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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT
Progress Report

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Progress Report

TITLE: METAL-FREE PHTHALOCYANINE

PERIOD COVERED: APRIL, 1951 - FEBRUARY, 1953

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INTRODUCTION

The Pigments Department used to market a metal-free phthalocyanine of Orchem manufacture, as BT-198-D. This product, a very desirable green-shade blue in the Peacock Blue range, was discontinued despite trade interest when Orchem abandoned the manufacture of phthalocyanines by the phthalonitrile route. It has always been recognised that it would be desirable to prepare metal-free phthalocyanine by the cheaper phthalic anhydride route.

The preparation of metal-free phthalocyanine directly from o-cyanobenzamide and from phthalimide by treatment with antimony, has been disclosed (U.S. Patents Nos. 2,000,051 and 2,000,052). In the latter patent, ammonia is used along with phthalimide. It is further disclosed that phthalic anhydride may also be used, since the anhydride will form phthalimide by reaction with ammonia. The yield of metal-free phthalocyanine by the process of either patent is 30-40% based on the starting phthalic anhydride.

SUMMARY AND CONCLUSIONS:

A novel approach to the synthesis of metal-free phthalocyanine by the phthalic anhydride-urea process involving "in-process" reduction was investigated. Metal-free phthalocyanine in good yield has been obtained by the use of ammonium chloride in conjunction with antimony metal as ancillary agents in the phthalic anhydride-urea process. A hexadecachlor metal-free phthalocyanine has, likewise, been prepared.

Calcium phthalocyanine has been synthesized by the phthalic anhydride-urea process in poor yield by the use of organic reducing agents.

Attempts to synthesise some labile-metal phthalocyanines in good yield by the phthalic anhydride-urea process were not successful.

The use of partially halogenated copper phthalocyanines as blending materials with standard copper phthalocyanines in attempts to match the shade of metal-free phthalocyanine yielded dull products.

PATENT SITUATION

It is believed that the use of ammonium chloride in conjunction with antimony metal as ancillary agents in metal-free phthalocyanine synthesis by the phthalic anhydride-urea route is patentable.

DISCUSSION OF RESULTS:

Two approaches to the development of a process for the synthesis of metal-free phthalocyanine (MFPC) have been investigated: the synthesis of labile-metal phthalocyanines which can be demetallized to give MFPC, and direct-synthesis methods. In addition, attempts have been made to synthesize substituted copper phthalocyanines which might approach the green-blue shade of metal-free phthalocyanine.

LABILE-METAL PHTHALOCYANINES

Calcium Phthalocyanine

This phthalocyanine has not hitherto been made by the phthalic anhydride-urea-solvent route, but has been synthesized in fair yields from phthalonitrile.

Calcium phthalocyanine has been prepared by the phthalic anhydride-urea route in kerosene in 18.2% and 24.3% crude extracted yields using phenylhydrazine and diethylenetriamine, respectively, as reducing agents in the synthesis. Calcium oxide was used as the metal source. Diethylenetriamine appears to be the more effective reducing agent for these purposes.

The yield of calcium phthalocyanine by the urea route has been increased from 24.3% to 31.4% (crude extracted) using DET in the synthesis. Cyclohexylamine and methyl glucamine are less effective. The use of DV-17 (Loral methacrylate, diethylaminoethyl methacrylate co-polymer ex Orchem) dispersing agent, and Paranox 441 (2,6 di-tert-butyl p-cresol) anti-oxidant does not appear to offer any great advantage. Calcium oxide is superior to anhydrous calcium chloride as the metal source. Other variables such as the order of addition of the reactants and the temperature of addition do not materially affect the yields.

Various calcium salts have been tried as the metal source (e.g. carbonate, acetate, sulfide, sulfite, arsenate, fluoride, nitrate); but none is as effective as calcium oxide (31.4% highest crude extracted yield). In most cases, no phthalocyanine formation had occurred at all, and only trace formation in others.

Barium phthalocyanine has been synthesized in low yield (impure) by the urea-kerosene process.

Magnesium Phthalocyanine

The preparation of magnesium phthalocyanine (of interest as a possible route to metal-free phthalocyanine and to polychlor metal-free phthalocyanine) was studied. Of all the synthesis media used to date (kerosene, nitrobenzene,

trichlorbenzene, α-chlornaphthalene, and Arochlor 1248, a polychlorinated polyphenyl), the last appears to be the most desirable, insofar as it seems to be a crystallizing solvent for the MgPC. In no case, however, has a yield in excess of 35% been obtained. Anhydrous magnesium chloride obtained from Newport (ex Ti-metal process) was used in the synthesis.

Yields of 40% magnesium phthalocyanine were obtained by the urea-kerosene process using magnesium metal powder as the sole metal source.

In kerosene, magnesium phthalocyanine was prepared by the phthalic anhydride process in 17.2 and 24.3% yields, using phenylhydrazine and diethylenetriamine, respectively, as reducing agents. Magnesium chloride (ex Newport) was used as the metal source. Diethylenetriamine appears to be the more effective reducing agent for these purposes. Subsequently, magnesium phthalocyanine was prepared in 43.6% yield using diethylenetriamine as reducing agent and in 17.4% yield in the absence of the agent. (Magnesium oxide used as metal source).

Further attempts to improve the yield of magnesium phthalocyanine have not been successful. Hydroxylamine sulfate and hydrochloride were ineffective as replacements for diethylenetriamine (DET). Hydrazine sulfate was more effective, although less so than DET. Alpha-chlornaphthalene appears to be less desirable than kerosene as a synthesis medium for MgPC under the conditions of test.

Arsenic trioxide, arsenic pentoxide, and antimony trichloride did not serve as ancillary agents for the synthesis of magnesium or calcium phthalocyanines. Arsenic trioxide, however, when used in a catalytic amount, gave a 28.8% yield of magnesium phthalocyanine.

Manganese and magnesium phthalocyanines were prepared by the fusion bake process in 59.3 and 53.7% of theoretical yield, respectively.

Attempts to demetallise these phthalocyanines by acid-pasting caused the destruction of a major portion of the phthalocyanine to phthalimide.

Manganese and Tin Phthalocyanines

Some attempts were made to improve the yields of dichlor-tin phthalocyanine and manganese phthalocyanine by the phthalic anhydride-urea process.

Trichlorobenzene appears to be more suitable than kerosene as the reaction solvent for these phthalocyanines with respect to the physical characteristics of the reaction slurry. With respect to the latter, $SnCl_2 \cdot H_2O$ and $MnCl_2 \cdot 4H_2O$ appear to be superior to the respective anhydrous salts.

Dichlor-tin phthalocyanine yields slightly in excess of 60% have been obtained using the Orchem process (81.2% process yields reported). A crude extracted yield of 72.3% of manganese phthalocyanine has been obtained. The product analyzed for 9.2% manganese (theory = 9.68%). A repeat synthesis gave a yield of 68.9%.

Attempts to prevent the decomposition of manganese phthalocyanine during demetallization by acid-pasting were not promising and confirm ICI experience in this respect (25-40% yield). Reducing materials such as cyclohexanol, oxalic acid, potassium oxalate, or ferrous sulfate present during the acid-pasting did not materially prevent the destruction of the pigment.

Acid-pasting of dichlor-tin phthalocyanine gave near theoretical yield of metal-free phthalocyanine. The product (alpha phase) was v. v. green and weak vs. BT-297-D and v. green and weak vs. alpha phase metal-free PC ex phthalonitrile (Orchem). The solvent-milled counterpart (beta phase) was v. green and weak vs. BT-297-D and red and weak vs. beta phase metal-free PC ex phthalonitrile (Orchem).

Substituted Copper Phthalocyanines

Octachloro-copper phthalocyanine was synthesized in a crude extracted yield of 92.2% and was investigated as a possible blending material for chlorine-free CPC or LB/CPC to produce a shade equivalent to that of metal-free phthalocyanine.

Co-solvent milling of blends of both CF/CPC and LB/CPC with octachloro-CPC yielded products progressively greener with increasing chlorine content, but progressively weaker and duller. The CF/CPC blends were greener than the corresponding LB/CPC blends. In those cases where the products appeared as green as, or greener than the alpha or beta phase metal-free phthalocyanines, the products were weaker and duller. Likewise, co-solvent milled blends of polychlor CPC with both CF/CPC and LB/CPC yielded products weak and dull against the metal-free standards. The CF/CPC blends were greener and more intense than their LB/CPC counterparts.

An LB-type synthesis series using 25, 30, 35, 40 and 45 mol percent of 4-CPA (LB/CPC requires approximately 18 mol percent) yielded products in good yield, green, strong and intense versus BT-304-D (lot 90719) standard, and v. strong and red versus BT-297-D (lot 373).

LB-type syntheses using 50, 55, 60, 65, 70 mol percent of 4-CPA yielded products in good yield and on the green side of BT-297-D. All the products were dull. The 65 mol percent material was 6-6½ strong, green and only a trace dull versus BT-297-D (lot 373).

Monophenyl copper phthalocyanine was synthesized in 90.3% crude extracted yield by the standard kerosene synthesis, using 25 mol percent of 4-phenyl phthalic anhydride obtained from the Chemical Department, Experimental Station. The product, finished by solvent-milling was very dull vs. BT-297-D (lot 373).

Direct Synthesis Methods

A phthalocyanine-like blue, presumably the metal-free phthalocyanine (acid-pastes to a distinct blue), was obtained in crude extracted yield of 1-4% of theory by the use of hydrogen sulfide gas or organic reducing agents such as hexamethylene diamine or triethylene tetramine on the reaction product of phthalic anhydride, urea, and ammonium molybdate in trichlorbenzene. Hydroquinone was not

effective. In one series, the reactants were heated to 195°C and then the reducing material was added. In another series the reactants were heated at 125°C for an extended period, to form the iminophthalimidine (ICI recipe), and then the organic reducing agent was added. Inorganic reductants such as sodium hydrosulfite, sodium sulfide or sodium thiosulfate do not appear to be effective under the conditions of test.

Attempts to prepare metal-free phthalocyanine directly by the urea-phthalic anhydride process using organic reducing agents such as diethylene-triamine, cyclohexylamine, and methylglucamine, gave distinct evidence of color, although only in trace amounts.

A dry-bake of phthalic anhydride, urea, ammonium molybdate, boric acid, and antimony metal powder yielded on acid-pasting a product in approximately 10% yield and tentatively identified as metal-free phthalocyanine. A control run without antimony metal powder yielded no colored matter. In TCB as a reaction solvent, a yield of approximately 20% was obtained (crude extracted; some antimony metal still present). In kerosene reaction medium, pelletization of the product was observed. Both antimony oxide and antimony sulfide were not effective in this synthesis.

An analogous synthesis in trichlorbenzene using tetrachlor phthalic anhydride, yielded a product in 16.8% yield and tentatively identified as polychloro metal-free phthalocyanine.

A series using antimony metal (20 mesh or finer) in increasing quantities for the synthesis of metal-free phthalocyanine by the phthalic anhydride route indicated some yield increase with increased antimony usage. The yields, however, were only in the 10-20% range.

A low yield of metal-free phthalocyanine was obtained in a phthalic anhydride-urea synthesis using antimony metal powder precipitated from an antimony chloride solution.

Attempts to prepare metal-free phthalocyanine by the phthalic anhydride-urea process (in TCB) using oleic acid plus antimony metal (a hydrogen source), antimony chloride alone or with antimony metal, silica gel as a catalyst, or potassium carbonate plus iodine as catalyst, were not successful. Some distinct evidence of color formation (by acid-pasting) was observed in the case of the run containing antimony metal and $SbCl_3$.

The use of antimony metal powder in conjunction with ammonium chloride (presumably a proton donor in molten urea) was investigated as a means for synthesizing metal-free phthalocyanine by the phthalic anhydride-urea process. This method has given encouraging results. The use of antimony metal alone invariably gives a lesser yield. Acid-pasting of the crude extracted (NaOH and dil. H_2SO_4; 54.9% of theoretical yield on this basis) material indicated a synthesis yield of 42.8% of theoretical. Analysis of the acid-pasted material showed it to contain 69.7% of a blue material presumably metal-free phthalocyanine, analyzing for 0.15% antimony, and a quantity of inorganic antimony. The over-all acid-pasted and hydrochloric acid extracted yield is, therefore, 29.8% of theoretical. Excess ammonium chloride usage returns a lower yield. Likewise, the use of ammonium

chloride in conjunction with antimony metal returned a higher crude extracted yield than did antimony metal alone in tetrachlorphthalic anhydride condensations (47.9% vs. 35.9%) to produce a polychloro metal-free phthalocyanine.

Metal-free phthalocyanine synthesized from phthalic anhydride (antimony metal plus ammonium chloride method) in 29.8% yield, acid-pasted, and hypochlorite treated, rubbed vvs weak s. green and vvs intense against α-phase metal-free phthalocyanine ("Monastral" Fast Blue G prepared at Orchem from phthalonitrile). The solvent-milled counterpart (not hypochlorite treated) was weak, green and dull.

Antimony metal-ammonium chloride syntheses have yielded products analyzing as follows:

Run	Impure Crude Yield	Total % Sb in crude	% Sb in crude expressed as SbOCl	Crude purity (%) assuming SbOCl	Pure Yield % Theoretical
4A	62.2%	11.9	16.9	83.1	51.7
4B	60.8%	12.9	18.3	81.7	49.7

Run	% Sb in residue after Conc. HCl extraction	% Sb in residue after acid-pasting
4A	0.32	0.32
4B	0.32	0.32

The analytical data suggest that even the impure crude products contain insufficient antimony to be accounted for as antimony phthalocyanine (SbClPC analyzes for 18.2% antimony). Either acid-pasting or concentrated HCl extraction yields a product which is essentially antimony-free (0.32% Sb) and which appears to be metal-free phthalocyanine. The acid-pasted products (not hypochlorite-treated) were equal in strength, green, and dull versus "Monastral" Fast Blue G (α-phase). The solvent-milled counterparts (not hypochlorite-treated) were vs weak, dull and green versus β-phase metal-free phthalocyanine (Orchem manufacture ex phthalonitrile; solvent-milled).

The yields of 51.7% and 40.7% of theoretical reported above (based on antimony analysis and presuming its presence as SbO Cl) were essentially confirmed by extracted solids analyses. Actual yields, therefore, were 49.9% and 49.2% of theoretical, respectively. A pure yield 54.8% of theoretical has since been obtained (higher urea usage, longer reaction time).

Variable studies indicate that lower yields are obtained at 175°-185° synthesis reaction temperatures, and at approximately 210°C. Ammonium nitrate is less effective than ammonium chloride. One kerosene run (in place of trichlorobenzene) gave an extracted yield of 49.8%. The use of kerosene as a reaction diluent does not permit dispersion of the product and considerable gumming up and caking (final product a single solid lump) of the synthesis mas was experienced.

A crude extracted yield of 61.2% metal-free phthalocyanine was obtained by increased ammonium chloride usage (in conjunction with antimony metal). The purity of the product was verified by titration with ceric sulfate using ET-198-D (Lot 55, MFPC ex phthalonitrile) as a standard. This represents the highest yield obtained to date. An optimum NH_4Cl usage seems to be indicated, inasmuch as a subsequent series using still greater amounts of ammonium chloride showed a decreasing yield (antimony metal usage, however, was also increased in this series.) The indications are that excessive use of both antimony metal and ammonium chloride is deleterious to yield.

By acid-pasting and subsequent hypochlorite treatment, the above product obtained in 61.2% yield was approximately equal in strength, dull and red versus α phase MFPC ex phthalonitrile (Lot 55). Solvent-milling followed by hypochlorite treatment yielded a product vvs strong, s. dull and red versus β phase MFPC ex phthalonitrile. The product was vvs weak, s. dull and green versus α phase MFPC. The dispersion-milled material (hypochlorite-treated) was approximately equal in strength, dull and red versus β phase MFPC.

Iminophthalimidine was prepared by standard process (± 85% yield) and subsequently employed for metal-free PC synthesis to determine the necessity for preforming this intermediate prior to the introduction of antimony and ammonium chloride to the synthesis mass. If the Sb plus NH_4Cl in the presence of urea or its decomposition products perform a chemical reduction service, the low yields may possibly be attributed to over-reduction (persistent water-soluble red and yellow colored impurities in the product) or to insufficient reduction (consumption of urea may prevent the action of the ammonium chloride as a proton donor).

Metal-free phthalocyanine was synthesized in 4.1% of theoretical yield starting with Phthalogen Brilliant Blue F3G (diiminoisoindoline, ± 75% purity) in a process analogous to that used for the preparation of metal-free PC from phthalonitrile using cyclohexylamine as reducing agent.

NOTEBOOK REFERENCES:

1425, 1454, 1465.

APPENDIX

2 Direct-Synthesis of Metal-free Phthalocyanine

The following ingredients are charged to a 2-liter glass reactor fitted with an anchor-type agitator, thermometer, and air condenser:

166.6 gr. phthalic anhydride
333.2 gr. urea
1.0 gr. ammonium molybdate
900 ml. trichlorobenzene

The charge is first heated to about 155°C. over a period of about 2 hours and held between 155°C. and 160°C. for one hour. 51.5 grs. of powdered antimony and 67.7 grs. of crystalline ammonium chloride are then added, followed by heating to about 200°C. The mixture is cooled, filtered and washed with trichlorobenzene and then washed with acetone. The resulting filtercake is added to 4 liters of water con-

taining 100 grs. of sodium hydroxide and the residual solvents are removed by steam distillation. The metal-free phthalocyanine is decanted from the antimony powder, filtered, and washed alkali-free. The product is separated from antimony salts by heating in 500 ml. of concentrated HCl for 1/2 hour followed by washing with concentrated HCl and finally with water. After drying, 96.2 grs. of metal-free phthalocyanine of 92% purity (ceric sulfate titration) is obtained. This amounts to 61.2% of the theoretical yield.

The product is acid-pasted by dissolving 25 grs. of powder in 250 grs. of 100% sulfuric acid at 0°-5°C. After stirring for 2 hours, the cold solution is added dropwise into 2500 ml. of boiling water. The hot slurry is filtered and washed free of soluble salts.

The product can be further purified by hypochlorite treating as follows:

Reslurry the acid-pasted filtercake in a one liter of water containing 25 ml. sodium hypochlorite solution (5-25%) and 1.5 gr. sodium carbonate. Agitate at room temperature for 3 hours adding sodium hypochlorite solution and sodium carbonate as required to maintain an excess at all times. Filter and wash chloride free.

C O P Y

E. I. du PONT de NEMOURS & COMPANY

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PIGMENTS DEPARTMENT

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File 7.3

Newport, Delaware
February 18, 1954

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DR. J. H. COOPER
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METAL-FREE PHTHALOCYANINE - COST ESTIMATE

Tabulated below is a rough cost comparison of standard type chlorine-free CPC with a metal-free BG. The MF-PC cost estimate is based upon a laboratory formula (NB-1425-80BPH) and the following assumptions (as supplied by Dr. Ehrich):

1 - Assume plant use of 12:1 acid:CPC for acid pasting.
2 - Assume 5% yield loss due to acid pasting.
3 - Assume 10% yield loss due to hypochlorite treatment.
4 - Assume no significant changes in batch size or operating cycles.
5 - Assume use of a 10% HCl extraction.

The laboratory product is approximately 35% strong versus BT-297-D.

Item		Blue BG	MF
Ingredients		$ 61.7/cwt.	$180.5/cwt.
Operating & Distrib.		127.3/cwt.	138.5/cwt.
	Total	$189.0/cwt.	$319.0/cwt.

These data indicate the metal-free product would cost roughly $1.30/lb. more to produce than solvent milled BG. This cost penalty is largely due to low synthesis yield (50%), yield loss due to acid pasting (± 5%) and hypochlorite extraction (± 10%), and waste disposal.

No attempt was made to estimate the additional investment required in view of the high manufacturing cost.

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March 1, 1954

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METAL-FREE PHTHALOCYANINE - COST ESTIMATE

As requested, a rough cost estimate has been made for manufacture of metal-free phthalocyanine from phthalonitrile by an Orchem process (see attached). Tabulated below is a comparison of the MF-PC cost data with Newport solvent milled BG. In making this estimate the following assumptions were made:

1 - Same batch sizes as chlorine-free crude.
2 - 75-76% yield (Orchem data).
3 - TCB loss equal to kerosene loss.
4 - Satisfactory quality by acid pasting.
5 - 12:1 acid; DPC for acid pasting; ±5% yield loss.
6 - Phthalonitrile available at $0.75, $1.25, and $2.00 per lb. (see below).

Item	Blue BG	MF-PC
Ingredients	$ 61.7/cwt.	$162.8/cwt.
Operating & Distributives	127.3	115.8
Total Mfg. Cost	$189.0/cwt.	$278.6/cwt.*

*This is the cost using phthalonitrile at $0.75/lb. The total manufacturing cost would be $345.0 and $445.0/cwt. using phthalonitrile at $1.25 and $2.00/lb. respectively.

The higher cost of MF-PC versus BG is largely due to lower yield (±75%) and high ingredient cost due to phthalonitrile and acid pasting.

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EFKJr:ad
Attach.

ORCHEM PROCESS

(JLR-59-1-B, No. 15; NB-4448-187 & NB-4554-140)

Phthalonitrile 1 part

Trichlor Benzene 3 "

Cyclohexylamine 0.1 "

Heat to 200-210°C and hold at temperature 12 hours (still kettle, open to atmosphere)

Filter warm

Wash with solvent

Dry

Yield = 74-77.5% of theory