Action of Reducing Agents on Copper Phthalocyanine and its Chlorinated Derivatives

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(Received September 19, 1958)

Although copper phthalocyanine is a very stable organic pigment, it is decomposed by oxidizing agents in its dissolved state in strongly acid solvents. However, it has been considered so far that copper phthalocyanine is stable toward reducing agents. The author examined the action of reducing agents on copper phthalocyanines containing chlorine in the range of naught to sixteen atoms per molecule and found that they were easily attacked by reducing agents, while copper phthalocyanine containing no chlorine was not. When copper phthalocyanine is chlorinated into " copper phthalocyanine green ", its color is darkened from bright green to dark green. The cleavage of phthalocyanine nucleus was not caused by reducing agents, although it was caused by oxidizing agents.

Experimental

Materials.—Syntheses of copper phthalocyanine and chlorinated copper phthalocyanines were carried out as follows.

Copper phthalocyanine.—A mixture of phthalic anhydride, urea and cuprous chloride was heated at about 190°C for 3 hr.[1] The reaction product was treated with 5% hydrochloric acid and 2% sodium hydroxide The precipitate was filtered off, washed with water and ethanol, and dried.

Chlorinated copper phthalocyanines.—One part of copper phthalocyanine was dissolved in 6 parts of a eutectic mixture of aluminum chloride and sodium chloride (9:2, by weight, m. p. 145°C) at 150∼160°C, and chlorine gas was introduced at a given flow rate and samples were taken out at regular intervals. These samples were washed with 5% hydrochloric acid, 2% sodium hydroxide, water and ethanol, and nine kinds of chlorinated copper phthalocyanine with chlorine content ranging from 2.91% to 44.97% as the degrees of chlorination were prepared. Copper hexadecachlorophthalocyanine (sample XI in Table I) was prepared by chlorinating copper octa-(3,6)-chlorophthalocyanine[2].

The results of chlorine analysis (micro-Carius method) for eleven samples thus prepared are given in Table I.

Methods.—*Particle size reduction.*—The particle size of these samples prepared as above were too large to be used as pigments. Therefore, the particle size of these samples was reduced

TABLE I. CHLORINE CONTENTS OF THE SAMPLES

Sample	Cl %	Cl atom/mol.
I	0.11	0
II	2.91	0.5
III	15.15	1.8
IV	24.05	5.1
V	25.44	5.5
VI	33.71	8.2
VII	39.57	10.6
VIII	42.86	12.1
IX	43.63	12.5
X	44.97	13.2
XI	50.32	16.0

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

[2] M. Shigemitsu, ibid., **62**, 110 (1959) (presented at the Autumnal Joint Meeting of Chemical Societies of Japan, Tokyo, 1957).

by the acid pasting method[3]. One part of the sample (I~V) was dissolved in 5 parts of 98% sulfuric acid, while 1 part of the sample (VI~XI) was dissolved in 3 parts of chlorosulfonic acid. Each solution was poured into 70 parts of ice water with stirring. Fine crystals precipitated were filtered off, washed free from acid with water and dried at about 60°C.

*Treatment by reducing agent, rongalit**. — A mixture of 1 g. of the sample treated as in the above section and 30 cc. of 20% aqueous solution of rongalit was heated at 150~155°C for 20 min. in a stainless steel autoclave equipped with a stirrer. The product obtaind was filtered off, washed with water and dried at about 60°C.

Measurement of the spectral reflectance curves. —One part of the sample treated as in the above section and 1.5 parts of polymerized linseed oil were mixed, made into paste by grinding 400 rounds in a Hoover automatic muller. To one part of this paste were added 70 parts of zinc white paste obtained by grinding 2 parts of zinc oxide with 1.5 parts of polymerized linseed oil. Then the mixed paste was applied 0.5 mm. thick on a coated paper with a "bladeoapplicator" (Gardner Laboratory), and the specimen was dried at room temperature. The spectral reflectance of the specimen prepared thus was measured with a General Electric recording spectrophotometer.

Electron microscopic observation of particle forms and measurement of particle size distributions.—To the samples (VI, VII, VIII, IX and X treated as in the above section was added 0.1% aqueous solution of a non-ionic surface active agent and the pigment was thoroughly dispersed with agitation. A drop of the dispersed solution was placed on a collodion film and dried. The electron microphotographs were taken at 2,000 magnification with an electron microscope of Hitachi Works, and the 20,000 magnification was obtained by enlarging photographs ten times. Three hundreds particles photographed were taken out at random, and particle size distributions were calculated by measuring their shorter and longer diameters.

Results

Variation in Chlorine Content.—Chlorine contents of the samples heated in the aqueous solution of rongalit are given in Table II.

TABLE II. VARIATION IN CHLORINE CONTENT

Sample	Cl %	
	Original sample	Sample treated by rongalit
I	0.11	0.12
II	2.91	2.86
III	15.15	15.09
IV	24.05	24.12
V	25.44	25.38
VI	33.71	33.32
VII	39.57	39.15
VIII	42.86	42.41
IX	43.63	43.10
X	44.97	44.30
XI	50.32	49.76

As is clear from Table II, samples I to V do not vary in their chlorine content. But samples VI to X, which have greater chlorine contents, show some decrease in chlorine content by the treatment in rongalit. The greater the chlorine content of the sample, the greater the decrease in the chlorine content by the treatment. However, copper hexadecachlorophthalocyanine (XI) shows somewhat smaller decrease in chlorine content.

Variation in Color.—The luminosity Y, purity P_e and dominant wavelength λ_D calculated after the C. I. E. coordinate system from the spectral reflectance data are given in Table III.

TABLE III. LUMINOSITY, PURITY AND DOMINANT WAVELENGTH OF THE PIGMENTS

Sample		Y %	P_e %	λ_D mμ
I	original	24.80	48.7	479.0
	treated	22.78	40.3	478.8
II	original	19.07	54.2	478.5
	treated	24.13	48.0	479.4
III	original	18.45	56.0	478.2
	treated	21.62	53.7	478.9
IV	original	19.75	58.3	481.0
	treated	21.87	56.0	481.2
V	original	21.77	54.0	482.2
	treated	23.08	52.0	482.0
VI	original	25.13	49.5	484.8
	treated	23.90	47.3	483.3
VII	original	25.63	46.0	486.9
	treated	21.75	45.5	485.2
VIII	original	26.83	40.3	489.8
	treated	20.48	37.0	486.8
IX	original	26.80	41.0	490.8
	treated	20.07	38.5	487.4
X	original	30.33	37.0	491.4
	treated	20.15	39.0	487.5
XI	original	30.34	36.8	492.6
	treated	22.18	39.1	488.9

It is evident from Table III that the variation of color becomes greater with the increase in the chlorine content and diminishes again in copper hexadecachlorophthalocyanine (XI). The relationship between the luminosity change (ΔY%)

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[3] H. A. Lubs, "Chemistry of Synthetic Dyes and Pigments", Reinhold Publishing Corp., New York (1955), p. 587.

* addition compound of formalin and sodium hydrosulfite.

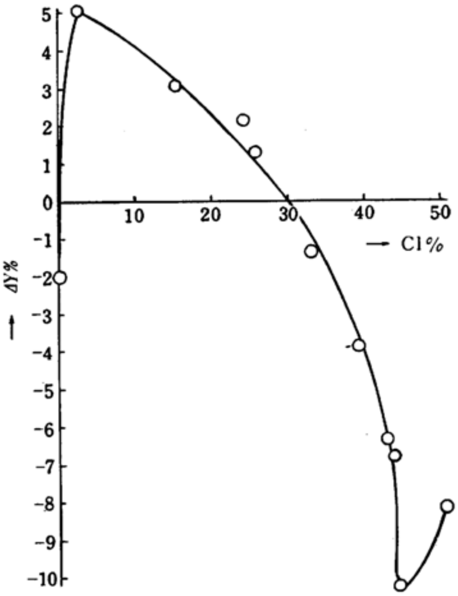

Fig. 1. Relationship between luminosity change and chlorine content.

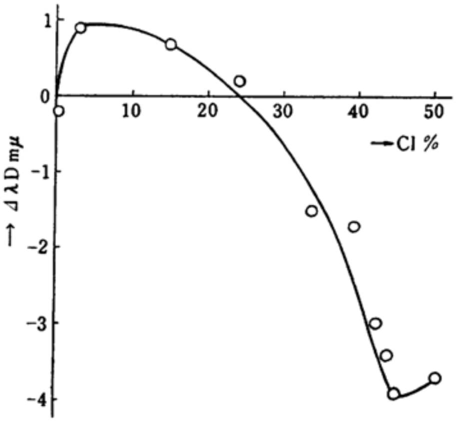

Fig. 2. Relationship between the shift of dominant wavelength and chlorine content.

or shift of dominant wavelength ($\Delta\lambda_D$ mμ) and the chlorine content are shown in Figs. 1 and 2.

It is to be noted that the sample with a greater chlorine content shows a lower brightness in color and shorter dominant wavelength.

Particle Size Distribution of Samples Subject to Remarkable Discoloration.—It is inferred from the above results that darkening of the color of samples treated with reducing agents is accompanied with the change in chemical composition of pigments. However, as the color of pigments, unlike dyes, is largely influenced by the form and the size of particles. particle size distribution of samples subject to remarkable discoloration (VI, VII, VIII, IX and X) was measured. The results are given in Table IV in which d_{mp} denotes the most probable value and d_m the average particle diameter. The value of d_m was calculated from

TABLE IV. PARTICLE SIZE DISTRIBUTION

Sample	Diameter mμ	d_{mp} mμ	d_m mμ	$\pm\delta$ mμ	Form
VI original	110～340	207	235	50	leaflet
	225～450	325	337	49	
VI treated	118～329	213	220	44	〃
	225～452	318	360	59	
VII original	103～370	208	219	52	〃
	230～480	342	343	44	
VII treated	110～370	220	223	48	〃
	240～485	350	354	59	
VIII original	115～320	200	202	45	〃
	220～479	320	337	55	
VIII treated	112～302	210	201	39	〃
	210～480	335	328	47	
IX original	120～322	208	207	42	〃
	240～460	345	339	50	
IX treated	114～330	212	222	44	〃
	250～472	340	347	52	
X original	121～300	204	216	42	〃
	220～450	330	313	54	
X treated	110～302	208	217	38	〃
	243～448	315	331	39	

$$d_m = 1/100\sum_i f_i d_i \text{ }^{4)}$$

where f is frequency and d particle diameter. "$\pm\delta$" in Table IV denotes deviation, that is, average deviation value from d_m, which was calculated from

$$\varDelta = 1/100\sum_i (d_m - d_i)^2 f_i \text{ }^{4)}$$

It is obvious from Table IV that variation in form or aggregation of pigment particles did not occur by the treatment of pigments in the aqueous solution of rongalit. Namely, as already described, it was confirmed that the variation of color was due to the change of chemical composition.

Summary

Action of reducing agents on copper phthalocyanine and its chlorinated derivatives was studied, and it was found that, while copper phthalocyanine containing no chlorine did not suffer from discoloration, the color of its polychlorinated derivatives darkened. The discoloration, was most conspicuous when 13 to 14 chlorine atoms per phthalocyanine molecule were contained. The chlorinated copper phthalocyanine become stable toward reducing agents when it was exhaustively chlorinated.

It was confirmed that the darkening of the color of pigments was caused by the change of chemical composition, not by the change of size and form of particles.

The author extends his sincere thanks to Dr. Ryozo Goto, Professor of Kyoto University, for his kind guidance throughout the present study. The author's grateful thanks are also due to Dr. Takahisa Nakamura and Dr. Wataru Ishikawa, Toyo Ink Manufacturing Company, for the valuable advice and much help during the experiments.

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[4] E. Suito et al., presented at the 58th Meeting of Electron Microscope Committee of Japan, 1951.