

**From the Editor's Desk**

## Pilgrimage of Phthalocyanine Macromolecule Phthalocyanine Dyes (Part-II)

**Jain N.C.**

Our editor, Research Scientist, Maharaja Ranjit Singh College of Professional Sciences., Indore, INDIA

[drncjain.jain@gmail.com](mailto:drncjain.jain@gmail.com)

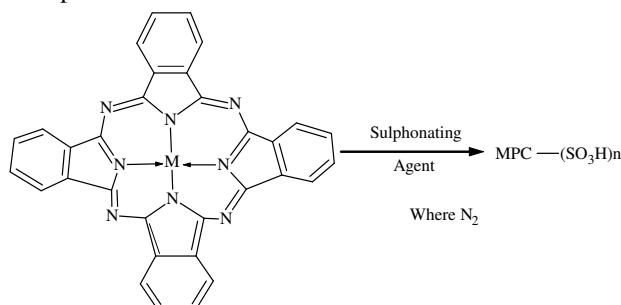
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### Introduction

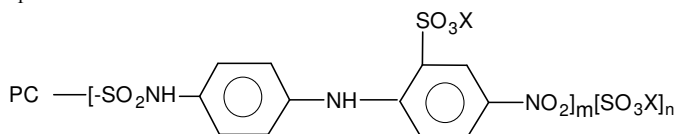
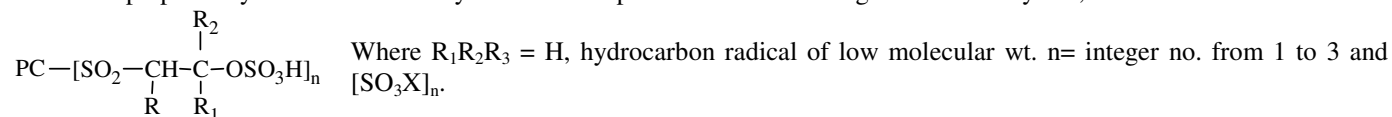
Metal free phthalocyanine (pc's), metal phthalocyanine (mpc's) and polyhalogenated (phmpc's) we have discussed so far are inert coloured substances (pigments) in nature and are bodily present with in a binding agent like plastic or resin etc. When certain auxochromic groups like -COOH, -OH, -NH<sub>2</sub>, -SO<sub>3</sub>H, -SH, are attached to these pigment molecules they function as dyes. These functional auxochromic groups attach themselves chemically to the substrate molecules to produce a tinctorially stable fast colour.

Phthalocyanine dyes are very important members of the colour industry. Many-thousand patents have been claimed all over the world with variations in the methods of their preparations and applications in different tinctorial forms. For convenience, we can divide them in series like, Sulphonic acid dyes, Sulphonic acid chlorides, Water soluble dyes without sulphonic groups, Quaternary and ternary dyes, Solvent soluble dyes, Sulphur dyes, Azo-dyes, Vat dyes, Leuco dyes, Chrome dyes, S-Triazine dyes, etc.

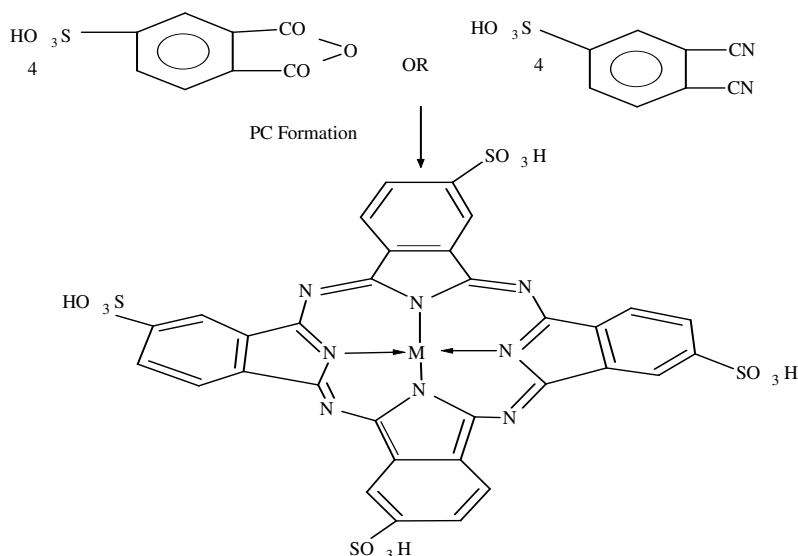
**Sulphonic acid phthalocyanine dyes:** They are prepared in two ways (First) by action of oleum of different concentrations on phthalocyanines or metal phthalocyanines at different temperatures and drawing the resultant slurry/solution in cold water. The precipitated sulphonic acid pc's are then treated with Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> solutions. The article is taken-out of the solution and dried. The articles thus dyed are generally sky-blue to blue-green in shade. The metals at the centre of the pc molecules also have their variable colour effect. They can be represented as under.



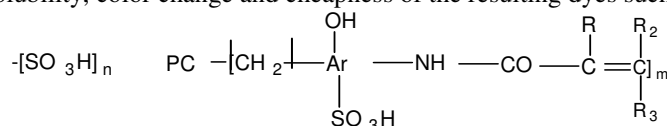
Another method of producing sulphonic acid pc is to start with already sulphonated starting materials such as 4 or 5-position sulphonated ortho-dicarboxylic/dinitrile derivatives. Such sulphonated pc's are having 4-SO<sub>3</sub>H solubilising groups and the shade and nature of the solubilising group may have different attachments like -SO<sub>3</sub>H, -SO<sub>2</sub>Cl, -SO<sub>2</sub>NH<sub>2</sub>, -SO<sub>2</sub>NHR etc. for varying the nature of the colour, solubility and applicability. Sulphonic pc dyes prepared in this way have better stability and fastness to light than those prepared by method. First many methods and patents came into being in successive years, such as under.



Where PC = Phthalocyanine Radical with or without metals like Cu, Co, Ni, Fe, Zn, Al, Sn, etc. , X = H, NH<sub>3</sub>, N<sup>R</sup>, ethanolamine, n = 1 or 2, m = 1, 2 or 3, n + m = 2, 3 or 4.



In some modified dyes, sulphonic acid groups are made to attach with some additional aromatic or elephatic groups to make desired changes in the dye molecule for solubility, color change and cheapness of the resulting dyes such as



Where Ar = aromatic radical that contains up to 2 benzene rings. R<sub>1</sub> and R<sub>2</sub> = H, alkyl group, hydroxyalkyl or halogen atom. R<sub>3</sub> = H, alkyl or hydroxyl group or halogen or -COOH, m = 1 to 8, n = 0 to 4

Many variations and methods of preparations and utility of pc sulphonic acid dyes are still in continuity in the present market also. These blue-green sulphonic pc dyes are so common and important in the market that everybody seems to prepare these dyes with a slight different method and get it patented in his own name.

**Sulphonic Acid Chlorides:** Although sulphonic acid groups impart H<sub>2</sub>O solubility to pc pigments/dyes, sulphonic acid chlorides are insoluble in H<sub>2</sub>O and organic solvents, but they are useful adjunct dyes, because they represent valuable starting materials for the preparation of dye-stuffs of pc series as their chlorine atoms are capable of being easily exchanged by other groups, for instance by reaction with alcohols, phenols and amines etc. They are easily prepared, for example: - A mixture of CuPC or any metal-pc and chlorosulphonic acid is heated and stirred for 1-2 hrs at 135-150<sup>0</sup>C. The mixture is cooled and stirred in ice water. The blue-green ppt is probably Cupc-tetrasulphonic acid chloride, is filtered off and washed to neutrality and dried.

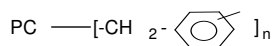
While many sulphonic acid groups on the parent pc molecule are not very necessary in sulphonic acid dyes, only two to three -SO<sub>3</sub>H are sufficient. The presence of 2 to 7 Cl atoms on the parent pc dye molecule along with -SO<sub>3</sub>H groups, though do not change the colour properties very much but are distinguished by evolved (improved) affinity to natural cellulose fibres. So, a combination of sulphonation and chlorination on the parent pc molecule along with some chlorosulphonation activity increases the utility of these brilliant sulphonic and chlorosulphonic acid derived dyes.

**Water Soluble Dyes:** Dyes soluble in H<sub>2</sub>O, other than -SO<sub>3</sub>H containing dyes have been prepared by various permutation and combinations, for example.

A mixture of Cupc and trichloroacetic acid is heated for 6 hrs at 170-180<sup>0</sup>C. The reaction mass is quenched in H<sub>2</sub>O. The residue boiled in dilute HCl, filtered and washed with ammonia solution, heated to 80-85<sup>0</sup>C, filtered and precipitated with acid. It dyes cotton green-blue shades which are fast to acid and very fast to light.

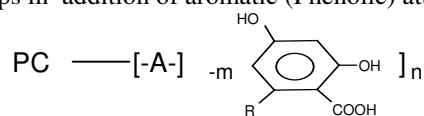
Poly carboxy pc's are also prepared by starting with poly carboxy benzene derivatives, such as pyromellitic and trimellitic acids etc. Such dyes are soluble in dil/warm alkali solution. These carboxy pc's react with amines and the resultant products are more or less soluble in alcohols.

PC dyes with following formula have also been prepared



This type of dyes are made from chloromethylphthalocyanines, anhydrous  $ZnCl_2$  and a phenol by heating the mixture of them at  $120^\circ C$  for 3 hrs and separating the blue solid. They are soluble in dilute aqueous NaOH and slightly soluble in alcohols, acetone etc. Their shades towards green-ness depends upon the number of  $-OH$  groups in their molecules. They are used for colouring shellac and nitro cellulosic articles and lacquers.

Dyes containing both  $-OH$  and  $-COOH$  groups in addition of aromatic (Phenolic) attached groups are also very common, such as:



Where PC= Phthalocyanineradical, A= is a bivalent bridge group, Ar=an additional aryl nucleus with  $-OH$  and  $-COOH$  groups,  $m = 1$  to 8,  $n =$  atleast one lower alkyl group. These dyes are completely soluble in aqueous alkali solutions because of the presence of multiple  $-OH$  and  $-COOH$  groups and are green in colour. They have exceptional fastness to light.

$H_2O$  soluble dyes of the formula:  $PC - [CH_2NH_2HX]_n$

Where, X = Halogen,  $n = 1$  to 8.

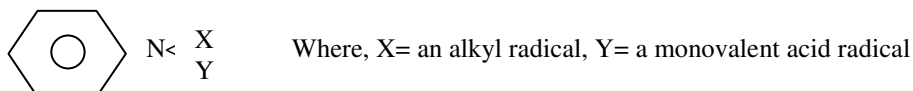
is another example of  $H_2O$  soluble PC dyes which do not have any sulphonic groups.

$PC - [-CH_2 - NH - CH_3]_n$ ,  $PC - [-CH_2 - N(CH_3)_2]_n$  and  $PC - [-CH_2OR]_n$  are also some examples of important  $H_2O$  soluble dyes.

All these enormous number of  $H_2O$  soluble dyes containing solubilising groups attached on the sides of the pc molecules are very common on the market. They are fast and stable dyes with various colour shades.

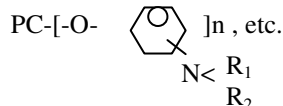
**Ternary and Quaternary compounds:** This type of quaternary ammonium compounds are soluble in water. These dyes are the products of pyridyl containing pc's and quaternizing agents such as dimethyl sulphate or an alkyl chloride etc. They are of intense blue-green shade and show a very good affinity to cotton, slick, paper or other cellulosic materials and are fast to light and washings.

Dyes containing pyridyl radical such as:



**Solvent soluble dyes:** Generally, presence of such alkyl attached side chains makes this type of dyes solvent soluble. These dyes are useful for colouring paper, wood, leather and nitrocellulose etc. This type of dyes give good colours with quite fast nature towards light. Variable chain lengths, variety of alkyl and aryl organic radicals have been utilized to produce such type of soluble dyes.

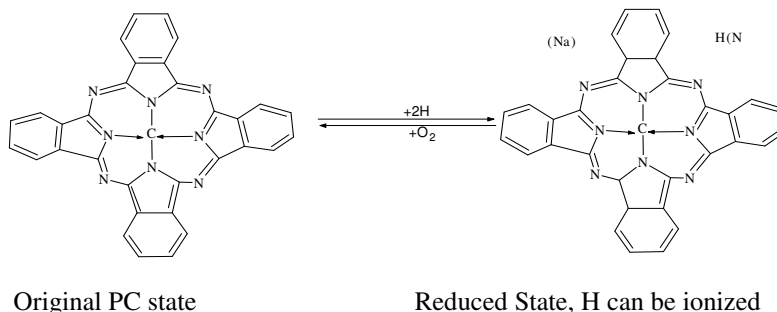
This type of dyes result by putting long alkyl groups on the pc molecules withauxochromic groups like  $-OH$ ,  $-NH_2$  etc. for example  $PC - [-OR]_n$ ,  $PC - [-N < \begin{matrix} R \\ R \end{matrix}]_n$ ,  $PC - [-CH_2OR]_n$ ,  $PC - [-CH_2 - N < \begin{matrix} R_1 \\ R_2 \end{matrix}]_n$ ,



**Sulphure dyes:** Mercapto ( $-SH$ )phthalocyanines are prepared from corresponding aminophthalocyanines by their conversion to diazo compounds followed by hydrolysis at elevated temperatures. The alkyli soluble mercaptophthalocyanines are oxidized by air/oxidizing agent to form  $H_2O$  insoluble dyestuffs. These dyes are reduced in aqueous sodium sulphite solution, forming a vat from which textile articles can be dyed in the same manner as by commercial sulphure dyes. Bluish green shades obtained on cellulosic material show out-standing fastness to washings and light and their clarity of shades is also out-standing.

Halomethylphthalocyanines also react with mercaptansto give sulphides, with sulphides to give ternary sulphonium salts and with thioureaisothiouranium salts. Also, phtalocyaninesulphonyl chloride is reduced to mercaptophthalocyanines by dilHCl and Zn dust. This has good affinity to cellulosic fibre after getting oxidized by arialoxidation. Condensation of such sulphonylphthalocyanines with hydrazine or primary/secondary amines and their substitution products result in green to blue-green shade dyes. Condensing halogenated pc's with mercapto compounds of aromatic series in presence of alcohols and catalysts give dyes of the general formula



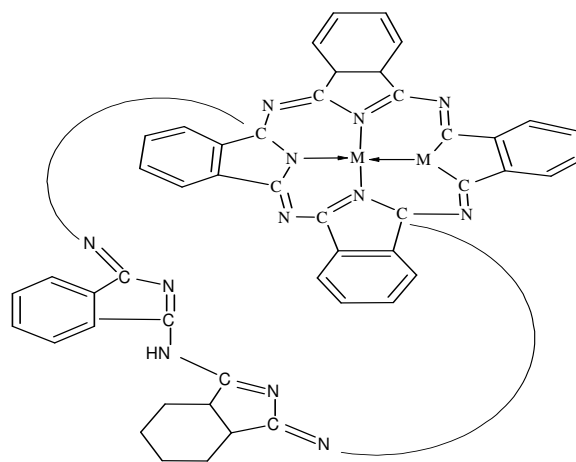


It has been found later on by McCormack, Stilmarand other workers that cobalt pc's vating and strength of dyeing can be improved by addition of the phosphorus acid groups – P(OH)<sub>2</sub> into the pc molecule up to the extent of 0.2 to 0.4 moles of –P(OH)<sub>2</sub> per pc molecule. Attempt to increase vating, solubility and stability can be introduced by introducing other solubilising groups like –SO<sub>3</sub>H, –SO<sub>2</sub>NH<sub>2</sub>, –COOH, CONH<sub>2</sub>, cyano, –OH, RONa, –SH, –NH<sub>2</sub>, –NHR etc. and such dyes dye the articles in slightly hot vats, even in very mild alkaline media such as NH<sub>4</sub>OH, dyeing all type of animal fibres.

Cobalt pc dyes containing from 1 to 4 moles of H<sub>2</sub>O solubilising groups like –R–COOH per mole, where R is an aliphatic radical specially –CH<sub>2</sub>–, CHCl or CCl<sub>2</sub> are soluble in alkaline hydrosulphite solution and colour cotton, cellulose, viscos and artificial silk in clear blue to green –blue shades. Many modifications in Cope's were made them perfect vat dyes, Co-pc's without solubilizing groups are treated with dispersing agents such as gum arabic, dextrin, tannin, saponin, sulphonated fatty acids, These are then finished with H<sub>2</sub>SO<sub>4</sub> and the dyeing material in vats easily applied to the textile objects in the usual manner in the alkaline hydrosulphite solution. Olive-green vat dyes cotton in strong, clear blue shade of good light and wash fastness. Cobalt pc's now are also formed in the fibre by preparation of complex cobalt compounds of phthalonitrile soluble in NaOH. For example:-

A mix of phthalic anhydride, urea, anhydrous CoCl<sub>2</sub>, ammonium molybdate and nitrobenzene is heated at 170°C for 10 hrs. The mass is cooled, diluted with MeOH and complex cobalt phthalonitrile paste is filtered off and purified by dissolving in aqueous NaOH /methanol solution followed by filtration and precipitation with CH<sub>3</sub>COOH. Conversion of such mass to cobalt-pc takes place. Such as by heating with NH<sub>2</sub>NH<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> in glacial CH<sub>3</sub>COOH for 0.5 hrs. or by refluxing in quinoline. This complex paste is used for printing and then steaming to produce the dye in the matrix of the articles. Other combination of cobalt dyes such as cobalt-iron dyes and putting different solubilizing groups in such pc vat dyes have been tried to introduce pc molecules successfully in the vat dyeing group of dyes.

**Leuco dyes:** Brooks has prepared a dye capable of generating phthalocyanine on the fiber by reduction of a solvent soluble form of CapC. Solvent soluble pc is prepared by reacting phthalonitrile with NH<sub>3</sub> and CaO / Ca(OH)<sub>2</sub>. The product seems to be made up of 6 phthalonitrile units, an atom of Ca and an NH<sub>3</sub> group. It also seems to have 3 moles of water of crystallization. The probable formula is – Ca(C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>)<sub>6</sub> NH<sub>3</sub> · 3H<sub>2</sub>O.

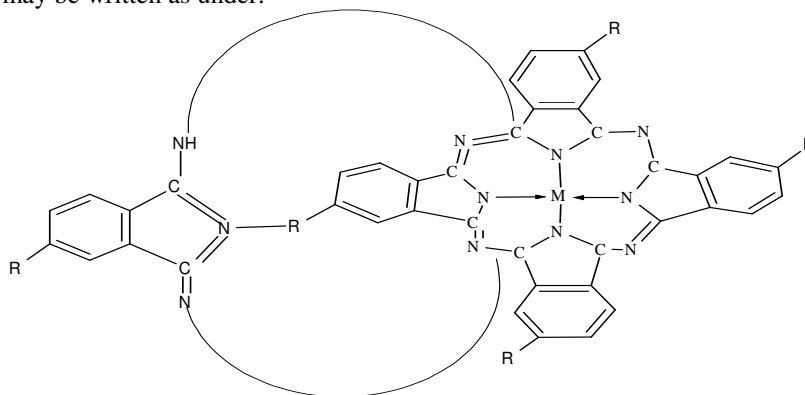


This leuco compound is soluble in alcohol, benzene and chloroform. It is barely a colored compound and has no tinctorial properties. Upon reduction, this leucoCa-pc decomposes to pc, NH<sub>3</sub> and a Ca salt of the reducing agent. Effective reducing agents are ascorbic acid, Na<sub>2</sub>S and NaHSO<sub>3</sub>. Later- on improvements produced this type of leuco PC's form many other metal PC's such

as CuPC, NiPC, CoPC, CrPC, etc. Baumann and Bienert prepared PC containing 6 moles of Phthalonitrile groups per atom of cobalt when cobalt salts were heated with phthalonitrile, phthalic acid/ anhydride and urea at a temperature of 160° - 170°C.

These copper and nickel leuco PC's are barely colored and possess no tinctorial properties. They are in the sense a higher oxidation stage than corresponding PC's, as they yield PC's upon treatment with reducing agents as compared to leuco vat compounds which is a reduction product of the dye, which gets oxidized on exposure to oxygen. The same scientist Brook has also synthesized useful halogenated Cu or Ni leuco PC's, where halogen atoms are Cl or Br, and where leuco PC's contain 6 phthalonitrile units and from 6 to 12 halogen atoms per molecule.

Perkins, Oken and Whelen have extended the shade range of leuco PC dyes by making noble precursor compounds of Cu and Ni Pc series which differ from above leucoPCs that they contain a phenyl substituent in atleast one of the Bz (phenylene) rings and by producing on the fiber dyes of shades varying from turquoise- blue to green. These noble precursors are also distinguished by having 5 phthalonitrile units in their complex formulae as compared to 6 units which characterize CuPC precursors. The structural formula of such precursors may be written as under.



Where, M=Cu/Ni, R=Phenyl radical, while other R's represented h/Phenyl.

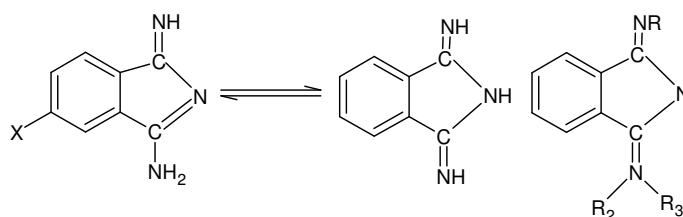
The molecular formula for leuco Cu pentaphenyl PC is  $Cu(C_6H_5.C_8H_3N_2)_5NH_3$

Other improvements later on in the series resulted in variety of dyes in this leuco PC series to give fast colors from water and solvent soluble precursor PC's used in dye industries.

**Precursor Dyes:** Some dyes were prepared to produce pc colours in the fibers themselves. In general, the derivatives of isoindolines are impregnated in the fibre, followed by chemical and heat treatments that convert the pc intermediates to pcs in a much easier way.

Chlorine bearing and NO<sub>2</sub> group bearing isoindolines may also be used as dye intermediates for printing & formation of dyes on the fabrics. For example phthalic anhydride is heated with stirring at 150-160°C for 20 hrs with urea, NH<sub>4</sub>NO<sub>3</sub> and Ammonium molybdate, forming amino-imino-isoindoline nitrate which is purified with a H<sub>2</sub>O wash.

Other isoindoline derivatives that have been prepared include



Where X= H or from 0 to 4 organic or inorganic radicals for example Alkyl, Alkoxy, Aroxy, Arylmercapto, Heterocyclic, Halogen or Acyl, -NO<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -SO<sub>2</sub>NH<sub>2</sub> etc groups.

R, R<sub>2</sub> and R<sub>3</sub> = H, organic or inorganic radicals such as alkyl, alkylene, aryl, other polycyclic radicals.

These isoindolines derivatives may later on prove to be useful in our pc polymer making techniques, which we will mention in the end of this discussion in the name of Nemi's half salt method & its uses for pc polymer formation (linear).

Continued-----