Synthesis of Metallophthalocyanines Starting from Phthalic acid,phthalimide dicynobenzene , Urea (2 mol.) and Metal salts (2 mol.) by using Ammonium Molybdate as a catalyst.

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Abstract :-

Metallophthalocyanine of Ni was synthesized by chemical reaction from phthalic acid, urea and Nickel Chloride by using Ammonium Molybdate as a catalyst. The sample preparation was done by using press technique, in the form of pellets. The synthesized compounds were confirmed by physical analysis.

Key words:- Phthalocyanine, Metal salts, Ammonium Molybdate.

Introduction:- Phthalocyanine is a conjugated heterocyclic 18-π electron containing compound. In Pc system, methane-bridges of porphyrin are replaced by azabriges and, therefore,[11] Pcs can be regarded as tetrabenzotetra-azaporphyrins.The name phthalocyanine was coined by scientist Linstead (1933) to describe both its origin from phthalic anhydride (*phthalo*) and its strikingly beautiful blue colour which was similar to *cyanine* dyes. Phthalocyanines (Pcs) are synthetic analogues of the porphyrins, such as chlorophyll, [9]cyanocobalamine (vitamin B_{12}) and haemoglobin. Pcs and their metallated forms (MPcs) are planar and highly conjugated electron systems The л-electron ring consists of alternating carbon and nitrogen atoms. Pcs are brightly coloured, with high tinctorial strengths. [3]They are the majority of the blue and green pigments used to make inks and car paints. Pcs have found commercial applications in photocopying, laser printing, information storage,odour removal, oil sweetening, computer disk writing and infrared security devices,display devices (electrochromism and electroluminescence), organic catalysis,electrocatalysis, photocatalysis, photovoltaic devices, lithium batteries, gas sensors and fuel cells.[10]Today they are being developed for high technology applications such as photodynamic therapy of cancer and non-linear optical applications (e.g. optical limiting). Phthalocyanines have found wide applications in diverse areas such as biomedical agents for diagnosis and therapy, chemical sensors, phothocatalysis, liquid crystals and dye stuffs .

Different approaches to the synthesis of copper phthalocyanine were reported in the literature, some of which were the fusion of phthalic anhydride or phthalic acid with urea and copper or copper salts. Copper phthalocyanine is the most stable compounds in the series of metal phthalocyanine and plays an important role in the field of dyes and pigments. In present paper phthalocyanine was prepared by the fusion of phthalic anhydride with urea and copper chloride in the presence of ammonium molybdate as catalyst.

Material and methods:-

Solvent free Process With Catalyst: [4]Synthesis of unsubstituted MPcs involves the chemical method starting from the phthalic acid and urea as the cheapest precursors and Nickel salt as a source for the central atom. The reaction scheme of phthalic anhydride urea process is given reaction. [7]Phthalic anhydride, urea and Nickel salt were mixed together, crushed into the form of fine powder and slowly heated with continuous stirring. [2]The reaction took place at about 197 °C and sufficient heat was generated to maintain the reaction temperature. After completion of the reaction, the product was washed with distilled water and methyl alcohol many times for purification and then air dried.

[5]Phthalimide, urea and Nickel salt were mixed together, crushed into the form of fine powder and slowly heated with continuous stirring. [1]The reaction took place at about 199 °C and sufficient heat was generated to maintain the reaction temperature. After completion of the reaction, the product was washed with distilled water and methyl alcohol many times for purification and then air dried. [8]Pthalic acid, urea and Nickel salt were mixed together, crushed into the form of fine powder and slowly heated with continuous stirring. The reaction took place at about 200 °C and sufficient heat was generated to maintain the reaction temperature.

[13]After completion of the reaction, the product was washed with distilled water and methyl alcohol many times for purification and then air dried. Uncorrected melting points were determined using simple melting point method.

Melt/Dry Process: [6]A mixture of 130 gm urea and 5 g of boric acid is melted at 130°C. 100 gm of phthalic acid and 20 gm of anhydrous cupric chloride is added. [2]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.

Using Microwave Irradiation Process: The Domestic variety of microwave oven of national model were use for synthesis by selecting mode of high 100% wattage.

Result and discussion:-

NiPc synthesized using phthalic anhydride urea route. The cyclotetramerization reaction took place at temperature 197,199 and 200 °C. The synthesized powder material was used for melting point.

Phthalic acid + Urea + Nickel chloride____ammonium molybdate___→Nickel Phthalocyanine
(2-mol) (2-mol) (2-mol)

Phthalimide + Urea +Nickel chloride ----ammonium molybdate--------→Nickel Phthalocyanine
(2-mol) (2-mol) (2-mol)

Dicyanobenzene (2-mol) +Urea (2-mol) + Nickel chloride(2-mol) ----- ammonium molybdate -------→Nickel Phthalocyanine

Sr.no	Reactants	Product	M.p in literature	Actual m.p	Obtained Yield
1	Phthalic anhydride	Nickel(ii) phthalocyanine	>300^{0}C	310^{0}C	5.7 g
2	Phthalimide	Nickel(ii) phthalocyanine	>300^{0}C	307^{0}C	4.3g
3	dicyanobenzene	Nickel(ii) phthalocyanine	>300^{0}C	309^{0}C	7.4g

Conclusion:

It concludes that from above methods of prepration, the yield obtained by using ammonium molybdate catalyst is greater than other catalyst.

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