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E. I. DU PONT DE NEMOURS & COMPANY
PIGMENTS DEPARTMENT
256 VANDERPOOL STREET
NEWARK, NEW JERSEY

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

General Patent Survey - Phthalocyanine Pigments.

Period Covered: May 1 - July 25, 1946

FILE: 223.4

DATE: 8-12-46

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10 - Dr. D. E. Killian, Newark
11 - Mr. J. P. Hancock, Wilmington
12 - Orchem Patent Service, Jackson Lab.
13 - Extra
14 - "

SUPPLEMENT TO HN-46-54

GENERAL PATENT SURVEY-PHTHALOCYANINE PIGMENTS

To be attached to page 5 of the report.

Since this report was issued on August 12, 1946 attention has been called to an error in the statement on page 5 that "There is no basic product claim on metal-free phthalocyanine". It has been pointed out that claim 18 of U.S. 2,000,052, although covering a product made by a different process than that commonly employed in the manufacture of metal-free phthalocyanine, nevertheless dominates metal-free phthalocyanine and is not limited to the process disclosed. Accordingly, the statement quoted above should be changed to read "Claim 18 of U.S. 2,000,052 is considered a valid product claim for metal-free phthalocyanine. This ICI patent is available for the use of Du Pont".

A. J. Stratton 10/11/46
A. J. STRATTON 10/11/46

APPROVED: A. Siegel 10/14/46

N39976.01

DUP050150213

Serial No. KN-46-54

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

Title: GENERAL PATENT SURVEY - PHTHALOCYANINE PIGMENTS.

Period Covered: MAY 1 - JULY 25, 1946

SUBMITTED BY: A. J. STRATTON A. J. Stratton 8/1/46 DATE SUBMITTED: 7-26-46

APPROVED BY: D. B. KILLIAN D. B. Killian 8/2/46 DATE ISSUED: 8-12-46

N39976.02

DUP050150214

PHTHALOCYANINE PIGMENTS - GENERAL PATENT SURVEY

INTRODUCTION:

Phthalocyanine pigments have been sold in the United States by the DuPont Company since about 1935. The manufacture of the pigment has, up to the present time, been carried out exclusively by the Organic Chemicals Department. However, the Pigments Department have used the pigment as a semi-finished product in the preparation of numerous modifications for special uses. During this period, extensive studies have been carried on in the laboratories of Orchem and of the Pigments Department and numerous reports are to be found in the files of each laboratory. These reports include a thorough review of the historical aspects of the development and this will not be repeated herein. For a brief review thereof, reference is made to Newark report KN-46-7.

Recently, a decision has been rendered to carry on research leading up to the full scale manufacture of phthalocyanine pigments within the Pigments Department. This research has now progressed substantially to the point of pilot plant operation, and, although numerous patent surveys have been made by the Jackson Laboratory of Orchem and the patent situation is fairly well understood by those interested in it, no such survey of the art has heretofore been made at Newark and it seems highly desirable to make such a complete survey from our own point of view.

With these facts in mind, the patent art has been thoroughly reviewed with particular reference to the preferred process at Newark, but a brief summary has also been included of the whole phthalocyanine art, in anticipation of a need for broadening this survey at some future date.

SCOPE OF THE REVIEW AND SOURCES:

As pointed out above, this review has been directed particularly towards one process now contemplated for use at Newark but has also included rather careful search of the art on the synthesis and finishing of copper phthalocyanine and its chlorinated derivatives. A somewhat less careful survey has been made of use patents and of patents covering other metal phthalocyanines as well as products in which the benzene nuclei contain various substituents. Although these latter products are not contemplated for manufacture at the present time, it seems highly probable that some of them may be of interest for future study.

As to the sources of this review, an attempt has been made to inspect all U.S. and British phthalocyanine patents which have been issued to date. It is believed that all such U.S. patents are available in the Newark Library and that substantially all British patents are also available. To insure this point, a careful search was made of Chemical Abstracts and, likewise, of the Jackson Laboratory patent files. A less careful search has been made of the French, German, and Swiss patents on this subject, with considerable dependence placed upon the Abstract Journals for information with respect to many of these foreign patents. However, since we are primarily concerned with domination, these patents are of minor importance in this search.

PROCESS:

Synthesis of Blue

There are two fundamentally different processes which have been widely used for the manufacture of copper phthalocyanine. In one, phthalonitrile is heated with a copper salt to about 180°C at which point a vigorous, exothermic reaction starts and goes to completion in a relatively short time. Because of the extremely vigorous nature of this reaction, it has been difficult to control and the addition of inert material, either salt, such as sodium chloride or high boiling liquid, such as kerosene or trichlorbenzene, has been common practice. This process has been used largely heretofore by Orchem and is still being used for the standard copper phthalocyanine pigment (BT-172-D) which is sold by the Pigments Department.

The other common process involves the reaction of phthalic anhydride, urea and a copper salt in the presence of certain catalysts at temperatures in the order of 200°C. Although this reaction may be carried out as a melt, which eventually sets up to a solid as the pigment is formed, it has been much more successfully handled in the presence of a liquid diluent such as kerosene or trichlorbenzene. It is this process using a purified grade of kerosene as the diluent, and ammonium molybdate as the catalyst, which Newark proposes to adopt. However, it is known that this process results in the formation of a chlorine-free blue which has certain undesirable characteristics, namely a loss of strength in the presence of hydrocarbon solvents for many uses. It is entirely satisfactory as a raw material for the subsequent manufacture of chlorinated green phthalocyanine and will be manufactured for this use. To manufacture a grade of phthalocyanine blue which is stable in the presence of hydrocarbon solvent, it is proposed to resort to the substitution of a minor proportion, about 15% to 20%, of 4-chlor phthalic acid for an equivalent amount of the phthalic anhydride used in the reaction. This results in the formation of a blue phthalocyanine containing approximately 4% of chlorine.

The process proposed for use at Newark is substantially identical with that used by I.C.I. in England for most of their phthalocyanine manufacture. They manufacture the chlorine-free grade under the designation "Monastral" Blue B and the grade containing chlorine under the designation "Monastral" Blue LB. Where the designation "Blue B" and "Blue LB" are used throughout this report, they will have meanings similar to those used by I.C.I.

Synthesis of Green Phthalocyanine

The only phthalocyanine green marketed in this country has been a highly chlorinated copper phthalocyanine containing between 14 and 15 atoms of chlorine per molecule of copper phthalocyanine (approximately 48% chlorine). The only process practiced commercially to our knowledge has involved the chlorination of Blue B suspended in the eutectic melt of anhydrous aluminum chloride and sodium chloride. It is an expensive process and difficult to control. Newark does not propose to use this process but will instead use sulfur dichloride as a combined carrier and chlorinating agent working under pressure and at relatively high temperatures. The details of the process are rather complex, and it has been practiced only on a laboratory scale, but it has shown much promise of substantial economy because of the relative ease with which the sulfur dichloride can be recovered for reuse.

Finishing Process

In the past, all commercial processes of which we are aware for the manufacture of phthalocyanine pigments involved the "so-called" acid pasting steps, in which the pigment is dissolved in highly concentrated sulfuric acid, or, in the case of the green, in a mixture of sulfuric acid and chlorsulfonic acid, and the pigment reprecipitated therefrom by diluting the acid solution with water. More recently, Orchem has developed a "so-called" salt milling process in which the pigment and a relatively large amount of an inorganic salt, such as sodium chloride or sodium sulfate, are ball milled together for a substantial period of time followed by extraction of the water soluble salt and isolation of the pure pigment. This process is under development for commercial operation by both Orchem and the Imperial Chemical Industries in England.

The Pigments Department does not propose to use either of these processes but have developed a new process which we have called "Solvent Milling". In this process, the pigment, either in the dry form (which may be a purified or simply a dried out crude), or in the form of a kerosene-containing filter cake from the synthesis step, is ground in a ball mill with a solvent such as kerosene or mineral spirits. After a suitable milling cycle (the unproven goal on a plant scale is a maximum of 48 hours), the mill charge will be dumped, separated from the solvent (probably by steam distillation) and extracted for the removal of any impurities such as the residual impurities from the synthesis stage, or impurities resulting from abrasion or corrosion of the grinding device.

In the case of the green, it seems desirable to add approximately equal quantities of an inorganic salt such as sodium sulfate to the grind and it seems necessary to use only hydrocarbon solvent for the liquid portion. The presence of even small amounts of water appears definitely harmful to the greens. On the other hand, in the case of the blue, it has been possible to get entirely satisfactory grinding with alcohols or other water soluble solvents containing up to as high as 40% of water. Even water alone has enabled a substantial improvement in strength, although, to date, the desired strength has not been obtained in this medium. Since grinds made in the presence of an appreciable amount of water suffer from a substantial corrosion problem in steel ball mills, the proposed process is at present restricted to the use of a hydrocarbon solvent.

Finally, it should be noted that the best results have been obtained when the grinds were made in the presence of an organic acid such as naphthenic acid or oleic acid, followed by steam distillation in the presence of certain treating agents, notably a combination of the TEA C_{12} Ester and glyceryl mono ricinoleate. The preferred agents have not been selected with certainty at this time, but it seems quite definite that some agent will be necessary in these steps.

SUMMARY & CONCLUSIONS:

Copper Phthalocyanine

1. There is no patent containing a product claim on copper phthalocyanine as such and none is possible at this time.

2. There is a patent containing a product claim covering monochlor copper phthalocyanine. It is assigned to I.C.I. and licensed to DuPont.

3. All practical processes for the synthesis of copper phthalocyanine are covered in patents either owned by or licensed to DuPont.

4. All important process patents are believed to be valid and to be rather universally respected in the industry.

5. The process for the manufacture of Blue LB is disclosed but not specifically claimed aside from the general process coverage.

Copper Phthalocyanine Green

1. A presumably strong product patent covering the highly chlorinated copper phthalocyanine is owned by General Aniline but licensed to DuPont outside of the DuPont - General CPC agreement. This is a non-exclusive license and, in the event that all of General's patents are thrown open to license by the Alien Property Custodian, the product might become available to our competitors.

However, there appears to be no reason to believe that our present license will be disturbed.

2. Both practical processes for the manufacture of copper phthalocyanine green, namely the aluminum chloride sodium chloride melt and the sulfur dichloride processes, are covered by presumably valid patents owned by DuPont, so that regardless of our lack of control of the product itself, our patent position seems quite strong.

Metal-Free Phthalocyanine

1. There is no basic product claim on metal-free phthalocyanine.

2. The commonly known practical processes for the manufacture of metal-free phthalocyanine are covered by patents either owned by or licensed to DuPont.

Finishing Steps.

1. There is no basic patent covering the acid-pasting procedure and none is possible at present. However, there are numerous patents on various details of the acid-pasting and subsequent drowning steps including the use of treating agents in the drowning step. Not all of these patents are available for the use of DuPont, but it is believed that there are none which will hamper any operations now contemplated. Since we do not propose to use acid-pasting in the Pigments Department, it is certain that none of them will disturb our operation.

2. DuPont owns a patent on the salt milling process which was issued quite recently but it is our opinion that this patent is quite weak in view of numerous references to similar processes in the art.

3. We have found no specific disclosures of solvent milling as we propose to practice it, and it is believed to be a patentable process. However, this will be made the subject of a separate report.

4. Miscellaneous Finishing Steps.

It is believed that our process may possibly be in conflict with U.S. 2,138,049 and 2,268,144 (owned by Harmon) if any of the solvent remains after steam distillation to be removed in the oven. However, negotiations which will give DuPont rights under these patents have been initiated at the present time.

We are informed by representatives of Orchem that the use of the TEA C_{12} Ester is under some patent restrictions. However, we are also informed by them that they have obtained licenses for the use of this material and it, therefore, is now open to our use. No effort has been made to locate the patent involved.

The general field of the use of various types of treating agents in the manufacture of pigments is one in which there are a great many patents but substantially all of these patents are of very limited scope. No extended search has been made in this field at the present time. However, the field has been broadly covered in previous searches made at Newark and we feel confident in the opinion that there are no insurmountable patent bars. Some of the more important patents in this group will be discussed in connection with the detailed description of the art.

DETAILED DISCUSSION OF THE ART:

In the following discussion of the patent art two main divisions will be recognized. The first will discuss in some detail those patents believed to be directly pertinent to operations of the DuPont Company in the manufacture of phthalocyanine pigments, with emphasis being laid on those which are particularly concerned with the operations of the Pigments Department. This group of patents will be further sub-divided under the four topics used above in the summary of the art.

The second main division will include in a much less detailed fashion substantially all of the remaining U.S. patents in the phthalocyanine field. It will also include many of the British patents and some reference will be made to other foreign patents. In addition to the four main sub-divisions referred to above, it will also include references to other metal phthalocyanines, to some patents on uses of phthalocyanines, and to a large group of patents concerned with products in which there are substituent groups on the benzene rings of the phthalocyanine molecule. This last group of patents will be listed by descriptive title only for the most part and are being included only for a ready reference in the future.

A. PATENTS OF MAJOR IMPORTANCE

1. Copper Phthalocyanine

U.S. 2,000,051, issued 5-7-35 to Thorpe, Linstead & Thomas of I.C.I.

This is the first phthalocyanine patent in the United States and covers a process of reacting o-cyanobenzamide with a metal or a metal compound under the influence of heat. A large number of metals including magnesium, copper and tin are disclosed as effective. Their use as pigments is disclosed as well as the process of acid pasting to obtain them in a fine state of subdivision. The possibility of removing some metals such as magnesium through the use of concentrated sulfuric acid to give a metal-free compound is recognized. There is no clear recognition of the structure of phthalocyanines as now accepted in this patent, but it is very closely approximated. The disclosure of this patent with respect to the compounds formed is basic to the whole phthalocyanine industry in the United States. However, the process is not currently used and there are no product claims independent of the process because of a prior disclosure in the literature.

U.S. 2,129,013, issued 9-6-38 to Linstead & Dent of I.C.I.

When phthalonitrile and cupric chloride are heated together above about 200°C. the resulting product is copper monochloro phthalocyanine. When cuprous chloride is used in place of cupric chloride, the product still contains chlorine but to a considerably lesser degree. The use of inert solvent is disclosed. Claim 3 covers copper monochloro phthalocyanine as a new product.

U.S. 2,197,458, issued 4-16-40 to Wyler of I.C.I.

This patent covers broadly the phthalic anhydride/urea fusion process, wherein phthalic anhydride, urea and a metal salt such as cupric chloride are heated to a temperature in the order of 200°C., whereby a solid pigmentary product is formed. The use of substituted phthalic anhydride, as well as the use of free acid, diammonium salts and certain other derivatives, is disclosed. The use of boric acid or ammonium sulfamate is recommended to improve yield and to prevent frothing. There is recognition of improved yields resulting from adding the urea to a molten mixture of the phthalic anhydride and to the metal salts. There is no disclosure of the use of a liquid diluent or solvent. This patent is basic for the process proposed for use at Newark.

U.S. 2,197,459, issued 4-16-40 to Wyler of I.C.I.

A phthalocyanine containing tin is obtained by the use of the phthalic anhydride/urea fusion process of U.S. 2,197,458 in the presence of suitable tin salts. The patent discloses, but does not claim, the preparation of a metal-free compound by the demetallization of the tin containing phthalocyanine through solution in concentrated sulfuric acid.

It discloses, but does not claim, the use of kerosene or other high boiling organic liquids as a diluent in the reaction. The disclosure of the use of kerosene is important to us but there is no protection. Otherwise, there is no direct interest to Newark at the moment but it is of direct interest to Orchem in their manufacture of a co-salt milled copper and tin dichloride phthalocyanine. It is of potential interest to both departments as a possible route for the manufacture of metal free phthalocyanine. Such a process is now used by I.C.I.

U.S. 2,214,477, issued 9-10-40 to Riley of I.C.I.

The efficiency of the phthalic anhydride/urea fusion process is materially increased through the use of certain salts of metals of groups 5 and 6 of the periodic tables as catalysts for the reaction. Ammonium molybdate is the preferred salt and is used in very small amounts. We propose to use this process at Newark.

U.S.Application, Serial #629,921, Application Date 11-20-45 by A. Siegel, assigned to DuPont

A coalesced phthalocyanine pigment is made by reacting phthalonitrile with a metal salt such as cupric chloride in the presence of a substantial amount of a calcined TiO_2 pigment as a substratum. The resulting product is satisfactory for use without any further conditioning steps. British patent 453,767 is very close art against this application but has not yet been cited in the prosecution, and it appears probable that a patent will issue. However, any patent which issues will probably have little value beyond that of a disclosure. The process is that formerly contemplated for use at Newark in the manufacture of Pigment BX-CR.

3. Phthalocyanine Greens

U.S. 2,195,984, issued 4-2-40 to Dent and Sylvester of I.C.I.

Phthalocyanine pigments may be chlorinated or brominated in hot molten phthalic anhydride using elementary chlorine or bromine. Although this is the first published patent on the process of halogenating a phthalocyanine pigment, it does not bear the earliest application date.

U.S. 2,214,469, issued 9-10-40 to Linstead and Dent of I.C.I.

This patent has a broad claim to the process of halogenating a phthalocyanine and discloses the use of a number of halogen carriers including aluminum chloride and sulfur chloride. This patent has the earliest application date of any patent on the direct halogenation of phthalocyanine but lost out as to the presently preferred product in an interference with U.S. 2,276,860 because it did not contain adequate

disclosure of the degree of halogenation necessary for the preferred phthalocyanine green.

U.S. 2,247,752, issued 7-1-41 to Fox of DuPont

This patent covers the aluminum chloride/sodium chloride eutectic melt process for the halogenation of phthalocyanine pigments. It is the process currently used by Orchem but is not contemplated at present for use at Newark.

U.S. 2,253,560, issued 8-26-41 to Detrick and Johnson of DuPont.

This patent covers the successive steps of synthesis from phthalonitrile in the presence of sodium chloride, mixing the reaction product with anhydrous aluminum chloride and chlorinating directly without any intermediate purification steps. The process is not contemplated for use at Newark.

U.S. 2,276,860, issued 3-17-42 to Niemann, Schmidt, Muehlbauer & Wiest, assigned to General Aniline

This patent has very broad coverage of halogenated phthalocyanine containing more than eight halogen atoms per molecule obtained by direct halogenation. It has both product and process claims. This patent issued following an interference with U.S. 2,214,469 mentioned above and is unquestionably a dominating patent in the field. However, the interference was settled on the basis of royalty free cross licenses between General Aniline and DuPont and we are free to manufacture the product.

U.S. 2,377,685, issued 6-5-45 to Fox & Jackson of DuPont

This patent covers the process of chlorination of phthalocyanine pigments by the use of sulfur dichloride, followed by recovery of the sulfur dichloride by sweeping with chlorine gas which reacts with the sulfur monochloride formed during the chlorination with regeneration of the sulfur dichloride. This is the process contemplated for the manufacture of phthalocyanine greens at Newark.

3. Metal Free Phthalocyanine

Attention is called to references to the manufacture of metal free phthalocyanine in some of the basic patents mentioned above. For instance, U.S. 2,000,061 discloses the demetallization of magnesium phthalocyanine and U.S. 2,197,459 discloses the demetallization of tin phthalocyanine. Both of these processes have been used in the past and the second is currently contemplated for use by I.C.I. The following patents more specifically cover the manufacture of metal free phthalocyanine.

U.S. 2,116,602, issued 5-10-38 to Heilbion, Irving & Linstead of I.C.I.

This patent covers the process of forming a metal free phthalocyanine by heating phthalonitrile with alkali metals or their compounds, ammonia or certain tertiary organic bases. It is understood that this

process is highly inefficient.

U.S. 2,155,084, issued 4-18-39 to Lowe of I.C.I.

In a modification of the previous patent phthalonitrile is heated with an ethanol amine to form a metal free phthalocyanine.

U.S. Application, Serial #679,332, filed 2-22-46 by Palmer & Gross of DuPont

Metal free phthalocyanine may be made by reacting phthalonitrile, a solid inert diluent such as sodium chloride or titanium dioxide and a solids alkaline agent such as calcium oxide in the presence of small amounts of methylglucamine at a temperature of about 200°C. When the reaction is carried out in the presence of a water soluble agent as NaCl and under conditions whereby some grinding action occurs during the reaction, such as in a rotary baker, little if any conditioning of the final product other than extraction of soluble impurities is needed. It is believed that this process is currently being practiced by Orchem but is not contemplated at present for use at Newark.

4. Finishing Steps

U.S. 2,138,049, issued 11-29-38 to Vesce of Harmon

A water immiscible organic liquid such as toluene is added to a pigment slurry which is then stirred to emulsify the liquid and the whole dried at a temperature below the boiling point of water to give a dried pigment of improved texture. There is specific disclosure of the application of this process to phthalocyanine pigments and it has been rather broadly interpreted as covering any process in which a water immiscible organic liquid is intimately mixed with a pigment slurry before drying. This patent is included in a cross licensing agreement under negotiation between DuPont and Harmon and is accordingly available for our use when negotiations are completed.

U.S. 2,173,699, issued 9-19-39 to A.Siegel of DuPont

This is the patent covering our "Ramapo" Blue pigment and covers broadly a water insoluble phthalocyanine pigment intimately associated with an alkaline earth rosinate. Since this patent was included in the DuPont/General Aniline agreement on phthalocyanine, it has been considered as available to all purchasers of phthalocyanine paste from General and no attempts have been made to enforce it by DuPont, altho it is believed that all large scale manufacturers of phthalocyanine pigments have practiced the process.

U.S. 2,213,693, issued 9-3-40 to Davies, Hailwood and Todd of I.C.I.

This patent covers the use of the sodium salt of the formaldehyde condensation products of Naphthalene Sulfonic Acid (Compound #8) in the acid-pasting step of finishing phthalocyanine pigments. There is a product claim to the combination of the pigment and the condensation product without limits to the method of manufacture and there are broad

process claims to the precipitation of an acid solution of phthalocyanine in the presence of a water soluble, non-hygroscopic dispersing agent. There is disclosure of ball milling in water and in the presence of the dispersing agent after acid pasting to get further particle size reduction. This patent may be sufficiently broad to cover some of our products but it is probably relatively unimportant to us.

U.S. 2,268,144, issued 12-30-44 to Vesce of Harmon

This patent is similar to U.S. 2,138,049 but differs in that a definite emulsion of the volatile oil is separately prepared and added to the pigment slurry, followed by stirring until the emulsion breaks, after which the slurry is filtered and then dried. The process is disclosed and specifically claimed as applied to copper phthalocyanine as well as being claimed broadly. This patent is also included in the cross license agreement with Harmon and is available to our use, when negotiations are completed.

U.S. 2,305,379, issued 12-15-42 to Detrick & Lang of DuPont

This patent covers Orchem's use of the so-called $TEAC_{12}$ ester in the manufacture of a soft powder phthalocyanine pigment. The claims cover pigment particles coated with the insoluble reaction product of a poly-alkanol amine with a higher aliphatic acid. The process is specifically applied to phthalocyanine pigments by using the agent to emulsify an organic liquid such as toluene in a process essentially similar to that of Harmon in the preceding patent. It is entirely possible that our products may come within the claims of this patent.

U.S. 2,327,472, issued 8-24-43 to Vesce & Stalzer of Harmon

A non-flocculating copper phthalocyanine is made by incorporating therein in the wet state a major proportion of aluminum benzoate as a substratum. The disclosure of this patent is quite accurate and products of this type have been marketed by Harmon but they are believed to be fundamentally high in cost and not a serious threat to our business. However, the goal is highly desirable and, at present, no other good solution is known.

U.S. 2,402,167, issued 6-18-46 to Lang & Detrick of DuPont

This patent is an attempt to cover Orchem's salt-milling process for finishing phthalocyanine pigments. Because of very close prior art the claims are limited to a process using more than four parts of a water soluble salt per part of pigment and to the use of an apparatus which grinds by attrition and shearing as distinguished from impact. It is doubtful if this patent has more than a publication value.

U.S. Application, Serial #664,434, filed 4-23-46 by Robbins of DuPont

1-naphthalene sulfonic acid is added to (or formed in situ) the sulfuric acid solution of a phthalocyanine pigment prior to drowning to give a soft-textured pigment. The agent is used in amounts of from 1 - 2-1/2 times the weight of the pigment. The true significance of this process is not clear at present but it is not now contemplated for use at Newark.

British Patent 569,402, issued 5-22-45 to Moilliett and Todd of I.C.I.

This is I.C.I.'s salt milling patent and includes a small quantity of a fatty acid or ester thereof with the salt. The preferred procedure uses anhydrous sodium sulfate with a small amount of oleic or linoleic acid.

B. PATENTS OF LESSER IMPORTANCE

1. Synthesis of Copper Phthalocyanine

U.S. 2,000,052 - I.C.I. - covers the reaction of phthalimide with a metal in the presence of ammonia.

U.S. 2,075,043 - I.C.I. - CPC is formed by reacting an ortho-halogen benzamide with cuprous cyanide.

U.S. 2,124,742 - I.C.I. - Copper phthalocyanine may be formed by heating a metal-free phthalocyanine with copper or copper salts.

U.S. 2,138,413 - Interchemical - A pigment which does not need acid pasting is prepared by reacting phthalonitrile and copper salts in the presence of aliphatic di- or trihydric alcohols or alcohol poly ethers.

U.S. 2,153,300 - DuPont - The violently exothermic reaction between phthalonitrile and the copper salts is controlled by adding the reactants portion-wise to the rotary baker.

U.S. 2,154,912 - General Aniline - Phthalonitrile is heated with a metallic cyanamid to form a phthalocyanine pigment.

U.S. 2,160,837 - DuPont - Phthalonitrile and metallic copper may be caused to react at a temperature of 160-170°C in the presence of small amounts of chloride of amphoteric metals or ammonia.

U.S. 2,166,213 - I.C.I. - This is the basic patent for the reaction of phthalonitrile with a copper producing agent to form copper phthalocyanine.

U.S. 2,194,280 - Interchemical - This covers an apparatus for the manufacture of phthalocyanine pigments by the reaction of phthalo-nitrile vapors with a polished metal surface.

U.S. 2,202,632 - I.C.I. - Ortho-arylene di-cyanides are heated with a compound of a metal of the second group of the periodic table.

U.S. 2,212,924 - General Aniline - Phthalonitrile is heated with an amide and a metal salt.

U.S. 2,216,761 - I.C.I. - Covers the use of ammonium sulfamate as a catalyst in the phthalic anhydride/urea process.

U.S. 2,216,867 - I.C.I. - Covers broadly the use of amino sulfonic acid in place of urea in the manufacture of phthalocyanine.

U.S. 2,216,868 - I.C.I. - Covers the use of ammonium sulfamate in place of urea in the phthalic anhydride process for cobalt, nickel or iron phthalocyanine.

U.S. 2,242,301 - I.C.I. - Is a belated issuance of one division of the basic patent for heating phthalonitrile with a copper salt and involves the use of a neutral organic solvent.

U.S. 2,245,008 - Interchemical - Covers the reaction of phthalonitrile vapors with a polished metal surface followed by scraping off the pigment thus formed.

U.S. 2,276,598 - S.C.I. - The presence of small amounts of NaOH, CaO or Na_2CO_3 improves the efficiency of the reaction between phthalonitrile and metal compounds in the presence of liquid diluents.

U.S. 2,302,612 - American Cyanamid - Chlorine-free CPC is prepared from phthalonitrile and cupric chloride by reacting in the presence of anhydrous ammonia.

U.S. 2,318,785 - American Cyanamid - Chlorine-free CPC is prepared by reacting phthalonitrile with anhydrous copper sulfate in the presence of nitrobenzene and anhydrous ammonia under pressure.

U.S. 2,318,787 - American Cyanamid - Also covers the reaction of phthalonitrile with cupric sulfate in the presence of ammonia.

U.S. 2,375,780 - Interchemical - Phthalocyanines may be prepared by heating phthalic anhydride, ammonia and a metal salt of cyanuric acid.

U.S. 2,382,441 - Interchemical - Phthalonitrile and metal compounds are reacted in the presence of such limited quantities of hydroxy aliphatic solvents that the major portion of the solvent is evaporated during the reaction.

U.S. Application, Serial #403,866 - APC - Benzoic acid and related compounds are effective in preventing the foaming of a phthalic anhydride/urea fusion synthesis.

In listing the following British patents, those patents which have substantially equivalent U.S. disclosure have been, for the most part, omitted.

British 322,169 - Scottish Dyes (I.C.I.) - This is the first disclosure of phthalocyanines in English and covers a process in which ammonia is passed into molten phthalic anhydride in the presence of a metal to give a blue solid which may be purified by precipitation from sulfuric acid.

British 453,767 - I.G. - Phthalonitrile is heated with metals or metal compounds taking part in the formation of the dyestuff in the presence of an oxide or salt of a metal of groups 1 to 4 of the periodic system, which salt is solid at the reaction temperature and inert and is used as a diluent. This is the best prior art against our Pigment BX-CR process, but there is no U.S. equivalent.

British 457,786 - I.C.I. - Ammonium phthalate or its derivatives may be heated with a metal salt in the presence of an amino sulfonic acid to give a phthalocyanine.

British 458,754 - I.G. - Phthalonitrile and copper salts are heated in the presence of tertiary bases under special conditions of pressure and concentration.

British 459,780 - I.G. - A high boiling diluent other than a tertiary base is added to the process of the preceding patent.

British 462,[illegible] - I.G. - Phthalonitrile is heated with metal amides or cyanamides together with high molecular weight alcohols or mercaptans.

British 482,387 - I.G. - Phthalonitrile is heated with metal compounds in the presence of diluents free from nitrogen and hydroxyl groups but under pressure.

British 503,029 - Montecatini - Phthalic anhydride and copper compounds are heated in the presence of di-cyano-diamides.

British 552,124 - DuPont - Covers the use of infra-red heating in the phthalonitrile process for phthalocyanine. The U.S. application has been finally rejected.

2. Phthalocyanine Greens

U.S. 2,227,628 - DuPont - Phthalocyanines may be fluorinated by treatment with fluorine in liquid hydrogen fluoride.

British 470,079 - I.G. - Simultaneous halogenation and formation of the phthalocyanine by heating phthalonitrile with the halogenating a

agent in the presence of the metal halide.

British 499,415 - I.G. - Copper phthalocyanine may be chlorinated with chlorine gas in trichlorbenzene in the presence of antimony trisulfide under atmospheric pressure.

British 500,471 - I.G. - Phthalocyanines are halogenated in the presence of organic acid halides and with halogen carriers.

3. Metal Free Phthalocyanines

U.S. 2,153,620 - I.C.I. - Phthalonitrile is heated in an atmosphere of ammonia.

U.S. 2,182,763 - General Aniline - Phthalonitrile is heated with sodamide and dimethyl aniline in the presence of aliphatic alcohol.

U.S. 2,214,454 - I.C.I. - An alkali phthalocyanine is treated with methyl alcohol and then diluted with water to give a metal-free phthalocyanine superior to that from acid pasting.

British 476,168 - I.G. - Phthalonitrile is heated with phenols or naphthols.

British 480,249 - I.G. - Phthalonitrile is heated with a Grignard reagent and hydrolyzed with sulfuric acid to give a metal-free phthalocyanine.

4. Other Metal Phthalocyanines

Many metal phthalocyanines other than copper are disclosed in a number of the patents listed above but the following patents are limited to certain other metal phthalocyanines.

U.S. 2,056,944 - I.C.I. - Covers lead phthalocyanine.

U.S. 2,124,419 - I.C.I. - Covers iron, nickel or cobalt phthalocyanine prepared from phthalonitrile.

U.S. 2,155,038 - I.C.I. - Covers vanadyl phthalocyanine.

5. Miscellaneous Finishing Methods

U.S. 2,192,704 - DuPont - Covers co-acid pasting of two or more phthalocyanines.

U.S. 2,225,302 - Interchemical - Covers the formation of CPC sulfate by careful dilution of the sulfuric acid solution.

U.S. 2,238,243 - DuPont - Covers a can stable blue paint containing alumina hydrate and the barium lake of sulfonated CPC.

U.S. 2,238,275 - DuPont - Covers the precipitation of any soluble dispersing agent prior to the addition of the oil in a pigment flushing operation.

U.S. 2,276,175 - Allied Chemical & Dye - Covers the treatment with a mild oxidizing agent as NaOCl after acid pasting.

U.S. 2,282,006 - DuPont - Covers the use of cation active agents plus volatile water immiscible organic liquids in making soft, dry pigments including phthalocyanine.

U.S. 2,282,303 - DuPont - Covers the use of nitrogen bases to improve texture.

U.S. 2,284,665 - DuPont - Is another patent on the isolation of CPC sulfate as a step in the acid pasting procedure.

U.S. 2,291,452 - DuPont - Covers drowning CPC from solutions in acids in the presence of lauric acid and the like.

U.S. 2,334,812 - DuPont - Covers turbulent flow drowning of an acid pasted phthalocyanine.

U.S. 2,359,737 - American Cyanamid - Covers drowning sulfuric acid solutions in water in the presence of an inert water immiscible organic liquid not sulfonated.

U.S. 2,365,464 - DuPont - Another patent on the isolation of the crystalline CPC sulfate.

U.S. 2,367,519 - Sherwin-Williams - Covers boiling the pigment suspension resulting from the drowning of an acid pasted phthalocyanine.

British 454,858 - I.G. - Covers drowning a sulfuric acid solution of a phthalocyanine in the presence of a dispersing agent and either in the presence of a substratum or under conditions which will simultaneously form a substratum.

British 466,042 - I.G. - Covers broadly the mixing or milling of a phthalocyanine with dispersing agents in the presence of water.

British 475,882 - I.G. - Is similar to the preceding patent but applied to a metal-free phthalocyanine.

British 502,623 - Montecatini - Phthalocyanine pigments are converted to the sulfate with sulfuric acid below 90% in strength and then hydrolyzed with water.

British 503,666 - I.G. - CPC is treated with 78% sulfuric acid at 45°C. and then with water to give soft powder.

British Application 5731 - 1944 - American Cyanamid - Halogen free phthalocyanine pigments are acid pasted, exposed to a crystallizing solvent, then salt-milled to the desired fineness and again exposed to the solvent. The product has 70% the strength of the acid pasted

material but no longer grows crystals in the solvent. Reference is made to two crystal forms of CPC. The crux of the invention seems to be an implication (without a definite statement) that, if crystals which have been grown in solvent are mechanically reduced in size, no further growth in crystals will occur. No U.S. equivalent of this patent has appeared although it was filed under convention in England.

6. Use Patents

U.S. 2,167,514 - I.C.I. - Phthalocyanines in a rubber dispersed master batch.

U.S. 2,168,576 - General Aniline - Vulcanized rubber colored with phthalocyanine colors.

U.S. 2,192,705 - I.C.I. - Rubberized fabric colored with CPC.

U.S. 2,317,371 - Interchemical - Use of phthalocyanines in pigment printing using a liquid volatile pine terpene to avoid crystal growth.

U.S. 2,339,739 - I.C.I.- Impregnating a fiber with a diazo of an amino phthalocyanine and developing with a coupling component.

U.S. 2,339,740 - I.C.I. - Impregnating a fiber with a diazo of a poly-amino phthalocyanine and decomposing to deposit insoluble phthalocyanine.

British 435,614 - I.C.I. - Use of phthalocyanines in nitrocellulose coating compositions.

7. Substituted Phthalocyanines

U.S. 2,099,689 - General Aniline - Water insoluble metal salts of phthalocyanine sulfonic acid.

U.S. 2,099,690 - General Aniline - Lakes of the water insoluble salts of phthalocyanine sulfonic acid.

U.S. 2,116,196 - General Aniline - /Acylated phthalocyanine.

U.S. 2,117,720 - General Aniline - Phthalonitrile is reacted with benzanthrone and aluminum chloride to give a vivid green dyestuff.

U.S. 2,122,137 - General Aniline - Alkyloxy and aryloxy phthalocyanine.

U.S. 2,124,299 - General Aniline - Halogenated phthalocyanines react with organic hydroxy compounds to form an ether type derivative.

U.S. 2,133,340 - General Aniline - Acyl amino phthalocyanine.

U.S. 2,135,633 - General Aniline - Dyeing textiles with phthalocyanine sulfonic acid.

U.S. 2,150,741 - I.C.I. - A quaternary ammonium salt of a poly sulfonated metal phthalocyanine.

U.S. 2,163,768 - DuPont - Phthalocyanines are formed directly on the surface of a metal body to cover the same.

U.S. 2,166,240 - I.C.I. - A compound similar to phthalocyanine but with = CH - group in place of a = N - in the large ring.

U.S. 2,187,816 - General Aniline - Covers the reaction product of phthalocyanine sulfonic acid with organic basic compounds.

U.S. 2,197,860 - General Aniline - Phthalocyanines containing an oxazol, thiazol, or imidazol group on the benzene nuclei.

U.S. 2,213,517 - General Aniline - A CPC containing a phenyl group as a substituent on each of its four benzene nuclei.

U.S. 2,215,726 - I.C.I. - Phthalocyanines containing three carboxy groups.

U.S. 2,225,441 - General Aniline - Covers phthalocyanine containing trichlor-methyl groups in the nuclei.

U.S. 2,242,469 - General Aniline - Covers a phthalocyanine containing both a phenyl group and a carboxy group in each benzene nucleus.

U.S. 2,266,404 - General Aniline - Covers a metal phthalocyanine with both a sulfonic acid group and a naphthylamino group in each benzene nucleus.

U.S. 2,276,918 - General Aniline - Covers a metal phthalocyanine in which each benzene nucleus contains both a sulfonic acid group and an alkoxy or aryloxy group.

U.S. 2,277,588 - I.C.I. - Covers tetra-pyridyl phthalocyanines.

U.S. 2,277,628 - I.C.I. - Covers quaternary salts of tetra-pyridyl phthalocyanines.

U.S. 2,277,629 - I.C.I. - Covers pyridyl phthalocyanines.

U.S. 2,280,072 - I.C.I. - Covers tetra-amino-phthalocyanines.

U.S. 2,280,507 - General Aniline - Covers a sulfonated phthalocyanine obtained by sulfonating a phthalocyanine containing a phenyl group on each benzene nucleus.

U.S. 2,285,359 - General Aniline - Covers sulfonated phthalocyanines obtained by synthesis from sulfonated phthalic acid.

U.S. 2,286,679 - I.C.I. - Tetra-nitro-copper phthalocyanine.

U.S. 2,288,478 - General Aniline - Phthalocyanine sulfonic acids are treated with chlor-sulfonic acid.

U.S. 2,290,906 - I.C.I. - Water soluble sulfonium derivatives of phthalocyanines.

U.S. 2,300,572 - General Aniline - Phthalocyanines containing up to four sulfonamide groups on the benzene nuclei.

U.S. 2,342,662 - I.C.I. - Poly-sulfide dyes of the phthalocyanine series.

U.S. 2,342,663 - I.C.I. - A method of preparing copper phthalocyanine containing disulfide groups.

U.S. 2,349,089 - I.C.I. - Stabilized diazonium derivatives of phthalocyanine compounds.

U.S. 2,349,090 - I.C.I. - Stabilized poly-diazo phthalocyanines.

U.S. 2 349,091 - I.C.I. - Stabilized poly-diazo phthalocyanines.

U.S. 2,351,118 - I.C.I. - Water soluble dyes are obtained by coupling diazotized amino phthalocyanines with coupling components containing solubilizing groups.

U.S. 2,351,119 - I.C.I. - Poly-diazonium phthalocyanines are coupled with pigment coupling components such as beta-naphthol or aceto-acet-anilide to give water insoluble dyes.

British 460,152 - I.G. - Covers the preparation of pigments by the precipitation of water insoluble dyes on phthalocyanine pigments as substrate.

British 471,418 - I.G. - Heterocyclic dyestuffs of the phthalocyanine series are made using di-amino maleic acid dinitrile as a starting ingredient.

British 471,435 - I.G. - Halogen containing phthalocyanines may react with a primary or secondary amine to give products greener than the original.

British 487,261 - I.G. - Phthalocyanines may be heated with trichlor-acetic acid and the like to give a halogen containing alkali soluble phthalocyanine.

British 490,744 - I.G. - Cyclic-ortho-dichloro compounds are heated with cuprous cyanide in the presence of an organic nitrogenous base.

British 492,177 - I.G. - A phthalocyanine containing halogen is heated with a mercaptan.

British 492,194 - I.G. - Phthalonitrile is heated with halides of polyvalent metals in the presence of bases such as pyridine or quinoline.

British 496,663 - I.G. - Phthalic acid-4-sulfonamides are reacted with copper salts in the presence of urea and with the usual catalysts.

British 496,683 - I.G. - Phthalocyanines are heated with aromatic compounds containing halogen in a side chain to give new compounds.

British 496,819 - I.G. - Diphenyl-3-4-dicarboxylic acid containing a further carboxy group is heated with urea and a metal salt to give a water soluble phthalocyanine.

British 514,857 - I.G. - Phthalocyanine sulfonic acids are treated with halogenating agents.

The following two German patents are cited as interesting disclosures in the general field without comparable disclosures in English.

German 657,628 - I.G. - Discloses combinations of phthalocyanines with other water insoluble colors obtained by precipitating the second color on the phthalocyanine. The disclosures include Hansa Yellow types, Red 2B, and Chrome Yellow.

German 696,592 - I.G. - Copper phthalocyanine is heated with anthraquinone acid chloride to give vatable dyes.