



From the Editor's Desk

The Pilgrimage of the Wonder Macromolecule: Phthalocyanine

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Industrial Production

Though, phthalocyanines (PC) have been prepared from almost every metal of the periodic table but the metal free phthalocyanine, Copper phthalocyanine and poly halogenated copper phthalocyanine are the three products of this series which have attained good commercial importance. Their commercial manufacture is also governed by the same general methods of preparations described earlier, but their utility for various industrial and domestic end- uses depends upon the different practices used for finishing the resultant products in various industrial processes.

1. Metal-free Phthalocyanines: They are produced by two slightly different methods, the direct method and the indirect method. The direct method includes heating phthalonitrile to 350 – 360° for 6-7 hrs, in a sealed vessel, heating phthalonitrile in triethanolamines at 170-180° for 4 hrs or heating phthalonitrile in an inert solvent in presence of cyclohexyl amine or pyridine etc.

In the indirect method, the metal phthalocyanine with a replaceable metal is prepared 1st and the metal is removed by an acid. Heating phthalonitrile with sodium-alcoholate and sod-cyanamide in a solvent, heating with calcium metal in an alcohol, heating with calcium or barium oxides in methyl glucamine with an alcohol or heating with mg and a solvent under pressure are the few methods for introducing replacable Na, Ca, Mg and Ba metals in the phthalocyanine molecular centre. These central metals are then removed by boiling in an alcohol or treating with an acid. In one other method Mg or Ca-phthalocyanines are prepared by Wyler's urea method and the resultant metal (replacable) phthalocyanine is treated with an acid to give the metal free phthalocyanine.

A less expensive practical method for large scale preparation of metal-free phthalocyanine is to mix CaO and Phthalonitrile with formamide in a wooden barrel. An exothermic reaction sets in and completes in 15-20 minutes. The Temperature control and stirring is not required. The product cooled and grinded, extracted with H₂O and boiled with 6 to 15% HCl to remove calcium.

2. Copper Phthalocyanine: The commercially used CuPC is a Metastable product generally called α -type which is produced by pasting the dull peacock-blue β -form, prepared by various methods. Pasting is done by dissolving or mixing the β -form with H_2SO_4 of high concentration and drowning into H_2O . Filtration from H_2O solution gives the α -form with better appearance and tinctorial properties.

Two basic groups of chemicals are used in the production of copper-phthalocyanines:

i. Phthalonitrile and allied chemicals: Includes bake/dry process and a solvent process.

Bake/Dry Process : 4 moles of phthalonitrile and 1 mole of cupric chloride are mixed and heated up to 200-250°C for 2 to 6 hrs in an autoclave in an inert atmosphere (N_2) to give about 70 – 75% yield of the CuPC. In an improved method developed in Germany, the mixture of phthalonitrile and anhydrous CuCl was placed on block iron trays, heated in a closed baker from which air was partially withdrawn. Exothermic reaction takes place at 140-145°C and the temperature reaches to 300°C. The product from the cooled trays is discharged and worked up. The yield approaches up to 90%.

Solvent Process: The phthalonitrile, pyridine and either nitrobenzene, or trichlorobenzene, mono chlorobenzene are used under pressure. Heating phthalonitrile with Cu-powder or Cu-salt in ethyleneglycol with catalytic quantities of a chloride of Cu, Sb, Al or ammonium and heating phthalonitrile with Cupric chloride or cupric sulphate in nitrobenzene in presence of NH_3 in an autoclave are the two methods, which give up to 90-95% yields. A 98 to 100% yield producing method is as under:-

This method is sometimes used for checking the purity of the technical phthalonitrile.

A 100% yield method: 100 cc of Nitrobenzene, 20 gm of CuCl and 16 gm of pyridine are heated at 100°C. At this temperature 250cc of more nitrobenzene is added, followed by the addition of 51.2 gms of technical grade phthalonitrile. The charge is heated in an oil bath to 190-200°C and kept at this temperature for about 1½ Hrs. 200 c.c. of nitrobenzene is then distilled off and the charge is filtered hot. The cake washed with little nitrobenzene and then with MeOH, till the filtrate is colourless. The remaining mass is extracted twice with hot 5% HCl. The filtered mass is washed with H_2O acid free, followed by a washing with MeOH and acetone and dried at 100°C. The yield is 99-100% of the theoretical technical grade phthalonitrile (95%). The product shows a high tinctorial strength as compared with that obtained by dry process. The purity of technical grade phthalonitrile is calculated according to following formula:

$$\% \text{ Purity} = \frac{\text{yield} \times 100}{57.5}$$

ii. Phthalic anhydride/imide and allied chemicals: Phthalic anhydride– urea process developed by Wyler, uses cheaper starting material as compared to phthalonitrile material and though gives fewer yields but is commercially viable. This also is divided into the melt/dry process and the solvent process.

Melt/Dry Process: A mixture of 130 gm urea and 5 gm of boric acid is melted at 130°C. 100 gms of phthalic anhydride and 20 gm of anhydrous cupric chloride is added. The mass then heated at 200°C until colour formation is complete. The cooled product is ground, slurried with dil. NaOH, filtered, slurried in 5% H₂SO₄, filtered and dried. The finishing was done by Pasting in conc. H₂SO₄ and drowning in hot H₂O. This process gave upto 70-75% yield in large operations. A continuous production is also possible with this method. Attempts in varying phthalic anhydride material and the catalyst improved the yield to some extent.

Solvent process uses high boiling organic solvents like tri-chlorobenzene, nitrobenzene and diethylephthalate etc. which improves the yield from 10 to 15% as compared to dry process.

In a method developed in Germany, 500 gm phthalic anhydride, 1050 gms of urea, 10 gms of CuCl and 1500 cc. of TCB are mixed. After heating the mixture to 130°C a mixture of 125 gm of anhydrous AlCl₃ and 50 gms of anhydrous FeCl₃ are added in small lots and then the reaction mass is heated to 180–200°C for 6–7 Hrs. Removal of solvent and isolation of CuPC results in 93% yield in the laboratory and 86 to 88% yield in the plant.

In another process 100 gms phthalic anhydride, 23 gm of CuCl₂, 150 gms of urea, 2.5 gm of boric acid and 0.25 gm of Ammonium Molybdate in 400 cc of TCB are heated up to 190-200°C for 4 to 6 Hrs. The CuPC is recovered from this product by adding 120 gm of 98% H₂SO₄ at 140–150°C with stirring for 2 hrs. The CuPC tetrasulphate is filtered and washed with 200cc of isopropanol. The filter cake is slurried with 500 cc of H₂O, neutralized with NaOH, filtered and dried after washing with H₂O.

A Newer Horizon in Phthalocyanine Chemistry: Dr. N.C. Jain, a research Scientist in the Chemical section of Maharaja Ranjeet Singh College of professional Sciences Indore (INDIA). Has recently developed a new method with his colleagues Dr. Mrs. A. Phadnis and Dr. Dipak Sharma for the preparation of metal Phthalocyanines. The method includes heating a modified stoichiometric mixture of phthalimide, phthalic anhydride and urea in a high boiling organic solvent (Trichlorobenzene). A moderately high temperature of 170 – 200°C and 2 hrs heating time with stirring has been used here as compared to 200 to 300°C temperature and 4 to 6 hrs time in other processes. The end-yield obtained in the few attempted reactions so far is about 85% with good quality product (CuPC).

By this method, this Laboratory has attained good success in preparing some symmetrically substituted CuPC's and putting some auxochromic groups like –COOH and –NH₂ on the opposite sides of the 4 benzene entities of the metal-phthalocyanine molecule. After successfully

putting different auxochromic groups on the opposite sides of the CuPC molecule, a trial of creating polymerization in MPC series is being made through condensation polymerization method with the opposite-natured auxochromic groups.

Finishing Processes: Products obtained from phthalonitrile or Phthalic anhydride-urea process are generally in the dull β -morphological form and have to be converted in the α -form or suitably modified by different undermentioned tectics to improve their tinctorial properties and stabilities for different industrial end-uses.

Acid Pasting: The manufactured product is slurried/dissolved in various concentrations of Conc. H_2SO_4 . The resultant slurry after keeping for some time is drowned in to water, filtered and dried. Sometimes some Co-precipitants are also used to increase the dispersibility of the resultant product.

Grinding with Salts: PC's or MPC's obtained from different production procedures are grinded with variety of salts of inorganic and organic acids with or without organic solvents to stabilize the β -form or to convert it to the usable α -form.

Pigment treatment: Semi-dried press-cake of PCc's and MPC's are milled with various dispersing or emulsifying agents like oyl alcohol, ethylene oxide, sodium salt of sulphonated naphthalene formaldehyde condensation products, oily substances, resinous products and compatible colours to make them acceptable for diferent marketabilities.

Non-crystallizing and non-flocculating activities: CuPC may exist in three different morphological modifications α , β and γ . Metastable α -form is obtained by acid pasting, stable β -form is obtained by solvent grinding or by heat treatment and γ -form is obtained by slurring in 60-65% H_2SO_4 .

Crystallization is a tendency of CuPC blue pigment fine particles to grow in size in different solvents such as benzene, toluene, alcohols, esters and ketones, resulting in loss of colour strength and shift in hue from blue-green towards red. While flocculation is a tendency of formation of clusters of pigment particles in the vehicles used. This also causes reduction of tinctorial strength and hue changes. Both these tendencies are checked by adding some lacquers, partial chlorination or sulphonation of the main product or admixing small quantities of PC's containing other metal in the centre. PC's/MPC's formation reactions when run in presence of (0.01 to 0.15) amounts of tertiary bases like pyridine or quinoline also give good non-crystallizing-non-flocculating substances. Heating PC's and MPC's in small quantities of $AlCl_3$ -NaCl eutectic mixture also produce non-crystallizing-non-flocculating products.

3. Polyhalogenated Phthalocyanines: Though, polybromo PC's and MPC's and polychloro-bromo PC's and MPC's have been prepared, but main polyhalogenated PC's and MPC's are the polychlorinated ones. Replacement of 16 hydrogen atoms of the four benzene-portions of the PC

and MPC molecules by chlorine atoms move towards green colour. Though the first few additions do not produce any colour effect but 10 chlorine atoms onwards rapidly increase the green colour which is perfect by the inclusion of 14 atoms. No colour change effect is noticed by 15th and 16th chlorine atoms. Chlorinated industrial products generally contain 12 to 14 Cl atoms. These chlorinated green products have high resistance to acids, alkali's and bleeding. The two methods of their preparation are:

Starting from halogenated phthalonitrile or phthalic anhydride reactants: Urea-Phthalic Anhydride method uses tetrachlorophthalic anhydride/imide, CuCl, urea and a catalyst (ammonium molybdate). Chlorides of zirconium, titanium, antimony and arsenic are also used as catalyst for increasing yields and colours strength.

Halogenation of the finished PC molecules: Direct Chlorination by Passing Chlorine gas in an eutectic mixture of AlCl₃/NaCl at 180-200⁰C give 14-16% Chlorine atom substituted PC's. Chlorination in TCB, molten phthalic anhydride, CCl₄ underpressure and phthallylchloride are few other methods used for the introduction of 12 to 14 chlorine atoms. Finishing methods of polyhalogenated green pigments are the same; acid pasting and salt grinding with or without solvent with slight variation in the methods used for finishing PC's and MPC's. Green PC's and MPC's are more persistent in colour, intensity and flocculation etc. properties as compared to PC's and MPC's.

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