

Pilgrimage of Phthalocyanine Macromolecule

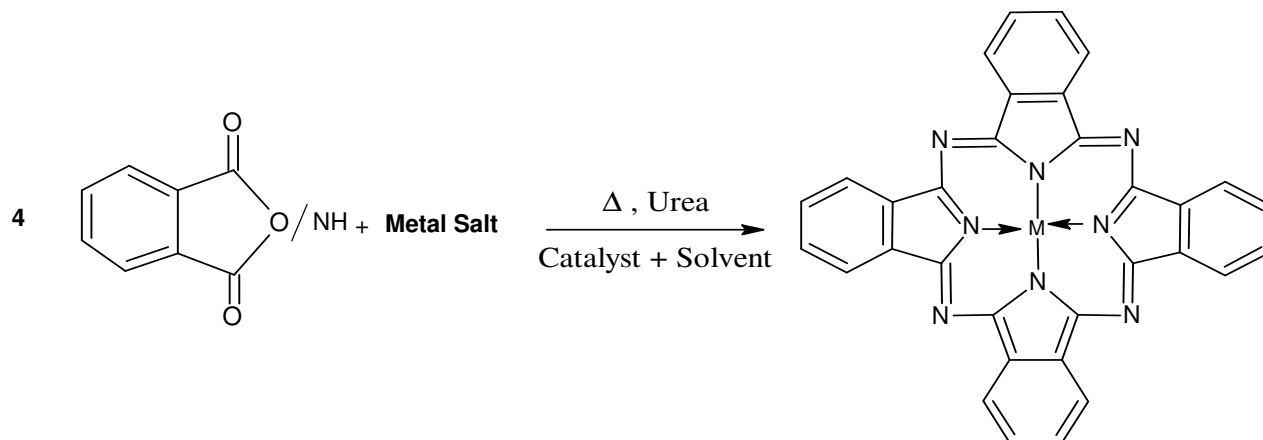
Jain N.C.

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

Available online at: www.isca.in, drcnjain.jain@gmail.com

A New Era in the Preparation of Phthalocyanine Macromolecule (Part-IV)

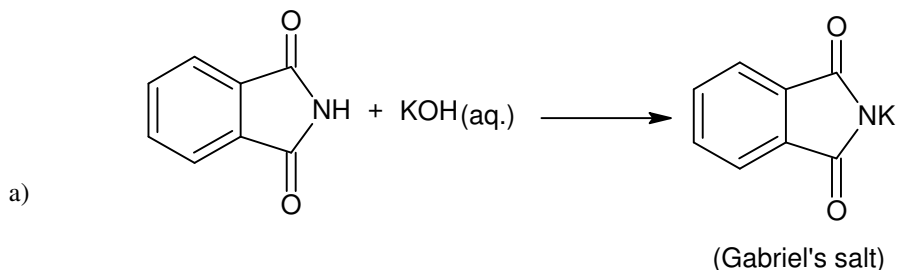
In the previous accounts (part-I, II and III), you can observe that all phthalocyanines, metallo-phthalocyanines and substituted metallo-phthalocyanines have been prepared by a common tetra cyclisation method starting from 4 moles of different starting compounds with or without a metal, in presence of a catalyst to give rise the desired final PC compound. If the phthalic anhydride/emide starting reacting entity has any substituent group and tetra cyclised, these substituted groups will invariably appear on all the 4 benzene rings of the phthalocyanine molecules as-

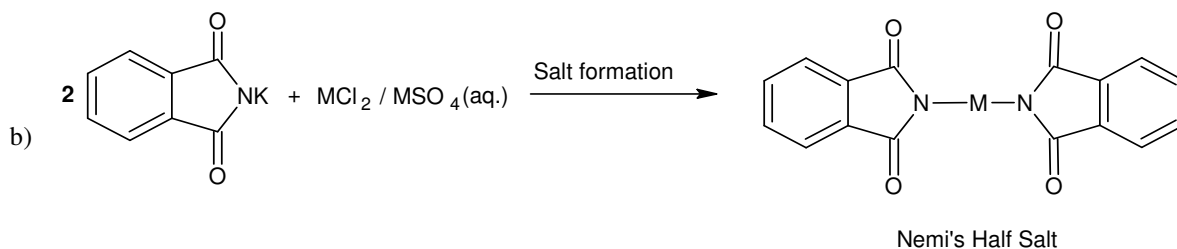


If we start with differently substituted phthalic acid starting materials, these substituent groups will also appear on all the four benzene rings of the resultant PC molecules, but their specific positions will not be known and the resulting PC's may be a mixture of many permutation-combination compounds.

Looking forward for an easier and more comprehensive headway (advancement) in the synthesis of a phthalocyanine molecule which is day-by-day advancing its tentacles in various modern technical activities, our group started experimenting some newer ideas in our laboratory and finally we have been able to give an altogether new approach for the derivation of this phthalocyanine wonder molecule.

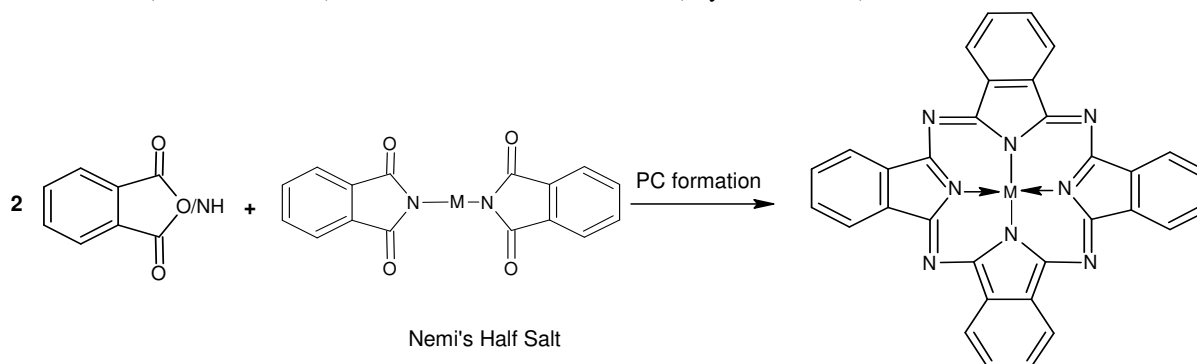
For this purpose, we divided the PC formation method in two parts: The first part includes the preparation of the one-half of the total PC molecule, by simple ionic reaction of phthalimide (acidic in nature) with an alkali (K or Na) hydroxide. The resultant phthalimide soluble metal salt was then treated with the solution of a higher group (periodic table) metal salt, such as Cu, Zn, Ni, Co, Fe, etc. in the form of chloride or sulphate. The two soluble salts on mixing precipitated a metal phthalimide salt in simple ionic fashion.



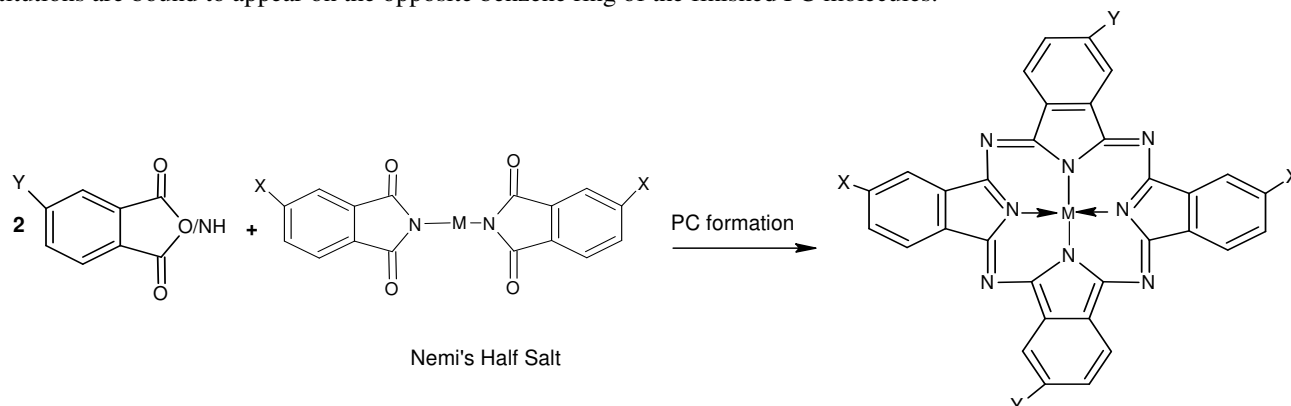


Here, M is a higher metal in the periodic table. We have mainly experimented with Zn, Ni, Co & Fe salts with special emphasis on copper salts, because the copper phthalocyanines are comparatively superior in stability and colour sheds. The dibasic metallic salts of different elements with phthalimide (Nemi's Half Salt) are supposed to be the one-half of the total PC molecule, in addition to the attachment of the central metallic part of PC molecule.

The second part of the procedure includes the condensation of the Nemi's half salt with 2 molecules of phthalic anhydride/ emide in stoichiometric ratio (as the other half) in usual PC formation reaction (Wyler's Method).

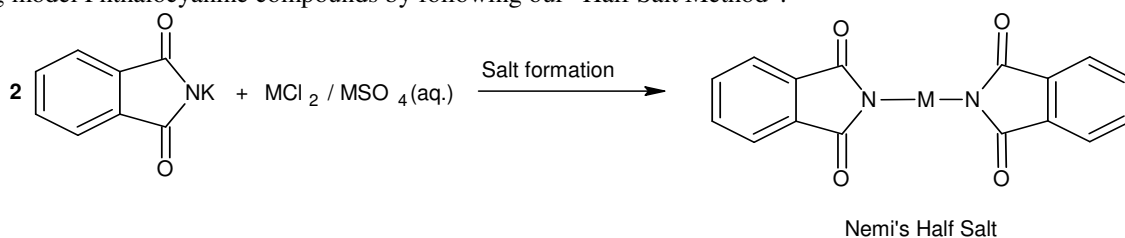


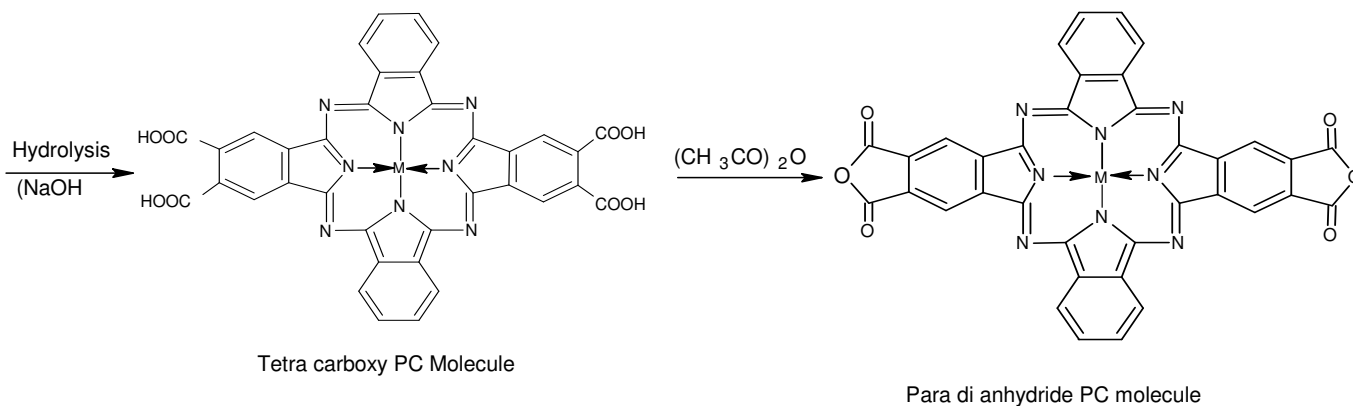
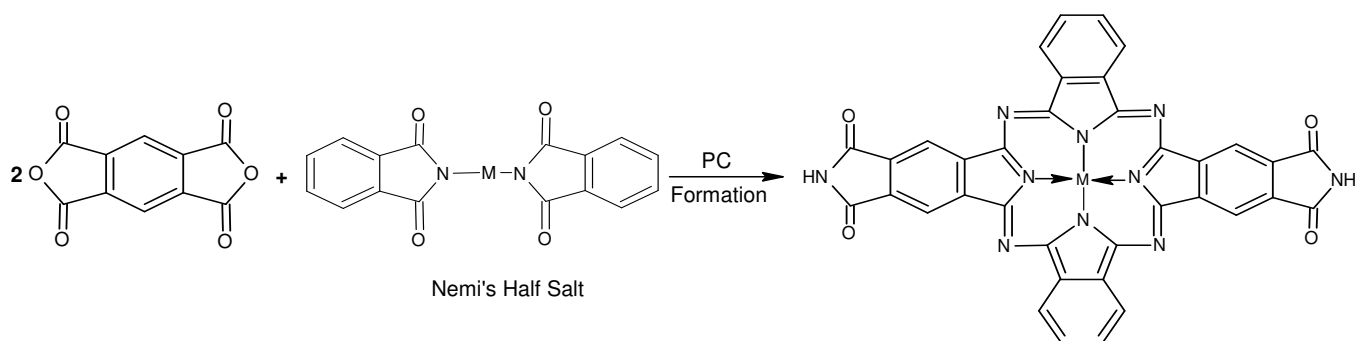
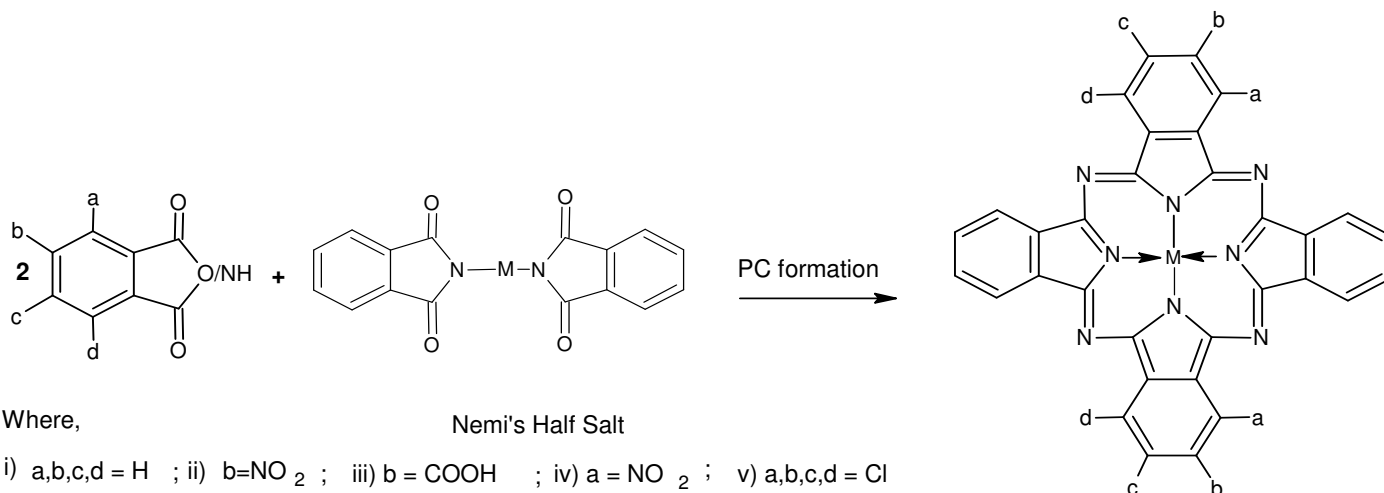
Now, if the Nemi's Half Salt or the additional 2 phthalic acid reactants have substitutions on any of their 3, 4, 5 or 6 positions, these substitutions are bound to appear on the opposite benzene ring of the finished PC molecules.



X, X and Y, Y are the positions well fixed on the finished PC molecule, because of their fixed positions on the starting reactants. By such combination of Nemi's Half Salt (half of the PC molecule) and the stoichiometric quantities of 2 molecules of substituted or unsubstituted phthalic acid derivatives, we can obtain PC molecules with definite group substitutions on the opposite side benzene rings of the finished whole PC molecule.

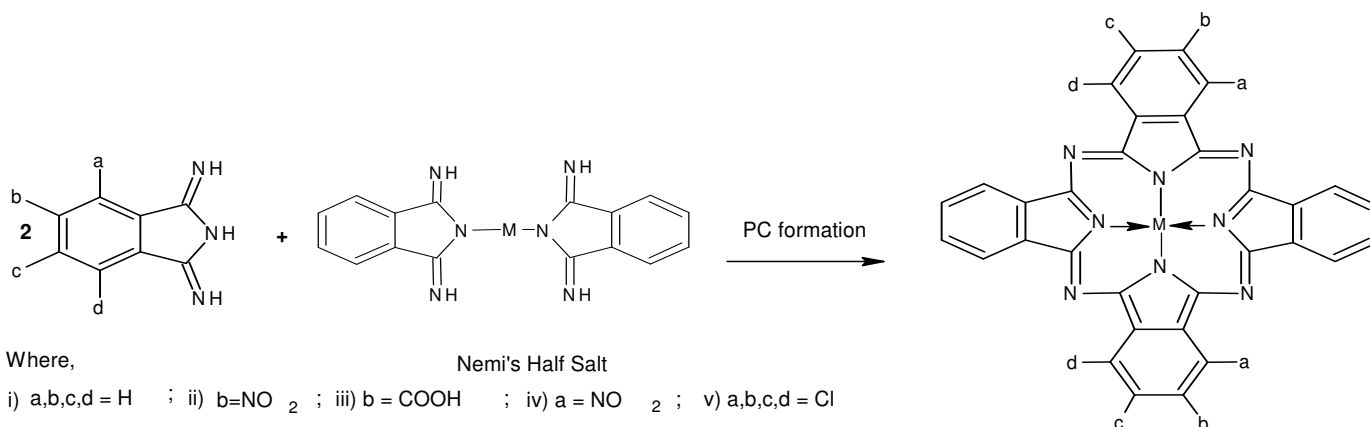
This Half Salt Method invention of synthesis of PC molecules with substitutions on the opposite side benzene positions of the resultant PC's, gives us a tool to easily prepare many desired compounds in the Phthalocyanine series. We have readily prepared the following model Phthalocyanine compounds by following our "Half Salt Method".



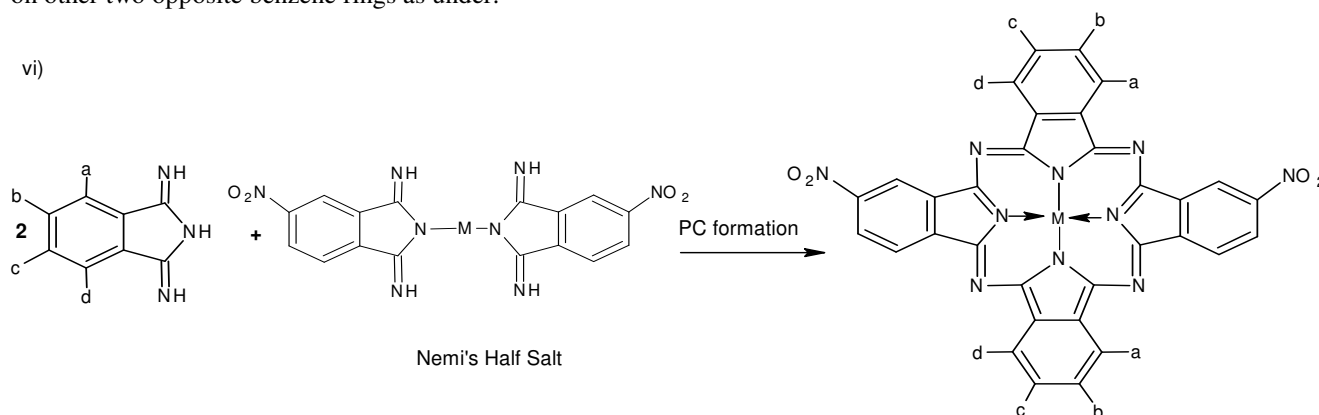


'En Somme', we can enter into the synthesis of substituted phthalocyanine molecules by this half-salt method by using any metal salt of elements like Cu, Zn, Ni, Co, Fe, etc. of the periodic table at the centre of the resultant PC molecule and desired substitutions on the periphery of the PC molecule. This gives us a great opportunity to enhance our knowledge of preparation and utility of phthalocyanines needed for newer future uses.

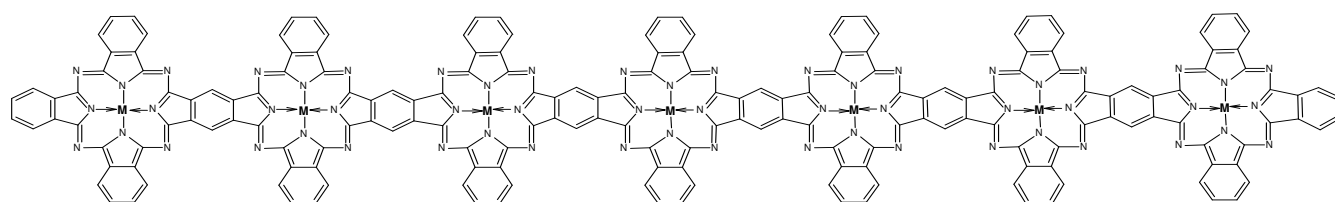
We have also entered through our half salt method in the iso-indoline series for obtaining similar substituted phthalocyanine molecules, using similar line of actions as in phthalic anhydride/ emide reactants and Nemi's Half Salt. Though we have only performed our experiments in this iso-indoline series with copper metal, but similar procedure can easily be adapted with Zn, Ni, Co, Fe, etc. metal salts as well. The iso-indoline entry into the PC series is comparatively more facile because such equivalents are more reactive and give the product PC molecules by just heating them in lower boiling solvents or just by heating the mixed ingredients without solvent, or just pasting the Nemi's Half Salt material and the other iso-indoline starting ingredients on a surface (like cloth) and subsequently just warming it to generate the PC molecule. Our lab has performed the following experiments in this series.



vi) Along with the choice substitutions on the two phthalic acid derivatives, which will appear on the two opposite benzene ring of the finished PC molecules. At the same time we can also put some substitutions on Nemi's Half Salt. Which inturn will appear on other two opposite benzene rings as under.

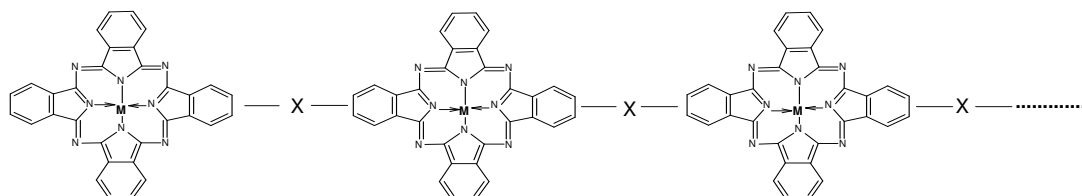


Either we start with Nemi's Half Salt in the phthalimide series or with the Nemi's Half Salt in the iso-indolin series, this approach of dicyclisation is definitely superior to the tetra cyclisation approach. Not only that, but this half-salt method ensures very much, the placement of desired substituent groups on the desired fixed positions in the PC molecules. These para-substituted PC molecules in turn may be used as precursors for different future products, including the most important derivations for soluble and insoluble polymers and coloured polymer fibres like-



M = Ni, Cu, Fe, etc.,

Seven membered phthalocyanine unbroken staple fibre (blue)



Intermittently joined PC Polymer

These types of polymerising attempts are being made in our laboratory.

The salient features of Nemi's half salt method of synthesis of PC molecules are as under: i. Nemi's half salt preparation is an ionic reaction without any energy or time consumption. ii. The half salts are ionic solid salts which can be stored safely to any extent of time without any damage. iii. Since, Nemi's half salt represents the half of the total PC molecule and carries the central metal atom attached to it, the introduction of the second half part is very easy and effective. iv. Temperature in this type of procedure is reduced from 180/200⁰C to 150/160⁰C. v. Time required for completion is reduced from 2/3 hr. to 1/1/4 hr. vi. There are multiple options of putting desired substituent groups on desired fixed positions on the periphery of the PC molecule. vii. The yields in all such experiments performed in our lab are in the range of about 80% which may be improved by further improving the procedural activities. viii. The most impotent part of this half salt method procedure lies in the placement of fixed substitutions on the positions of the opposite side benzene ring entities of the PC molecule which in turn can be chemically changed as per need of the future products. ix. Peripherally situated groups open a ground for multiplication of compounds by their extension on both linear and bifacial sites. x. With very minor variation of colour due to the central metal atom, the colour of all finished PC molecules is bound to remain near blue or green. xi. This procedural approach opens a very good possibility of the synthesis of soluble or in soluble coloured polymer products including coloured fibres as well, which are very much needed advancements. They may very well replace the present natural and manmade white coloured fibres on the market.

So this new simple invention of ours has a power of very much modifying the chemistry of phthalocyanine coloured products. So much so that it may be called an era change in the future PC molecule formation for various technical utilities.



NEMI CHAND JAIN studied chemistry at Birla College of Science Pilani (Rajasthan, India) and obtained Ph. D. in the year 1964. Later, he joined RIT Jamshedpur (Bihar, India) as lecturer. He worked as post doctoral research fellow (1967-69) with Prof. J.N. Chattergia of Patna University, India. After voluntary retirement, he has run his own small scale recovery plant in the name of KESARI ORCH. CHEM. INDUSTRY at Kota, Rajasthan, India and a small preparation unit NEMI SYNTHETICS for the α - Pigment blue and its sulphonated derivatives. He joined (as an immigrant) in the year 1991 with the group of Dr. F. X. Garneau, Professor and Head, Department of Chemistry, Quebec University at Chicoutimi Canada for extraction & purification of taxol an anti cancer drug. Back to India guided a tissue culture program in the native area of his district Kota, Rajasthan, India.

Presently 2 years back he has joined as research scientist in department of chemical sciences, Maharaja Ranjit Singh College of Professional Sciences, Indore, India. With a running research project entitled "Modification and Polymerisation of Phthalocyanine Macromolecule", (Funded by MPCST, Bhopal, M.P. India) he has developed a new specific simple NEMI'S half salt method for the preparation of Phthalocyanine molecules. His near future interest is to extend this self designed half salt method for the preparation of linear phthalocyanine polymers for solar energy absorption and coloured textile fibre end-uses.

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