

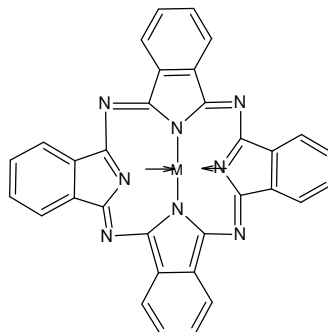
From the Editor's Desk

The Pilgrimage of the Wonder Macromolecule: Phthalocyanine

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This wonder Macromolecule was given birth accidentally in the year 1928 at the works of Scottish Dyes Ltd. When Ammonia gas was being passed on molten phthalic anhydride in an iron vessel for the preparation phthalimide, there appeared a blue coloured impurity in the reaction mass. Proper repetition of the reaction of phthalimide with iron compounds by Dunworth and Dreseher established the preparation of this blue substance and in the preceding year 1929 the 1st patent was issued with respect to compounds that we now known as phthalicyanines, to Dandrige, Drescher and Thomsan of Scottish Dyes Ltd. with the claim of the reaction of ammonia or primary monoamines of aliphatic series or of benzene or naphthalene series on phthalic anhydride, phthalimide or mono or diamide of phthalic acid in presence of Fe, Ni or Co in the form of metal or compounds.

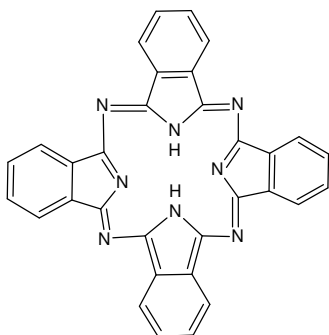
Up to 1929 to 1933, none of the blue colour observing scientist's attempted to determine the structure of this compound when prof. Linstead and his students at the University of London determined and announced the structure of phthalocyanine and several metal phthalocyanines in the year 1933 and 1934. Thus the discovery of phthalocyanine class of organic compounds terminated in 1934. This was the new class of organic compounds as well as a new class of coloured matter or chromogen.

1934, onwards many attemptes have been made by different scientist's and dye companies of the world to construct the phthalocyanine colouring mater but it was the Imperial chemical industries London which in the year 1935 started a full manufacture of the principal colouring blue pigment "copper – phthalocyanine" and named it Monstral Fast Blue BS. In 1936 I.G. Farben industry at Ludwigshaten and in the late 1930's du point and deep water point New Jersey began to produce Cu-PC. The standard ultramarine and colour company began production of this substance (pigment blue) in 1949.

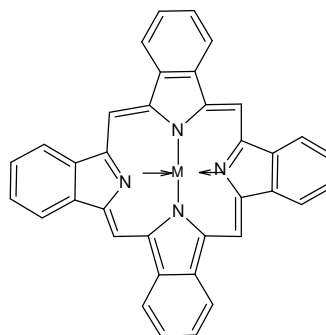
Successive chemical and physical studies of these chromogens by the world scholars have opened many new horizons for the utility of these pigments in variety of important fields other than colouring and now presently phthalocyanines occupy almost 60-70 of the total words production of the pigment and dyes.

Today about 60 million tons of pigment phthalocyanine colouring matter is being produced in different countries of the world including few large scale producers in our own country.

Structure: Analysis indicates that phthalocyanine has a molecular formula $C_{32}H_{18}N_8$ or $(C_8H_4N_2)_4H_2$ and has a grouping of 4 isoindoline units arranged in the form of a planner ring structure. The corresponding formula for metal phthalocyanine is derived by the replacement of the two hydrogen atoms in the centre by a metal atom.



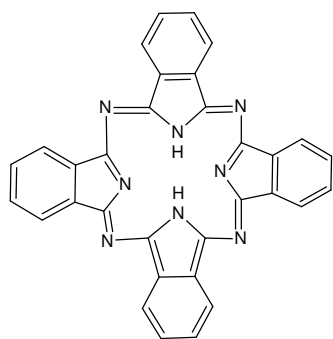
Phthalocyanine



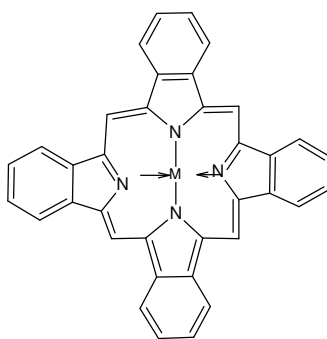
Metal-Phthalocyanine

Almost all metals of the periodic table have been put in the centre of the phthalocyanine ring structure with slight variation in the preparation methodology. The colours of the resultant phthalocyanine changes with the presence of the particular metal atom in the centre. Generally the phthalocyanines and metal phthalocyanines are stable colour pigments. Copper phthalocyanine with its peacock blue colour and high tinctorial value occupies the top position. It is very stable against heat (sublimes at $550^{\circ}C$), oxidation, reduction, acids, alkalis and other wear and tear activities.

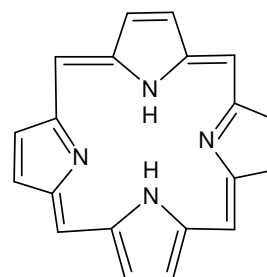
Phthalocyanine macromolecule resembles very much to other naturally occurring coloured compounds, like red hemin of haemoglobin of red blood cells and green chlorophyll of all green plants. The inner chemical structure of all these coloured substances is the same and in each of them 4 pyrole units join to the central metal atom through their nitrogen atom. Phthalocyanines differ only by the presence of 4 benzene rings on the periphery of the pyrolianic ring structure and perhaps this symmetrical peripheral presence of 4 benzene entities presence make phthalocyanine much more stable as compared to the Porphyrines in general. Molecular similarity is very well judged by their structural formulae as under:



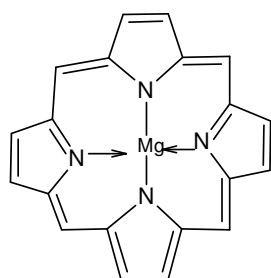
Phthalocyanine



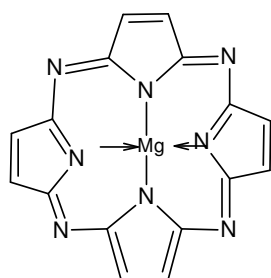
Metal-Phthalocyanine



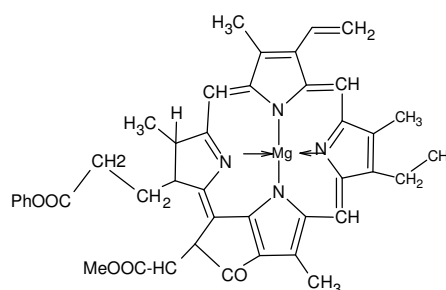
Porphine



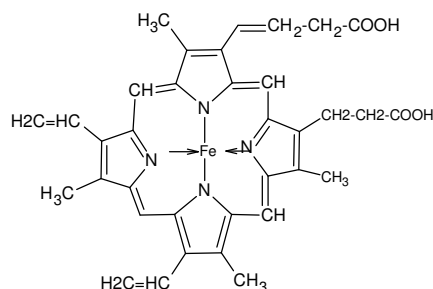
Mg-Porphine



Metal Tetra-azo Porphine



Chlorophyll



Hemine

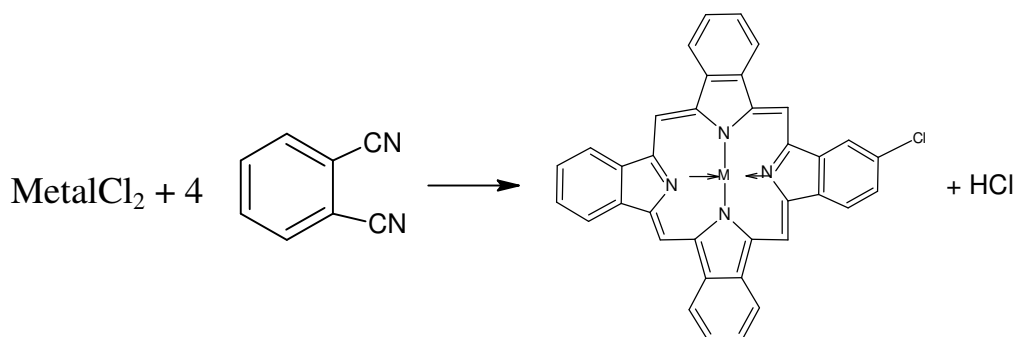
General methods of preparation: Phthalocyanines with almost all metals of the periodic table in their centre are prepared by slight variation in the following methods of preparation:

The reaction of phthalonitrile with metal or metal salts.

The reaction of phthalic anhydride, phthalic acid or phthalimide, urea, metal salt and catalyst.

The reaction of (metalless) phthalocyanine or replaceable metal phthalocyanine with a higher metal in the periodic table.

In method-1: 4 moles of phthalonitrile are heated with one of the metal or metal chloride to 180-190°C for atleast 2 hrs in quinoline or a mix of quinoline and trichlorobenzene. The tetracyclisation reaction may be denoted as under:

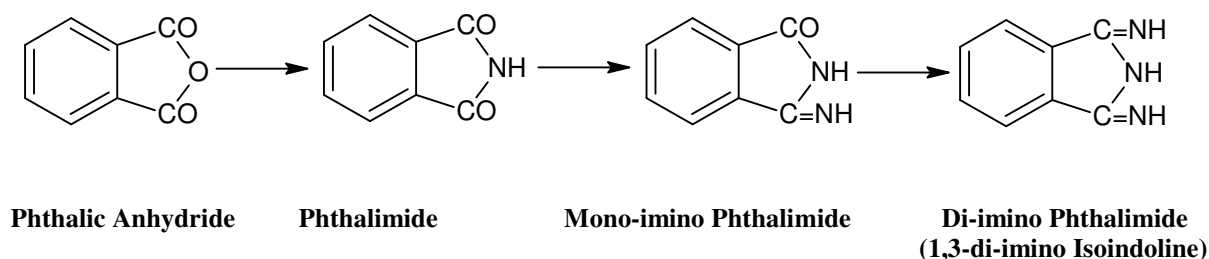


Co, Ni, Cr, Fe, Vanadyl, Chloroaluminium, and Ti-phthalocyanines have been made by this method. Quinoline or urea decomposition products act as halogen absorbing materials in the absence of which the halogen atom enters in the PC Molecules.

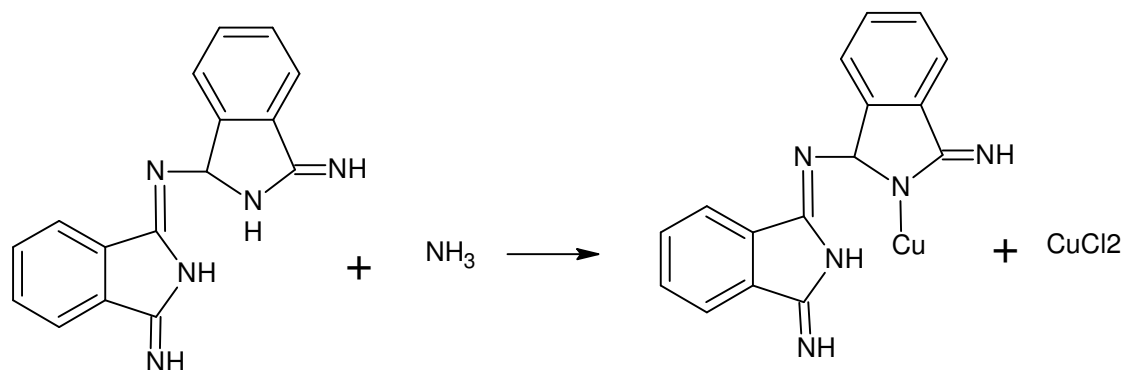
Method-2: uses, the phthalic anhydride/imide, a metal salt, urea and a catalyst. The reaction here completes in about four hours heating at 170-200⁰C. A reaction medium such as trichlorobenzene, nitrobenzene or chloronaphthalene is generally used in the reaction. The yields in this reaction are generally about 85%. Catalysts include Am. molybdate, boric acid, ferric chloride or the pre-made metal PC itself. Cu, Co, Ni, Fe, Sn etc metal phthalocyanines are generally prepared by this method.

Method-3: The method involves boiling of phthalocyanine and a metal in quinoline or benzophenone. A variation of this method is a double decomposition of a labile metal phthalocyanine with a metal salt forming its more stable metal phthalocyanine molecule. For example a dilithium metal phthalocyanine complex soluble in alcohol is added CuCl₂ and the Cu-Phthalocyanine which precipitates immediately is filtered and dried. Reaction medium other than alcohol, such as dimethyl formamide and dimethyl sulphoxide are also equally effective. Heavy metal phthalocyanines from uranium, lead, thorium, lanthanum, gadolinium etc. metals are prepared by thus method.

The chemistry of the formation of phthalocyanine involving the union of four isoindoline units symmetrically about a centre atom in one reaction system (step) is indeed a remarkable process. In the phthalic anhydride, urea, Cucl and Catalyst process, the formation of phthalocyanine molecule probably undergoes through the following steps.



And now the mono or the di-imino phthalimide condenses with itself to form for example:-



I

II

Followed by subsequent condensation of I and II to form Cu-phthalocyanine and ammonia. Indeed phthalocyanines have been made from mixtures of phthalimide urea, mono and diimino phthalimide and also the phthalimide and monoiminophthalimide have been isolated from the reaction maas in the formation of phthalocyanines.

Continued