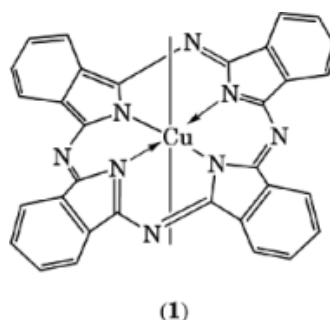


PHTHALOCYANINE COMPOUNDS

Phthalocyanine[574-93-6], $C_{32}H_{18}N_8$, compounds have found widespread acceptance in a variety of applications. The discovery of iron phthalocyanine [132-16-1] and the elucidation of its structure led to the commercial application of copper phthalocyanine [147-14-8] (1).

Copper phthalocyanine (1) was developed in the 1930s and is the most commonly used blue organic pigment in the coatings (qv), paint (qv), and printing inks (qv) industry. Phthalocyanine forms complexes with numerous metals. Various complexes with 66 chemical elements are known (1–7). The coordination number of the metal in the phthalocyanine complexes ranges from 4 (Cu, Li, Pd) to 5 (U), or 6 (metals with two additional ligands such as H_2O or NH_3) to 8 (Nd(III) HPC_2 or U(IV) Pc_2) (8–13), where Pc represents the phthalocyanine ligand. Polymeric phthalocyanines can also be synthesized (Si, Ge, Sn) (14–17). Metal-free phthalocyanine, H_2Pc , in which the central copper atom in (1) is replaced by two hydrogen atoms, has interesting photosensitive and semiconductor properties (1). Phthalocyanines are structurally related to naturally occurring dyes such as hemoglobin and chlorophyll A (18).



1. Physical Properties

The density of β -phthalocyanine, H_2Pc , is 1.43 g/cm^3 ; β -copper phthalocyanine [14832-14-5], $CuPc$, 1.61 g/cm^3 ; and polychloro-copper phthalocyanine, 2.14 g/cm^3 . The color of most phthalocyanines ranges from blue-black to a metallic bronze, depending on the manufacturing process and the chemical and crystalline form of the material (19). The colors of the finely divided pigment forms vary from dark blue to green, as phthalocyanines absorb in the visible region at $600\text{--}700\text{ }\mu\text{m}$ (2). Most compounds do not melt but sublime above 200°C . $CuPc$ can be sublimed without decomposition at $500\text{--}580^\circ\text{C}$ under an inert gas and normal pressure and at 900°C under vacuum (20). It decomposes vigorously, however, at $405\text{--}420^\circ\text{C}$ in air and in nitrogen between $460\text{--}630^\circ\text{C}$ (21, 22). The thermodynamic stability of the five crystalline forms of $CuPc$ increases in the sequence $\alpha = \gamma < \delta < \epsilon < \beta$ (23, 24). The solubility of most phthalocyanines in water and organic solvents is very low. The α -form, however, is slightly soluble in polar solvents and converts rapidly to the β -form (25, 26). Three

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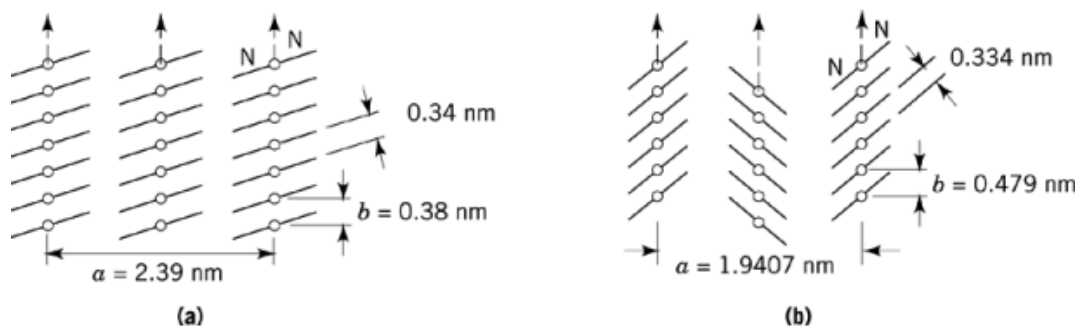
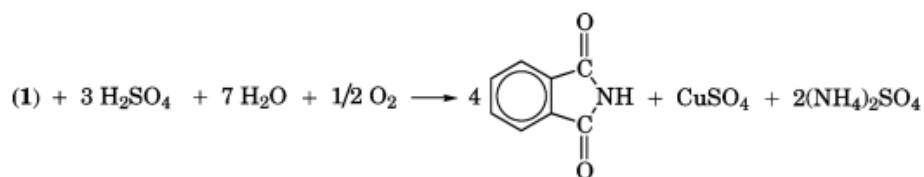


Fig. 1. Arrangement of the copper phthalocyanine molecule in the (a) α - and (b) β -forms.

modifications of H_2Pc , α , β (27, 28), and X (29) have been found. Polychloro CuPc has only an α -modification (30). The arrangement of the planer stackings differs as illustrated by the structures of α - and β -CuPc in Figure 1 (27, 28).

2. Chemical Properties

The chemical properties of phthalocyanines depend mostly on the nature of the central atom. Phthalocyanines are stable to atmospheric oxygen up to approximately 100°C . Mild oxidation may lead to the formation of oxidation intermediates that can be reduced to the original products (29). In aqueous solutions of strong oxidants, the phthalocyanine ring is completely destroyed and oxidized to phthalimide. Oxidation in the presence of ceric sulfate can be used to determine the amount of copper phthalocyanine quantitatively (30).



Oxidation can also occur at the central metal atom of the phthalocyanine system (2). Mn phthalocyanine, for example, can be produced in these different oxidation states, depending on the solvent (2, 31, 32). The carbon atom of the ring system and the central metal atom can be reduced (33), some reversibly, eg, in vatting (34–41). Phthalocyanine compounds exhibit favorable catalytic properties which makes them interesting for applications in dehydrogenation, oxidation, electrocatalysis, gas-phase reactions, and fuel cells (qv) (1, 2, 42–49).

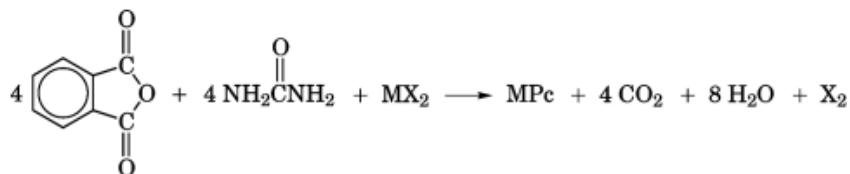
3. Manufacturing and Processing

Phthalocyanine compounds have been synthesized with various metals (1, 2, 4). The most important metal phthalocyanines are derived from phthalodinitrile, phthalic anhydride, Pc derivatives, or alkali metal Pc salts.

The route from *o*-phthalodinitrile [91-15-6] can be represented $4 \text{C}_8\text{H}_4\text{N}_2 + \text{M} \longrightarrow \text{MPc}$, where M is a bivalent metal, metal halide, metal alcoholate, or an equivalent amount of metal of valence other than two in a 4:1 molar ratio. If a solvent, eg, trichlorobenzene, benzophenol, pyridine, nitrobenzene, or quinoline, is used,

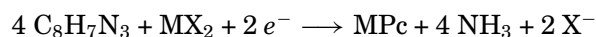
the reaction takes place at approximately 180°C. Without a solvent the dry mixture must be heated to ca 300°C to initiate the exothermic reaction (50).

The following shows the reaction of phthalic anhydride [85-44-9] with urea:



In this process, catalysts, such as boric acid, molybdenum oxide, zirconium, and titanium tetrachloride or ammonium molybdate, are used to accelerate the reaction. The synthesis is either carried out in a solvent (aliphatic hydrocarbon, trichlorobenzene, quinoline, pyridine, glycols, or alcohols) at approximately 200°C or without a solvent at 300°C (51, 52).

The synthesis from phthalimide derivatives, eg, diimidophthalamide (or phthalimide [85-41-6]) is usually carried out in a solvent such as formamide.



Metal phthalocyanines may also be prepared using alkali metal salts or from metal-free phthalocyanine by boiling the latter in quinoline with metal salt.

Industrial production of copper phthalocyanine usually favors either the phthalic anhydride–urea process (United States, United Kingdom) (1, 52, 53) or the *o*-phthalodinitrile process (Germany, Japan) (54, 55). Both can be carried out continuously or batchwise in a solvent or bake process of the solid reactants (56).

The crude copper phthalocyanine must be treated to obtain a satisfactory pigment in regard to the crystal modification and optimal particle size (1, 57) (see Pigments). The particle size of crude phthalocyanine can be reduced by chemical or mechanical methods. The former involves dissolving phthalocyanine in concentrated sulfuric acid and precipitating it by addition to water (1). Alternatively, it may be slurried in dilute acid, washed, and dried, but this process leaves the pigment partially undissolved. A grinding step might have to be added because different sulfuric acid concentrations yield different sulfate levels. The α -modification, which is obtained by these methods, is treated by adding chlorine or sulfuric acid to the phthalocyanine, either during or after the synthesis to prevent recrystallization into the more stable β -form (57, 58). This may be induced by heat or wet-milling in certain solvents (1, 58). Very unstable modifications, like the reddish, chlorine-free α -copper phthalocyanine, can be stabilized with amides or salts of copper phthalocyanine sulfonic acids (59–63). Mixture with other metal phthalocyanines, eg, tin, vanadium, aluminum, or magnesium, also inhibits crystallization change and poor performance in binders and prints (flocculation) due to the hydrophobic character of unsubstituted phthalocyanines.

The second process to finish phthalocyanine, which is more important for β -copper phthalocyanine, involves grinding the dry or aqueous form in a ball mill or a kneader (64). Agents such as sodium chloride, which have to be removed by boiling with water after the grinding, are used. Solvents like aromatic hydrocarbons, xylene, nitrobenzene or chlorobenzene, alcohols, ketones, or esters can be used (1). In the absence of a solvent, the crude β -phthalocyanine is converted to the α -form (57, 65) and has to be treated with a solvent to regain the β -modification. The aggregate structure also has an impact on the dispersion behavior of α - and β -copper phthalocyanine pigments (66).

Incorporation of less than a stoichiometric amount of alkyl sulfonamides of copper phthalocyanines into copper phthalocyanine improves the pigment's properties in rotogravure inks (67). Monomeric and polymeric

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phthalocyanine derivatives with basic substituents adsorb strongly to the pigment surface and promote the adsorption of binder molecules (68–72).

Performance in ink and coatings can be improved by addition of surfactants (qv), dispersants, resins, or copper phthalocyanine derivatives with long aliphatic chains, $\text{CuPc}(\text{CH}_2\text{-NHR})_3$ (68, 73), to stabilize the pigment in the binder system. Another possibility is wet-milling of aqueous pigment dispersions incorporating an organic medium, eg, glycols, polyethers, or surfactants (74).

γ -Copper phthalocyanine is obtained by treating the α -modification with 30% sulfuric acid and glycol monobutyl ether at 110°C (1, 75, 76). δ -Copper phthalocyanine is prepared by dissolving copper phthalocyanine in 98% sulfuric acid, adding water, benzene, and turkey red oil, washing with alcohol and water, and drying (77, 78). ϵ -CuPc is made by mixing urea, sulfuric acid, and CuPc made from the phthalic anhydride–urea process (1, 41).

Some references cover direct preparation of the different crystal modifications of phthalocyanines in pigment form from both the nitrile–urea and phthalic anhydride–urea process (79–85). Metal-free phthalocyanine can be manufactured by reaction of *o*-phthalodinitrile with sodium amylate and alcoholysis of the resulting disodium phthalocyanine (1). The phthalic anhydride–urea process can also be used (86, 87). Other sodium compounds or an electrochemical process have been described (88). Production of the different crystal modifications has also been discussed (88–93).

Perchloro- and perchlorobromo copper phthalocyanine [1328-53-6] are important organic green pigments. They are accessible through direct chlorination of copper phthalocyanine in a eutectic melt of aluminum and sodium chloride or in a chlorosulfonic acid medium (94, 95). Bromine can be used instead of chlorine in the AlCl_3 – NaCl melt to obtain polybromochloro copper phthalocyanine. Other synthesis paths have been disclosed (96–99). Solvents such as methanol (qv), butanol, ethylene glycol (see Glycols), esters (100), ketones (101), or benzoic acid (qv) (102) are used as finishing agents to convert the halogen phthalocyanines into the finely divided pigment forms.

Phthalocyanine sulfonic acids, which can be used as direct cotton dyes (1), are obtained by heating the metal phthalocyanines in oleum. One to four sulfo groups can be introduced in the 4-position by varying concentration, temperature, and reaction time (103). Sulfonyl chlorides, which are important intermediates, can be prepared from chlorosulfonic acid and phthalocyanines (104). The positions of the sulfonyl chloride groups are the same as those of the sulfonic acids (103). Other derivatives, eg, chlormethyl phthalocyanines (105–107), *tert*-butyl (108–111), amino (112), ethers (109, 110, 113–116), thioethers (117, 118), carboxyl acids (119–122), esters (123), cyanides (112, 124–127), and nitrocompounds (126), can be synthesized.

Polymeric phthalocyanines, which possess a higher stability compared to the monomers, can be obtained by combining a phthalocyanine with a polymer (1). The linking of the polymeric chain can occur at the central metal atom, the phenyl rings, through bridging or attachment to a polymeric chain (14, 17, 127–131). Various phthalocyanine analogues, which are potential pigments, have been studied (1). For example, the four-fused benzene ring systems can be replaced by other aromatic rings like naphthalene (132–135) or other heterocyclic systems (136–152).

4. Specifications, Standards, Analysis, and Quality Control

Testing of phthalocyanines includes crystallization (qv), flocculation, and application in paints, plastics (qv), and printing inks (1). The ASTM standard specifications include CuPc in dry powder form for various applications (153). The specifications cover color (qv), character or tint, oil absorption, reactions in identification tests, and dispersions and storage stability. Quantitative determinations are possible with ceric sulfate (30) or sodium vanadate (154). Identification methods are given (155), including tests for different applications.

5. Uses

Approximately 90% of the phthalocyanines (predominantly copper phthalocyanine) are used as pigments (qv). In addition, they have found acceptance in many types of dyestuffs, eg, direct and reactive dyes, water-soluble and solvent-soluble dyes with physical and chemical binding, azo-reactive dyes, azo nonreactive dyes, sulfur dyes, and vat dyes (1) (see Dyes; Dyes, reactive).

5.1. Available Forms

Phthalocyanines are available as powders, in paste, or liquid forms. They can be dispersed in various media suitable for aqueous, nonaqueous, or multipurpose systems, eg, polyethylene, polyamide, or nitrocellulose. Inert materials like clay, barium sulfate, calcium carbonates, or aluminum hydrate are the most common solid extenders. Predispersed concentrates of the pigments, like flushes, are interesting for manufacturers of paints and inks (156), who do not own grinding or dispersing equipment. Pigment–water pastes, ie, presscakes, containing 50–75% weight of water, are also available.

5.2. Colorants

The pigmentary forms of copper phthalocyanine are by far the most important commercial products of that class. They provide excellent color properties, excellent resistance to heat and light, acid and alkali, and are extremely insoluble in most solvents. They are less expensive than other organic pigments and color practically every type of printing ink, paint, plastic, and textile. Other uses include the coloring of roofing granules, cements and plasters, fine art paint, soaps, detergents, and other cleaning products (157). The two principal classes of copper phthalocyanine pigments are the blues and the greens. The blues may be further classified as the α - and β -crystal types, and the greens as the chlorinated and brominated derivatives.

5.3. Phthalocyanine Blues

α -Copper phthalocyanine blue is a reddish species used primarily in coatings and plastics. Several varieties are marketed. The basic form, the unstable Pigment Blue 15 [147-14-8] (CI 74160), is used in water-based paints, paints containing weak petroleum solvents, and in certain plastics, eg, PVC, that require mild processing conditions.

The unstable α -modification tends to crystallize in the presence of strong solvents or heat, which causes flocculation and a significant loss of color strength. Stabilized forms exist as the noncrystallizing (NC) types, eg, Pigment Blue 15:1, and the noncrystallizing, nonflocculating (NCNF) types, eg, Pigment Blue 15:2. Additives provide improved rheological properties and reduce flocculation. The NCNF types are stable to heat and a variety of solvents. Plastics and certain metal decorating inks are the main applications for the NC types, whereas the NCNF types are the preferred colorants for coatings, like industrial and automotive paints. Many multipurpose systems for architectural finishes, which come in contact with a variety of solvents and are used under varied conditions, are made, at least partly, of NCNF blues (see Paint, architectural).

β -Copper phthalocyanine blue (Pigment Blue 15:3) is characterized by the greenish hue and cleanliness of color tone, which is necessary for the cyan component in color process printing. It is, however, weaker in color strength than α -copper phthalocyanine blue. Used as the cyan in four-color process printing (yellow, magenta, cyan, black), all the spectral colors can be reproduced in the different printing systems, eg, letter press, gravure, flexographic, offset, screen-printing, and textile inks (see PRINTING PROCESSES). For applications incorporating strong solvents at higher temperatures (gravure printing), a nonflocculating (NF) type, Pigment Blue 15:4, is favorable. Relatively smaller amounts of β -copper phthalocyanine (compared to the α -modification)

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are used in coatings and plastics because of the lower color and strength. The color purity of β -CuPc is not required, since most systems for plastics and coatings are shaded with other pigments.

ϵ -Copper phthalocyanine blue 15:6 is significantly redder and slightly stronger in color strength than the α -crystal type. The ϵ -type can also be produced in a stabilized form, so that crystallization and flocculation are minimized in systems containing strong solvents (41), which makes applications in coatings and printing inks possible.

Metal-free copper phthalocyanine blue, ie, Pigment Blue 16 [574-93-6], is one of the earliest forms of phthalocyanine. Environmental concerns about copper in pigments tended to increase the use of metal-free copper phthalocyanine, but certain shortcomings (greenish hue, lack of stability in aromatic solvents) allowed only specialty uses (109). The stabilized α -NC-type is used in certain automotive coatings.

5.4. Phthalocyanine Green

The commercial development of the perchloro- and perchlorobromo copper phthalocyanine greens began in the 1930s. The predominant form of the halogenated derivatives of phthalocyanines is the chlorinated Pigment Green 7 [1328-53-6] (CI 74260). The blue hue shifts toward yellow when chlorine is replaced by bromine, eg, Pigment Green 36 [14302-13-7] (CI 74265). This form was first marketed in the late 1950s. Like nonhalogenated compounds, halogenated phthalocyanines must be converted to useful pigments by finishing in liquids, eg, methanol, butanol, or ethylene glycol. Phthalocyanine green pigments (158, 159) are used in a variety of paints and plastics. Because the green color in the printing process is predominantly obtained by combinations of yellow and blue, the application in printing inks is reduced to spot colors. Fluorine-treated pigments have been used as writing inks (160).

5.5. Phthalocyanine Dyes

In addition to their use as pigments, the phthalocyanines have found widespread application as dyestuffs, eg, direct and reactive dyes, water-soluble dyes with physical or chemical binding, solvent-soluble dyes with physical or chemical binding, azo reactive dyes, azo nonreactive dyes, sulfur dyes, and wet dyes. The first phthalocyanine dyes were used in the early 1930s to dye textiles like cotton (qv). The water-soluble forms like sodium salts of copper phthalocyanine disulfonic acid, Direct Blue 86 [1330-38-7] (CI 74180), Direct Blue 87 [1330-39-8] (CI 74200), Acid Blue 249 [36485-85-5] (CI 74220), and their derivatives are used to dye natural and synthetic textiles (qv), paper, and leather (qv). The sodium salt of cobalt phthalocyanine, ie, Vat Blue 29 [1328-50-3] (CI 74140) is mostly applied to cellulose fibers (qv).

Sulfonamide groups can be introduced into phthalocyanines to make them soluble in alcohols and glycol ethers. Their main applications are transparent paints, flexo and gravure printing inks, wood stains, plastics, and ballpoint inks. This includes products like Solvent Blue 24 (CI 74380), Solvent Blue 42 [1330-38-7] (CI 74180), and Solvent Blues 44, 46, and 52.

Incorporating additional tertiary or secondary amine groups, the sulfonamide group leads to dyes which are soluble in acidic media, eg, printing inks, ballpoint ink, ink ribbons, copying inks, and carbon paper. In contrast to the phthalocyanine dyes already mentioned, developing dyes do not contain any substituents and possess purer, more genuine colors, eg, Ingrain Blue 2:1 (CI 74160) (161–163). Derivatives of copper phthalocyanine sulfonates with diphenylguanidine are used for ballpoint inks (164, 165).

5.6. Other Uses

Phthalocyanines have interesting properties as catalysts, lasers (qv), semiconductors, lubricants, or as photographic components. Metal phthalocyanines catalyze dehydrogenations, oxidation, or gas-phase reactions. Catalysis by metal phthalocyanines was first discovered in 1936 in the exchange reaction between hydrogen

and water and the catalysis of water from oxygen and hydrogen (166). The catalysis of oxygen transfer reactions suggested the similarity of metal phthalocyanines to heme and enzymes like hydrogenase (167). A variety of chemical compounds, eg, alkanes, olefins, aromatics, alcohols, aldehydes, alkyl aromatics, phenols, thiols, cumenes, polymers, and sugar, are oxidized by molecular oxygen when iron, copper, or cobalt phthalocyanine are present (1, 43, 44). For example, cobalt phthalocyanine sulfonate [30638-08-5] and vanadium phthalocyanine sulfonate [42862-24-8] catalyze air oxidation of mercaptans and other sulfur compounds of petroleum (qv) (1, 168). They oxidize caustic solutions that are used to dissolve sulfur compounds from petroleum, hydrogen sulfide, and disulfides. Magnesium phthalocyanine [1661-03-6] and iron phthalocyanine [136-16-1] catalyze the oxidation of cumene by air (169). Cobalt phthalocyanine [3317-67-1] catalyzes the oxidation of liquid toluene and ethyl benzene to benzyl alcohol (170). Isopropyl alcohol has been oxidized to acetone with the use of copper or other metal phthalocyanines as a catalyst (171). In addition, hydrogenation, dehydrogenation, degradation, polymerization, isomerization, hydrogen-exchange reaction, reactive dehydrogenation, hydrogenative thermal cracking, autoxidation, epoxidation, decarboxylation, and Fischer-Tropsch synthesis are catalyzed by phthalocyanines (42–44). For example, a number of phthalocyanines are able to catalyze the hydrogenation of carbon monoxide to form C_1 – C_5 hydrocarbons (172), the formation of ammonia at room temperature from hydrogen and nitrogen in contact with a sodium film (173) or the polymerization of methacrylates, nitriles (qv), and polymethylenes (1). Phthalocyanines have been extensively studied for application in fuel cells (qv) (45–47). Cobalt phthalocyanine especially was studied to enhance the oxygen release or to act as an electrode. Iron phthalocyanine has even higher electrocatalytic activity (48, 174). Polymeric phthalocyanines exhibit even higher stability (175).

Air oxidation of dyestuff waste streams has been accomplished using cobalt phthalocyanine sulfonate catalysts (176). Aluminum has been colored with copper phthalocyanine sulfonate (177, 178). Iron phthalocyanine can be used as a drier in wood oil and linseed oil paints (179).

Metal-free, chloroaluminum phthalocyanine [14154-42-8], vanadyl phthalocyanine [13930-88-6], or magnesium phthalocyanines are sufficiently soluble in organic solvents and show enough bleachable absorption at 694.3 nm to serve as repeated Q-switching elements for ruby lasers (qv) (180). Phthalocyanines have been used in other lasers as well (181).

Phthalocyanines have been used to incorporate semiconductor properties in polymers (182) or to develop a thin-film transistor (183). Phthalocyanines and their derivatives can act as dyes in color photography (qv) (184) or electrophotography (185). Light-sensitive compositions for use on lithographic plates are comprised in part of copper phthalocyanine blue (186). Dichlorosilicon phthalocyanine [19333-10-9] has been used in the photoconducting layer in the target area of a television camera tube (187). Copper polyphthalocyanine can be prepared with an excess of copper which produces a material with *p*- or *n*-type conduction for use in photoelectric devices and solar cells (188). The conducting and photoconducting properties of metal-free phthalocyanine and of phthalocyanine containing less than the theoretical amount of copper have been studied (189). Doping of other semiconductors and general photoconducting properties of phthalocyanines have been disclosed (1, 185, 190).

Phthalocyanines are excellent lubricants at temperatures of 149–343°C (191). Combinations with other lubricants, like grease, molybdenum, or tungsten sulfides, have found applications in the automotive industry or professional drilling equipment (192–195). Further uses include indicators for iron(II), molybdenum(V), and uranium(IV) (196) or redox reactions (197), medical applications like hemoglobin replacements (198) or sterilization indicators (199), or uses like in gas filters for the removal of nitrogen oxides from cigarette smoke (200).

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Table 1. Worldwide Distribution of Crude Phthalocyanine Capacity

Country	Estimated capacity, t
United States, Canada	5,500
Western Europe	13,500
Eastern Europe	3,000
Japan, Taiwan, Korea, India	33,500
South America	1,500

Table 2. U.S. Production of Phthalocyanine Blue and Green Pigments, t

Colorant	1981	1983	1985	1987	1989	1991 ^a
Blue 15	412	631	354	564	195	221 ^b
Blue 15:1	476	429	452	432	380	503 ^b
Blue 15:2	548	357	258	229	198	199 ^b
Blue 15:3	3,720	3,956	4,196	5,752	8,017	8,460 ^b
Blue 15:4	^c	^c	580	661	644	609 ^b
<i>total</i>	<i>5,156</i>	<i>5,373</i>	<i>5,841</i>	<i>7,637</i>	<i>9,434</i>	<i>9,992^b</i>
Green 7	1,112	878	814	959	1,211	1,350
Green 36	99	89	66	43	42	38
<i>total</i>	<i>1,211</i>	<i>967</i>	<i>879</i>	<i>1,002</i>	<i>1,253</i>	<i>1,388</i>
<i>Total</i>	<i>6,367</i>	<i>6,340</i>	<i>6,720</i>	<i>8,639</i>	<i>10,687</i>	<i>11,388^b</i>

^aIn 1991, no detailed figures were published for phthalocyanine blue, but the total volume dropped 3.3% compared to 1990.

^bValue is estimated.

^cNo information available.

6. Health and Safety Factors

Phthalocyanines do not pose any significant risk to human health in the environment or the workplace. The blue and green pigments have LD₅₀ values of >10 g/kg body weight (201). Skin and eye irritation studies on CuPc (202) and the Ames test for mutagenicity were negative (203). In several studies, no carcinogenic risk or toxicity to humans was revealed. The FDA approved the use of CuPc in general and ophthalmologic surgery, for contact lenses, and food packaging (qv) (204). Phthalocyanine Blue [147-14-8] may be used as a colorant for coatings that are used in manufacturing, packing, processing, preparing, treatment, packaging, transporting, or holding food (205). The TLV value for CuPc is 10 mg/m³ (206). Other potential health hazards, which can be reduced to meet existing limits through protective equipment, have been discussed (207). A list of trace metals in typical commercial phthalocyanines has been given (208).

Polychlorinated biphenyls (PCBs) have been detected in pigments manufactured in trichlorobenzene, but not in those made with nonchlorinated solvents (209). High boiling hydrocarbons or esters are suitable replacements (210–212). Producers of copper phthalocyanine pigments may be faced with various regulations, based on the presence of copper in these pigments (201, 207), although the U.S. EPA has delisted Pigment Blue 15 as a source of copper for reporting under SARA III, Section 313. OSHA has established PEL of 0.1 mg/m³ for copper fumes (201). Other regulations deal with the issue of copper in waste water (EPA) (204) and solid wastes (RCRA) (201).

7. Economic Aspects

Phthalocyanine pigments account for approximately 23% of the total worldwide organic pigment consumption of 225,000 tons. Approximately 20,000 t are used in printing inks, 10,000 t in paints, 9,000 t in plastics, 3,000 t in textiles, 7,000 t in dyes, and 2,000 t in specialty uses. Table 1 shows the worldwide distribution of crude phthalocyanine capacity. The production history of phthalocyanine in the United States from 1980 to 1990 is given in Table 2 (161). The 1990 prices of phthalocyanine blue and green pigments were ca \$11–22/kg and \$21–27/kg, respectively.

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Dyes; Dyes, reactive