The History and Development of Phthalocyanine Chemistry

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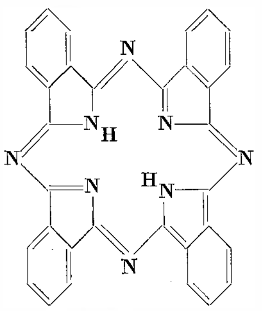
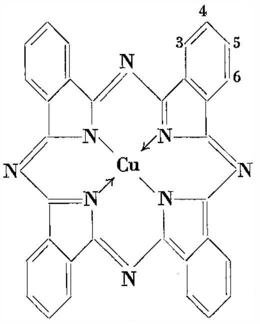
Discovery and determination of structure

The first three recorded preparations of phthalocyanines were all accidential. In 1907, **Braun** and **Tcherniac**,[1] reported that molten *o*-cyanobenzamide turned green and gave a small quantity of a blue, alcohol-insoluble, substance. The product obtained in this way is now known as metal-free phthalocyanine (I).



I

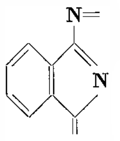


II

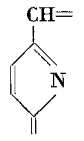
In 1927, **de Diesbach** and **von der Weid**,[2] at the University of Fribourg in Switzerland, prepared copper phthalocyanine (II; although several years were to elapse before the constitution was determined) by two methods. Firstly, by analogy with previous experiments with dibromoxylenes,[3] *o*-dibromobenzene was heated with cuprous cyanide in pyridine at 200 °C, but gave a blue product rather than the expected phthalonitrile. The same blue product was also obtained by heating phthalonitrile (which was therefore the likely intermediate in the first process) with cuprous bromide in pyridine at reflux temperature. This second process is obviously an improvement on the first and yields of about 70% of the theoretical can be obtained. The mode of formation of this new copper complex together with the elementary analysis suggested the formula $[C_6H_4(CN)_2]_2Cu(C_5H_5N)_2$, i. e. $C_{26}H_{18}N_6Cu$ rather than the correct $C_{32}H_{16}N_8Cu$. **De Diesbach** and **von der Weid** observed the remarkable stability of their product to heat, concentrated alkali and concentrated sulphuric acid and concluded «nous serions heureux si des collègues plus spécialisés dans l'étude des sels complexes voulaient bien éclaircir la constitution et les causes de la stabilité de ces nouveaux produits».

The story now moves to Grangemouth, Scotland, where early in 1928 a blue substance which had been observed in a phthalimide melt pot was separated and examined by **Dandridge**, **Drescher**, **Dunworth** and **Thomas**. The product was shown to be an iron complex which was readily obtained, albeit in comparatively low yield, by heating together either phthalic anhydride, iron and ammonia, or phthalimide, ferrous sulphate and ammonia. Similar copper and nickel compounds were obtained from phthalic anhydride or phthalimide by heating with ammonia and the appropriate metal salt. The results of this work were patented[4] without realising the significance of the earlier results reported in the literature since the starting materials were different.

Work during the ensuing six years served to link together these three separate observations and discoveries and the elucidation of the metal phthalocyanine structure finally realised **de Diesbach**'s wish, quoted earlier. In 1929, Scottish Dyes Limited (by this time part of Imperial Chemical Industries Limited, Dyestuffs Group) supplied samples of the iron and copper compounds to **Thorpe** and **Linstead** at the Royal College of Science. By 1933, **Linstead** was able to report to the "British Association" meeting[5] that the unit of phthalocyanine (as he then termed it) was III, by analogy with the porphin unit IV;



III



IV

the macrocycle formed with a divalent metal (M) having the formula $(C_8H_4N_2)_4M$. The work of **Linstead** and his co-workers which led to this conclusion, and also to the proposal of structures I and II, was fully reported in 1934.[6] Final confirmation of the macrocyclic structures soon followed with **Robertson**'s X-ray study of metal-free, nickel, copper and platinum phthalocyanines.[7]

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[1] A. **Braun** and J. **Tcherniac**, *Chem. Ber. 40* (1907) 2709.

[2] H. **de Diesbach** and E. **von der Weid**, *Helv. Chim. Acta 10* (1927) 886.

[3] H. **de Diesbach**, *Helv. Chim. Acta 6* (1923) 539.

[4] Scottish Dyes Ltd. (A. G. **Dandridge**, H. A. **Drescher** and J. **Thomas**), British Patent 322,169 (appln. 16.5.1928).

[5] R. P. **Linstead** (reported in), *Chem. Age 29* (1933) 228.

[6] R. P. **Linstead** *et al.*, *J. Chem. Soc. 1934,* 1016, 1017, 1022, 1027, 1031, 1033.

[7] J. M. **Robertson**, *J. Chem. Soc. 1935,* 615.

[8] C. J. T. **Cronshaw**, *Endeavour 1* (1942) 79.

Manufacture of copper phthalocyanine

Copper phthalocyanine was first placed on the market in 1935 as Monastral Fast Blue B (I.C.I.).[8] The first manufacturing process was carried out at Trafford Park Manchester and involved baking phthalonitrile with either copper bronze or cuprous chloride at 200 to 240 °C in copper trays. An ingenious process was discovered in 1936 based on the cheaper phthalic anhydride.[9] Cupric chloride was added to a molten mixture of urea and phthalic anhydride and the formation of product completed at 200 °C. Even though this process was more difficult to operate and gave lower yields than the phthalonitrile process it was immediately worked on the large scale. A study of the effect of catalysts on this process was made after it had been observed that the yield was dependent on the materials of construction of the vessel. This resulted in the discovery that molybdenum compounds were outstandingly good catalysts[10] and ammonium molybdate has since been used almost invariably in the phthalic anhydride-urea process. The use of a catalyst increased the manufacturing yield from 50% to 80%. The yield was then further increased by changing from the melt process to a more convenient solvent process. This is essentially the same reaction but carried out in a high-boiling organic liquid reaction medium such as kerosene or trichlorobenzene.

I. G. Farben manufactured copper phthalocyanine shortly after I.C.I. Ltd. and mainly because of the DE DIESBACH disclosure[2] were able to work a process starting from phthalonitrile. In fact, by 1945, a continuous bake process using phthalonitrile and cuprous chloride had been developed. This was preferred to the solvent urea process which was only used when there was a shortage of phthalonitrile.[11, 12] However, any comparison between the two main processes must ultimately depend upon the comparative costs of phthalonitrile and phthalic anhydride.

Polymorphism in copper phthalocyanine pigments

Until the 1950's the only commercial pigmentary form of copper phthalocyanine was the metastable (α-form) product obtained by reprecipitation of the crude pigment from concentrated sulphuric acid (acid-pasting) or by "salt-milling" with an inorganic salt which is subsequently washed out. The greener β-form (the stable polymorph) which is obtained directly from the manufacturing process requires purification by washing with dilute acid or dilute alkali, or both, and when used acid pasting acts as a further purification. One defect of the α-form pigment is its lack of stability in various media, particularly in those containing aromatic solvents; this is now known to be due to crystal growth accompanied by transition to the β-form (see Figure 1).

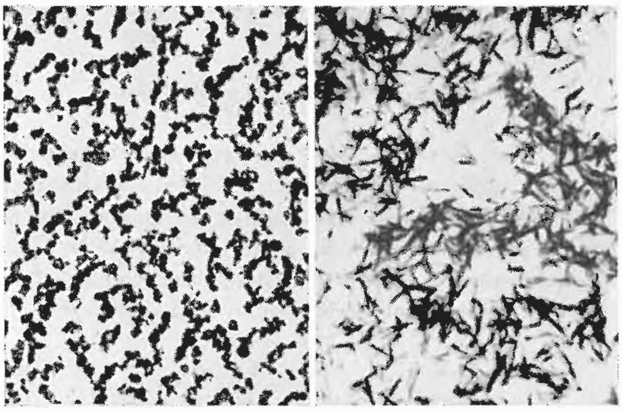

Figure 1. The crystallisation effect of aromatic solvents on copper phthalocyanine. Left: immediately after dispersion; right: after 72 hours

Special treatment is required to convert the highly crystalline β-form to pigment, for example it may be finely milled (< 2 microns) then given a controlled crystallisation treatment.[13] The increased stability of the β-form, combined with its greener and brighter shade make it of particular value in certain end-uses.[14] American markets, for which full figures are available, reflect the increasing importance of the β-form as shown by the production chart in Figure 2.

At least two other polymorphic forms of copper phthalocyanine are known, being distinguished by their

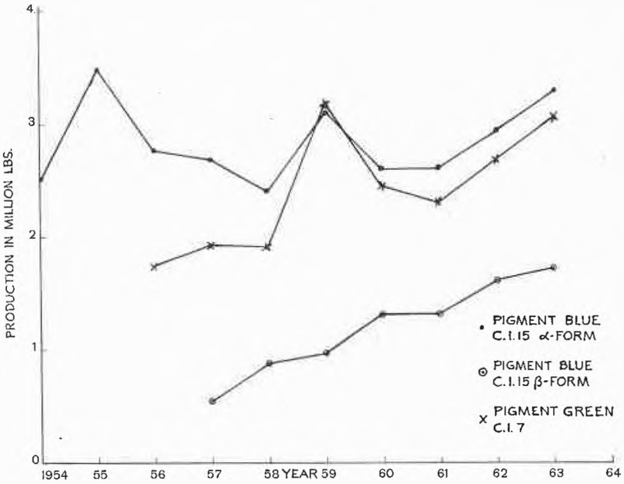

Figure 2. U.S. production of copper phthalocyanine and polychloro copper phthalocyanine pigments (prepared from U.S. Tariff Commission data)

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[9] Imperial Chemical Industries Ltd. (M. WYLER), British Patent 464,126 (appln. 10.7.1935).

[10] Imperial Chemical Industries Ltd. (A. RILEY), British Patent 476,243 (appln. 4.6.1936).

[11] BIOS Final Report No. 960, p. 33 *et seq.*

[12] FIAT Final Report No. 1313, Vol. III, p. 273 *et seq.*

[13] American Cyanamid Co. (R.H. WISWALL), British Patent 600,911 (conv. 12.3.1943).

[14] D.M. VARLEY, *Paint Manuf. 31* (1961) 373.

X-ray diffraction spectra. The γ-form is obtained by slurrying copper phthalocyanine, prepared in solvent medium, with 60% aqueous sulphuric acid,[15] and the δ-form is obtained by treating the α-form with benzene in aqueous sulphuric acid in the presence of a surfactant.[16] No commercial application of forms other than α- and β- is known at present.

Halogenated copper phthalocyanine pigments

The use of partially chlorinated copper phthalocyanine (containing about one chlorine per molecule) is technically the most important way of stabilising the α-form pigment. Preparation is effected by controlled chlorination or, conveniently by introduction of the appropriate quantity of 4-chlorophthalic anhydride into the phthalic anhydride-urea process.

Fully halogenated copper phthalocyanines are by far the most important phthalocyanine derivatives. Although a gradual change from blue to green is obtained by stepwise replacement it is not until 14 to 16 halogen substituents are present that the most important green pigments result.

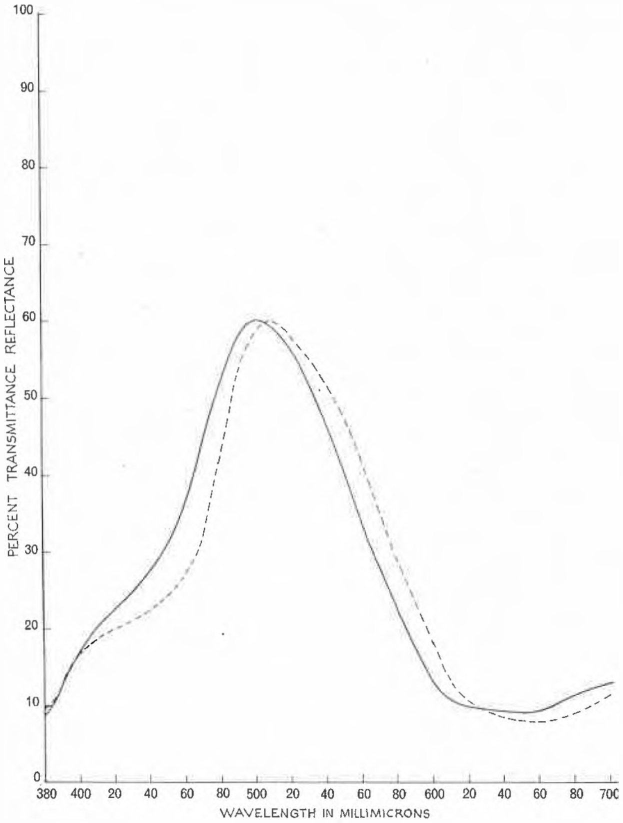

Figure 3: Reflectance spectra of $CuPcCl_{15}$ (——) and $CuPcBr_{15}$ (– – –)

In the absence of reliable world figures, the U.S. production of polychloro copper phthalocyanine green pigment is shown in Figure 2. The weight of copper phthalocyanine required for production of the green (i. e. about half the weight of green) together with the copper phthalocyanine used in the manufacture of other substitution products has to be added to the pigment production figures of Figure 2 to obtain the total production of copper phthalocyanine itself. Manufacture of the chloro green pigment started in the late 1930's and, although several alternative processes are available, the preferred method on the large scale is halogenation at 180 to 200 °C in a molten eutectic mixture of aluminium chloride and sodium chloride.[11] It required another twenty years before any significant technical advance was made in this field. Although it had been known for many years that brominated products were yellower in shade than the corresponding chlorinated products (see Figure 3 for a comparison) it was not until 1959 that a mixed bromochloro copper phthalocyanine was introduced commercially by General Aniline and Film Corporation.[17] The difficulties were mainly in achieving the optimum conditions for controlled simultaneous bromination and chlorination to give complete halogenation.[18] The first yellowish-green of this class contained 4 to 5 atoms of bromine and 9 to 11 atoms of chlorine and many other similar mixed products are now on the market, with the yellowest product containing 11 to 12 atoms of bromine and 3 to 4 atoms of chlorine per molecule.

Metal-free phthalocyanine

Only three phthalocyanine compounds achieved any commercial importance before 1940. Copper phthalocyanine (α) and polychloro copper phthalocyanine have already been discussed and (metal-free) phthalocyanine was next in importance. Phthalocyanine was first prepared by demetallising magnesium phthalocyanine with dilute acid. On the large scale it is best obtained from disodium phthalocyanine, which is prepared by heating phthalonitrile with the sodium derivative of a high boiling alcohol in excess of the alcohol.[11, 19]

Like copper phthalocyanine, metal-free phthalocyanine exists in several polymorphic forms. The α-form is greener than the α-form of copper phthalocyanine and even less stable. Although the β-form is greener still and solvent stable, manufacture of metal-free phthalocyanine in the United States apparently ceased with the advent of the cheaper β-form copper phthalocyanine to meet requirements for the greener-blue shades.

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[15] American Cyanamid Co. (J. W. Eastes), U.S. Patent 2,770,629 (appln. 8.1.1952).

[16] Imperial Chemical Industries Ltd. (B. P. Brand), British Patent 912,526 (appln. 19.2.1960).

[17] E. A. Wich, *Amer. Ink Maker 37* (8) (1959) 26; *Amer. Dyestuffs Rep. 48* (18) (1959) 42.

[18] E. I. du Pont de Nemours & Co. (A. L. Fox), U.S. Patent 2,247,752 (appln. 23.6.1937). Imperial Chemical Industries Ltd. (R. Fazackerley and A. Kershaw), British Patent 932,943 (appln. 11.11.1960).

[19] Imperial Chemical Industries Ltd. (I. M. Heilbron, F. Irving, R. P. Linstead, and J. F. Thorpe), British Patent 410,814 (appln. 16.11.1932).

Li	Be													
Na	Mg											$\underline{\text{Al}}$	$\underline{\text{Si}}$	
K	Ca		$\underline{\text{Ti}}$	$\underline{\text{V}}$	Cr	Mn	Fe	Co	Ni	Cu	Zn	$\underline{\text{Ga}}$	$\underline{\text{Ge}}$	
			$\underline{\text{Zr}}$	$\underline{\text{Nb}}$	Mo		Ru	Rh	Pd	Ag	Cd	$\underline{\text{In}}$	Sn	$\underline{\text{Sb}}$
	Ba	La (Lanthanides)	$\underline{\text{Hf}}$	$\underline{\text{Ta}}$			$\underline{\text{Os}}$		Pt		Hg		Pb	
			Th		$\underline{\text{U}}$									

Figure 4. The metals of which phthalocyanine derivatives have been reported

Phthalocyanines of other metals

Phthalocyanine derivatives of most metals are now known and Figure 4 lists these metals according to their arrangement in the periodic table. In most cases the metal is present in the mono- or di-valent state but those metals which are underlined give derivatives only in higher valency states and consequently require additional anionic ligands.

The type of metal to nitrogen bonding varies according to the metal. Generally, the transition metals are covalently bound to two anionic nitrogens of the phthalocyanine inner ring and the planar four-coordination completed through the two neutral nitrogen atoms. With non-transitional elements the bond is mainly ionic in character, with no further coordination, and this leads to a much lower order of stability; the metal being displaced from the salt-like compound by treatment with dilute acid. Additional stabilisation is possible where the transition metal has filled non-bonding *d*-orbitals since, although there is no supporting evidence,[20] the d_{xz} and d_{yz} orbitals are capable of forming π-bonds with the surrounding phthalocyanine macrocycle. This would support the increased bond strength apparent in metals (e.g. Pt) to the right of the transition series. The only transition-metal phthalocyanine which is readily demetallised is that of Mn(II); this degree of instability is much greater than would be expected from the Irving-Williams order and is more likely to be attributable to the exceptional affinity of manganese (II) phthalocyanine for oxygen.[21]

The most general method for the preparation of metal phthalocyanines is to use dilithium phthalocyanine as a labile intermediate. This compound (readily obtained from phthalonitrile and lithium in amyl alcohol) is soluble in alcohol and undergoes metathetical reactions with salts of other metals (e.g. Ag, Hg, Fe, and Pd).[22] Alternative methods involve heating phthalonitrile (or phthalic anhydride and urea) with a metal salt.[19, 23] In certain cases the free metal (e.g. Be, Mg, Zn, Mn, Fe, Co, Ni) can be heated with phthalonitrile or *o*-cyanobenzamide to yield the phthalocyanine, but it may be relevant to some of these examples that copper powder requires the presence of air before reaction takes place with phthalonitrile.[24]

A large number of phthalocyanines of different metals were prepared in the early days of phthalocyanine chemistry by **Linstead** and his co-workers.[25] Recent additions to the compilation include derivatives of the lanthanides,[26] titanium,[27] ruthenium,[28] gallium and indium,[29] silicon,[30] and germanium.[31] The last two are particularly interesting since substitution products of the type $M(OR)_2Pc$ (where M = Si or Ge; Pc = phthalocyanine; R = alkyl or aryl) can be prepared from the corresponding dihydroxy compounds; the higher (C_{18}) alkoxy derivatives have surprisingly low melting points (150 to 200 °C).

The notable spaces in Figure 4 are those of the metals tungsten, rhenium, iridium and gold. Preparation of phthalocyanine compounds with these metals may be difficult due to the particulare combinations of oxidation state, coordination number and stereochemistry which are required. The last of these requirements is dominated to such an extent by the rigidity of the phthalocyanine ligand that several metals [e.g. Fe(II) and Co(II)] do not form square planar complexes with any other ligand combination.

It will be seen then that phthalocyanine derivatives of about fifty different metals are now known. When

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[20] J.F. **Gibson**, D.J.E. **Ingram**, and D. **Schonland**. *Disc. Faraday Soc. 26* (1958) 72, 94.

[21] J.A. **Elvidge** and A.B.P. **Lever**, *Proc. Chem. Soc. 1959*, 195.

[22] P.A. **Barrett**, D.A. **Frye**, and R.P. **Linstead**, *J. Chem. Soc. 1938*, 1157.

[23] FIAT Final Report No. 1313, Vol. III, p. 308 *et seq.*

[24] H.Z. **Lecher**, H.T. **Lacey**, and H.P. **Orem**, *J. Amer. Chem. Soc. 63* (1941) 1326.

[25] R.P. **Linstead**, *Chem. Ber. 72 A* (1939) 93.

[26] U.S. Atomic Energy Commission (N.A. **Frigerio**), U.S. Patent 3,027,391 (appln. 28.8.1959).

[27] Union Carbide Corporation (J.C. **Burbach**), U.S. Patent 3,137,703 (appln. 23.12.1960).

[28] P.C. **Krueger** and M.E. **Kenney**, *J. Inorg. Nuclear Chem. 25* (1963) 303.

[29] D. **Colaitis**, *C.R. Acad. Sci. 242* (1956) 1026.

[30] M.E. **Kenney** and R.D. **Joyner**, U.S. Patent 3,094,536 (appln. 3.1.1961).

[31] M.E. **Kenney** and R.D. **Joyner**, U.S. Patent 3,094,535 (appln. 3.1.1961).

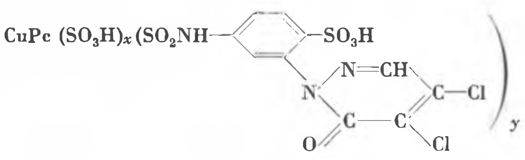
compared as pigments the copper compound is outstanding and is the only one used as such, since it combines maximum fastness properties together with economy. Many claims have been made for the exploitation of the other metal phthalocyanines, for example as adjuvants with copper phthalocyanine to resist crystallisation and flocculation, but very few have been made on the large scale. The use of several metal phthalocyanines (particularly those of iron and cobalt) as catalysts in oxidation or polymerisation processes has been patented. Nickel and cobalt phthalocyanines have limited outlets in the field of water-soluble dyes (see later).

Water-soluble dyes

The high fastness to light and the attractive shades offered by the phthalocyanine chromophore have served to stimulate the search for useful water-soluble derivatives ever since the first phthalocyanine patent,[4] which describes the sulphonation of copper phthalocyanine in oleum. Direct sulphonation gives substitution almost entirely in the 3-position, the water-soluble products derived from 4-sulphophthalic anhydride being considerably redder in shade (in aqueous solution or on the fibre) then their sulphonated isomers. This difference is due mainly to aggregation in solution.

Products from the sulphonation of copper phthalocyanine which contain between two and three sulphonic acid groups per molecule have been manufactured for over 25 years as direct dyes for cotton, paper and wool. Copper phthalocyanine tetra-4-sulphonic acid has also been marketed.[32] More important are the derivatives obtained through the chlorosulphonation[33] of copper phthalocyanine since a variety of dyes containing both sulphonamido and sulphonic acid groups (again in the 3-position) can be obtained, e.g. $[\mathrm{CuPc}(\mathrm{SO_3H})_x(\mathrm{SO_2NH_2})_y]$.[34] The extent of chlorosulphonation can be controlled (up to a maximum of four entering groups) and the nature of the amine and number of sulphonamide substituents modified to affect such factors as shade, strength and affinity.

More complex variations of this type of sulphonamide formation are of supreme importance in the field of reactive dyestuffs. Over 250 patents concerning the manufacture and use of phthalocyanine reactive dyes have been filed since 1956. Practically all known reactive groups have been attached to the phthalocyanine chromophore, in nearly all cases through a sulphonamide linkage. All the established ranges of reactive dyes contain at least one copper phthalocyanine derivative to meet the important requirements for turquoise shades. The following examples demonstrate the variation in reactive group and its mode of linkage to the chromophore ($x + y = 3$ or 4 with $y \geqslant 1$):



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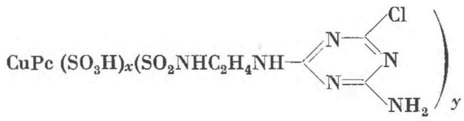

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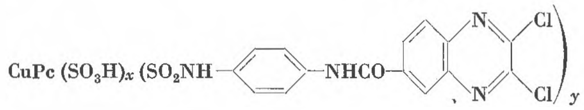

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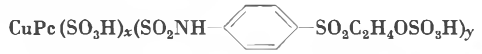
$\mathrm{CuPc}(\mathrm{SO_2NHC_2H_4OSO_3H})_3$ 38



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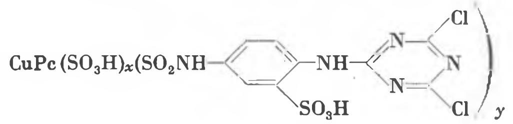

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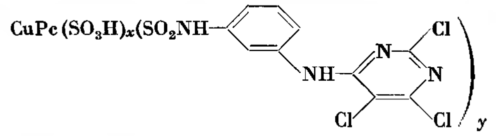

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Chlorosulphonation is effected by treating copper phthalocyanine with excess of chlorosulphonic acid at 130 to 140°C, complete conversion of the resulting $\mathrm{CuPc}(\mathrm{SO_3H})_x(\mathrm{SO_2Cl})_y$ to $\mathrm{CuPc}(\mathrm{SO_2Cl})_{3\ \mathrm{or}\ 4}$ is completed, if required, by the addition of an inorganic acid chloride such as thionyl chloride or phosphorus pentachloride. After reaction with an amine to the required y value any residual sulphonchloride groupings can be hydrolysed. Considerable variation in the values of x and y, which are precisely controlled in order to achieve optimum properties, is thus possible.

Phthalocyanines of some (but not all) other metals can be similarly chlorosulphonated and at least one dye based on nickel phthalocyanine has been manufactured,[38, 42] but its merits compared with the corresponding copper derivative have not been established. Green reactive dyes can be obtained either through the use of sulphonchloride derivatives of copper tetra(4)phenylphthalocyanine or by linking a yellow azo chromophore to the blue phthalocyanine through a chromophoric block.

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[32] *Colour Index*, 2nd Edition (1956) Vol. 3, p. 3569.

[33] I.G. Farbenindustrie AG, British Patent 515,637 (conv. 8.6.1937).

[34] I.G. Farbenindustrie AG, British Patent 520,199 (conv. 14. 10. 1937).

[35] Badische Anilin- und Soda-Fabrik AG (A. Tartter, H. R. Hensel, and H. Baumann), D. A. S. 1,123,065 (appln. 17.8.1959).

[36] Ciba Ltd., British Patent 866,513 (conv. 17.8.1956).

[37] E. I. du Pont de Nemours & Co. (J. E. Cole and W. H. Gumprecht), French Patent 1,359,644 (conv. 21.11.1961).

[38] Farbenfabriken Bayer AG (K. G. Kleb), D. A. S. 1,170,898 (appln. 15.7.1957).

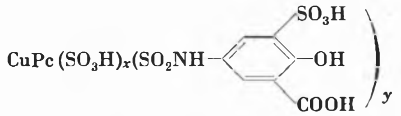
[39] Farbwerke Hoechst AG (J. Heyna, H. Springer, E. Schinzel), D. A. S. 1,179,317 (appln. 5.3.1960).

[40] Imperial Chemical Industries Ltd. (P. F. Clark, H. T. Howard, and J. Wardleworth), British Patent 805, 562 (appln. 14.3.1956).

[41] Sandoz Ltd., British Patent 916,094 (conv. 28.5.1958).

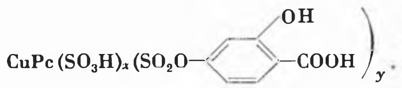
[42] H. Wagner and J. Pflug, *Melliand Textilber. 44* (1963) 281.

Dyes solubilised by carboxylic acid groups are not so widely used but copper tetra(4)phenyl phthalocyanine-tetra(5)carboxylic acid was manufactured by the I.G. (from 5-phenyltrimellitic acid) as a green dye for cotton. Chrome dyes of the type



$CuPc(SO_3H)_x(SO_2NH{-}C_6H_2(SO_3H)(OH)COOH)_y$

were also made by the I.G.[23] A variation on this last theme lies in the use of the related esters



$CuPc(SO_3H)_x(SO_2O{-}C_6H_3(OH)COOH)_y$ [43].

As distinct from the anionic direct and reactive dyes discussed above there is an important group of cationic phthalocyanine dyes. The evolution of these dyes started in 1939 with the investigation of the properties of copper tetra(4)pyridyl phthalocyanine and its quaternised derivatives. This led to the study of other 'onium' (quaternary ammonium, ternary sulphonium and isothiouronium) derivatives linked to the chromophore in a variety of ways.[44] The best linkage for this purpose proved to be methylene which it was found could readily be introduced into the system by controlled chloromethylation of the metal phthalocyanine by reaction with dichlorodimethyl ether in a flux made of aluminium chloride and a tertiary base such as triethylamine.[45] Subsequent reaction of the chloromethyl derivative (prepared under conditions appropriate for the introduction of between two and four substituents) with either a tertiary nitrogenous base or a thiourea produces a water soluble dye.[46] The latter type proved to be the most suitable for insolubilisation of the dyestuff on cotton, after dyeing or printing, by a heat or steam treatment and Alcian Blue 8G (first marketed by I.C.I. Ltd. in 1947) was the important outcome of all this work.

Temporarily solubilised dyes of the above type have been classified[32] as ingrain dyes, i.e. formed *in situ* in the substrate. Another type which could be similarly classified are represented by the Inthion dyes of Farbwerke Hoechst. Here insolubilisation is combined with polymerisation by co-application of a dye of the type $[CuPc(SO_2NHC_2H_4SSO_3Na)_x]$ with sulphur or a sulphur-containing compound.[47] These dyes are thus modified sulphur-dyes, the earliest example of which in the phthalocyanine series was the tetramercapto derivative of copper phthalocyanine. Although mercaptophthalocyanines can be prepared by (Zn/H_2SO_4) reduction of the corresponding sulphonyl chlorides the best method of obtaining the tetramercapto compound is by dissolving copper tetra(4)thiocyanophthalocyanine in sodium sulphide, oxidation of the resulting solution when impregnated on cotton then yields a fast green shade.[48] The thiocyano compound is obtained from copper tetra(4)-aminophthalocyanine [which in turn is obtained by reduction of $CuPc(NO_2)_4$] through its tetradiazotised derivative. Diazotised aminophthalocyanines have also been used in the preparation of azo dyes, the best products being obtained by reaction with azoic coupling components on the fibre.[44]

Early work on the construction of vat dyes containing the phthalocyanine chromophore together with an appended anthraquinone residue was fruitless owing to the inherent instability of the leuco forms.[44] Although it was known during the earliest work on phthalocyanines that metal phthalocyanines were "vattable"[4] it was not until 1948 that exploitation of this property was possible. Cobalt phthalocyanine, when sulphonated to contain 15 to 40% cobalt phthalocyanine monosulphonic acid, was found to have excellent properties as a blue vat dyestuff (Indanthrene Brilliant Blue 4G).[49] The structure of the leuco compound derived from cobalt phthalocyanine is likely to involve reduction with the formation of a second quinonoid ring in the macrocycle[50] but no investigation into the oxidation state of the metal has been reported.

There are thus six main classes of water-soluble phthalocyanine dyes (direct, reactive, after-metallisable, ingrain, sulphur and vat) and ingenious ways of identifying these on cellulose fibre (the most important substrate for these dyes) have been worked out.[42]

Solvent-soluble dyes

Solvent-solubility can be conferred through the introduction of suitable hydrocarbon residues either directly linked[51] or, more usually, through a linkage such as aminomethyl or aminosulphonyl. These last two types have the advantage that certain members with basic properties, e.g. $CuPc(CH_2NEt_2)_x$[52] and $CuPc(SO_2NHC_3H_6NMe_2)_x$[53] are also soluble in dilute acid and can be applied to textiles and paper. They can also be alkylated to give water-soluble quaternary ammonium derivatives.

The reaction of coppertetrachlorophthalocyanine with a mercaptan, such as *p*-thiocresol, in a high boiling alcohol gives green pigments with some applications which utilise their solvent solubility.[54]

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[43] Durand & Huguenin AG, British Patent 768,444 (conv. 8.1.1952).

[44] N.H. Haddock, *Research 1* (1947–48) 685.

[45] Imperial Chemical Industries Ltd. (N.H. Haddock and C. Wood), British Patent 586,340 (appln. 17.11.1944).

[43] *idem*, British Patent 587,636 (appln. 6.12.1944).

[47] Farbwerke Hoechst AG, British Patent 929,398 (conv. 8.8.1959).

[48] Imperial Chemical Industries Ltd. (N. H. Haddock), British Patent 541,146 (appln. 13.5.1940).

[49] Farbenfabriken Bayer, British Patent 704,310 (appln. 12.11.1948).

[50] E.E. Bowker, *Dyer 117* (1957) 355.

[51] Badische Anilin- und Soda-Fabrik AG, British Patent 694,072 (conv. 30.8.1950).

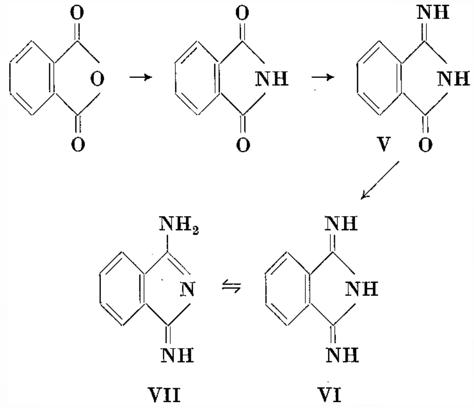
[52] Imperial Chemical Industries Ltd. (N. H. Haddock), British Patent 770,784 (appln. 22.10.1954).

[53] Farbenfabriken Bayer AG, British Patent 784,843 (conv. 21.12.1953).

[54] Sandoz Ltd., British Patent 588,231 (conv. 14.2.1944).

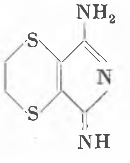
Phthalocyanine precursors

The formation of the phthalocyanine macrocycle in the phthalic anhydride-urea process involves the probable initial reaction sequence;



the urea supplies thus only three atoms of nitrogen per molecule of phthalic anhydride although the process is usually operated using about four molecules of urea per molecule of phthalic anhydride. The excess urea must have other functions in the system (e.g. removal of chloride ions) but the complete mechanism is not known. It has been proved however that the urea does not supply any carbon to the macrocycle.[55]

The early work showed that 1-keto-3-iminoisoindolenine (V) was formed in the process and although Haddock[56] suggested that diiminoisoindoline (VI) was a possible further intermediate it was the workers of the Leverkusen research group of Farbenfabriken Bayer who first separated this product in 1949.[57] 1-Amino-3-iminoisoindolenine (VII, tautomeric with VI) was introduced to the market in 1951 as the first of the Phthalogen range of dyestuffs. The generation of the metal (e.g. copper or nickel) phthalocyanine on cellulose from such precursors is readily achieved.[58] A further advance came in 1957 with the use of dicyanodithiacyclohexene for the preparation of a Phthalogen base (VIII); this extended the shade range obtainable from greens and blues to include violet, dark blue and black.[59, 60] A full account of the application of Phthalogen dyes has recently been given by Eibl.[61]



VIII

Conclusions

The development of phthalocyanine chemistry has to a large extent been dominated by technological requirements. This has resulted in a very full study of the chemistry of copper phthalocyanine with comparatively little work on the phthalocyanines of other metals. The four substitution reactions halogenation, sulphonation, chlorosulphonation and chloromethylation have been evaluated widely since they all lead to commercially important products. From a very large number of products that have been prepared from substituted phthalonitriles or phthalic anhydrides (or their analogues) only a small number have been of technical importance (e.g. tetranitro- and tetraphenyl-phthalocyanines).

A review[56] on phthalocyanines written twenty years ago concluded by pointing out some of the then outstanding targets. Considerable advances have since been made in the pigments field where the current major requirements must be for products outside the green to greenish-blue shade range. The requirement of bright blue shades for cotton which are fast to washing has been met with the ingrain and reactive dyes but the successful use of phthalocyanine dyes on wool and synthetic fibres is still somewhat problematical. Progress with these last substrates is continually being made through the preparation of novel dyestuffs and improvements in application conditions.

Clearly in an enormous field of chemistry and technology such as phthalocyanines now represent it is impossible to cover all facets in a paper of this sort. Discussion has therefore been restricted somewhat to cover mainly topics with commercial implications which lie almost entirely in the pigment-consuming and textile industries. The more recent applications of phthalocyanines to the technology of catalysts, lubricants, semiconductors or polymers are still in the comparatively speculative stage. For a complete bibliography (to 1961) on all aspects of the phthalocyanines the reader is referred to Moser and Thomas.[62]

The preparation of copper phthalocyanine by Henri de Diesbach in 1927 was proved by later developments to be of major importance. Since that time, considerable research has been undertaken on related macrocycles without any useful new chromophore emerging. The closest approach to an extension of the shade range available was probably the work on phthalocyanine precursors and further fundamental work in the future may yet lead to the desired red shade macrocycles.

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Inthion is a registered trade mark of Farbwerke Hoechst AG.

Phthalogen is a registered trade mark of Farbenfabriken Bayer AG.

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[55] S. M. Brumfield, V. W. Foltz, C. M. McGhee, and A. L. Thomas, *J. Org. Chem. 27* (1962) 2266.

[56] N. H. Haddock, *J. Soc. Dyers & Colourists 61* (1945) 68.

[57] Farbenfabriken Bayer, British Patents 698,039 and 698,049 (appln. 25.8.1949).

[58] F. Baumann, B. Bienert, G. Rösch, H. Vollmann, and W. Wolf, *Angew. Chem. 68* (1956) 133.

[59] Farbenfabriken Bayer AG, British Patents 881,408 (conv. 18.3.1957) and 881,410 (conv. 2.7.1957).

[60] W. Wolf, E. Degener, and S. Peterson, *Angew. Chem. 72* (1960) 963.

[61] J. Eibl, *Melliand Textilber. 45* (1964) 789.

[62] F. H. Moser and A. L. Thomas, *Phthalocyanine Compounds*, Reinhold Publ. Corp. (1963).