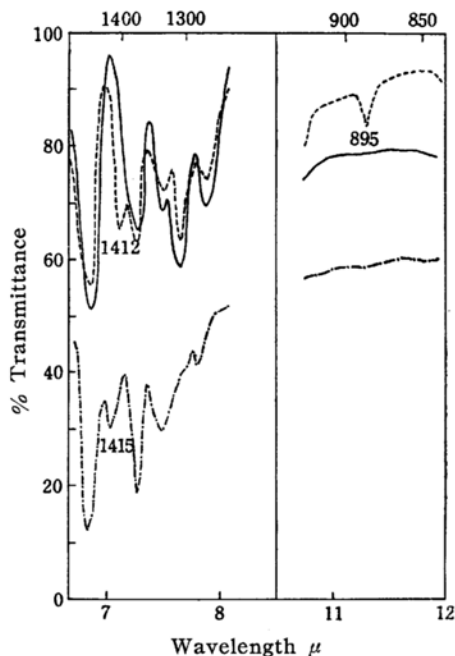


Fig. 9. Comparison of infrared spectra.  
— copper hexadecachlorophthalocyanine.  
----- reduced product of copper hexadecachlorophthalocyanine.  
- - - copper phthalocyanine.

C-H bond of copper phthalocyanine. It is further inferred that, since C-H bending vibration appears in the range of  $1475\sim 1300\text{ cm}^{-1}$ <sup>4)</sup>, this absorption band may be due to the same vibration.

Further, a new absorption band appears at  $895\text{ cm}^{-1}$  in II, but no such absorption band in I and copper phthalocyanine. Therefore, this absorption band may be attributed to the addition of hydrogen atoms. The position of the addition of hydrogen atoms is considered to be either C=C or C=N. Actually, the addition seems to proceed at C=N bond of the phthalocyanine nucleus, because the absorption band at  $895\text{ cm}^{-1}$  corresponds to N-H bending vibration according to Colthup<sup>4)</sup>.

Gund<sup>5)</sup> describes that cobalt phthalocyanine produces two N-H bonds when reduced. In the present experiment fourteen hydrogen atoms were added to phthalocyanine nucleus. Observing the absorption of C-H and N-H bonds which appeared in II, it is considered that twelve hydrogen atoms add to six C=C bonds and the remaining two hydrogen atoms, as inferred by Gund, produce two N-H bonds.

4) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

5) F. Gund, *J. Soc. Dyers and Colourists*, **69**, 671 (1953).

Thus, the chlorination of copper phthalocyanine seems to facilitate hydrogenation at C=C and C=N bonds of phthalocyanine, and the darkening of color occurs as is observed in the reduced vat dyes.

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