Serial No. KN-45-9

Copy No. 1

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

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

COALESCED PIGMENTS - LITERATURE SEARCH

Period Covered: JANUARY 1945

FILE: 150

DATE: March 4, 1945

Serial No. KN-45-9

Copy No. 1

Copy to:

#1 - Numerical File
2 - Research Office (150)
3 - Library File (150)
4 - John P. Hancock, Wilmington
5 - D. H. Dawson, Newark/Library File, Rec'd by library 3-30-45
6 - Extra
7 - "
8 - "

NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

COALESCED PIGMENTS LITERATURE SEARCH

JANUARY - 1945.

SUBMITTED BY: A. J. Stratton 3/3/45 DATE SUBMITTED: 2/27/45

APPROVED BY: D. H. Dawson 3/4/45 DATE ISSUED: March 4, 1945

COALESCED PIGMENT LITERATURE SEARCH

INTRODUCTION:

For the purposes of this report, "Coalesced Pigments" are considered to be those phthalocyanine pigments which are prepared by the reaction between phthalonitrile and copper salts in the presence of certain substrata which are desirably retained as part of the final pigment. More particularly, they are those phthalocyanine pigments which are prepared by the same reaction in the presence of pigmentary forms of titanium dioxide. There is also some interest in those pigments which contain zinc oxide or certain colored inorganic pigments as the substratum.

This literature search has been largely confined to that art showing the reaction between phthalonitrile and metallic salts either with or without added material. It has covered the patent files in the Newark Library (class 653.101, both main reference and cross reference files) and the indexes of chemical abstracts since 1936 under the heading "Phthalocyanine".

SUMMARY & CONCLUSIONS:

The reaction between phthalonitrile and metal or metallic salts (particularly metallic copper, cuprous chloride or cupric chloride) was recognized very early in the study of phthalocyanine pigments as an effective method of preparation. However, it was also recognized as a violently exothermic reaction which could easily get out of control to the serious detriment of the resulting pigment. Various methods of controlling the reaction have been proposed and they may be roughly classified into three groups. The first method proposed, and one which is apparently still in wide use, is to carry out the reaction in the presence of certain high boiling organic liquids which function both as diluents and as cooling agents. There are numerous patents covering a wide variety of such diluent liquids, some of which, such as nitro benzene, are presumably inert in the reaction, and others, such as pyridine or quinoline, which very probably take some part in the reaction, and still others, such as ethylene glycol, which play an uncertain role.

A second method of control, covered by a DuPont patent, involves the very carefully controlled stepwise addition of the reactants to the reaction zone. A modification of this general method involves the use of certain materials such as ammonium chloride or aluminum chloride in catalytic quantities so as to initiate the reaction at a temperature considerably below that at which it would normally begin.

The third method of controlling the reaction involves carrying out the reaction in the presence of certain inert solid diluents. These diluents may include water soluble materials such as sodium chloride or sodium sulphate which are readily removed from the resulting pigment by solution in water. On the other hand, the diluent may be water insoluble in which case a separation can be effected by solution of the phthalocyanine pigment in concentrated sulfuric acid with reprecipitation by drowning in water after separation of the diluent by filtration. Finally, the diluent may be a desirable addition to the pigment in which case the reaction product may be used as a pigment without further treatment other than pulverization and, possibly, extraction of any unreacted water soluble materials.

The use of solid diluents is covered quite comprehensively in British Patent 453,767 (I.G.). There are French, German and Swiss equivalents to this patent but none in this country. The disclosure is broadly to "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 oxide or salt is solid at the reaction temperature and is inert with respect to the reaction and is used as a diluent". The specific disclosures include such soluble salts as sodium or potassium chloride or sulfate, and a number of insoluble materials such as silicon dioxide, alumina, barium sulfate, and titanium dioxide. The disclosure also includes the separation of the dyestuff from water soluble materialsby extraction with water and the separation from insoluble materials by elutriation methods or by solution of the dyestuff in concentrated sulfuric acid. It also includes the following statement "when using inert substances which are insoluble in water it is preferable to select those which can serve as substrata for lake dyestuffs, as, for example, barium sulfate or alumina. In this case an after-treatment of the dyestuff formed on the substratum is no longer necessary". Example 3 is specific to the reaction of phthalonitrile and cuprous chloride in the presence of dry alumina. Barium sulfate and titanium dioxide are named as equivalents of the alumina.

As far as is known at the present, there is no other patent making claims to the use of any solid diluent for this reaction. Since there is no U.S.Patent on the process, we are free to operate it in this country and it is our understanding that the modification using sodium chloride as the diluent is a part of the standard Orchem process for phthalocyanine toners.

As to the possibilities of patent protection in this country for the coalesced pigment development, it must be admitted that there is very little chance for any broad coverage. Titanium dioxide, which is found in Pigment BX-CR, is specifically mentioned in the above patent and zinc oxide which is present in Green Z comes within the broad disclosure unless it can be argued that it is not inert at the reaction temperature. It has been suggested that, since some

forms of titanium dioxide are more effective in the preparation of a commercially valuable product than others, it may be possible to obtain protection on the use of these commercially valuable forms and it is proposed to attempt an application based on such a distinction. Since the reaction product in the presence of zinc oxide is unpredictably distinctive in character and since zinc oxide is not specifically mentioned in the British patent, it is also proposed to prepare an application covering that modification. Likewise, it is felt that an application based on the use of certain inorganic colored pigments as the substrata is worth filing since the products are distinctive in character and none of the substrata are specifically mentioned in the basic patent even though some of them come within the broad disclosure.

In passing it should be mentioned that there is prior art showing the use of metallic oxides as a source of the metal for reaction with phthalonitrile. One such patent includes a claim to the reaction between phthalonitrile and a metallic oxide of the second group of the periodic table. We propose to differentiate between this art and the present process for coalesced pigments by showing that the metallic oxide used does not furnish the metal for the reaction with the phthalonitrile.

REFERENCES:

Since this search is interested both in our freedom to operate and the possibility of patent protection, it has included the general literature and foreign as well as U.S. patents. As far as we have found, all foreign language patents on the subject have substantial equivalents in the English language, either British or American, so that no direct citations have been made therefrom.

Helv. Chim. Acta 10 886 (1927)
Authors - de Diesbach & von der Weid
Title - Some complex salts of o-dinitriles with copper and pyridine.
Abstract- This paper describes the reaction between phthalonitrile and cupric bromide and pyridine to give an indigo blue material stable to many reagents including conc. H_2SO_4. The authors described this blue material as a copper complex of phthalonitrile and pyridine but there is every reason to believe that their interpretation was incorrect and that they actually had copper phthalocyanine.

J. Chem. Soc. 137, 1022 (1934)
Authors - Linstead & Lowe
Title - Preliminary experiments on the preparation of phthalocyanines from phthalonitrile.
Abstract- The reaction between phthalonitrile and various metals and metal salts was studied comprehensively including the recognition of the extreme ease of reaction with copper salts and the violently

Abstract Cont'd.
exothermic nature of this reaction. This and other articles of a series published simultaneously describe the phthalocyanines of many of the common metals.

Berichte 72 93 (1939)
Author - Linstead
Title - Phthalocyanine and related compounds.
Abstract- This article in German is an excellent general review of the preparation and properties of phthalocyanine compounds. The following metals are known to form phthalocyanine compounds:

Hydrogen (metal-free)	Beryllium	Aluminum	Tin	Vanadium	Chromium	Manganese	Iron
	Calcium		Lead	Antimony	Molybdenum		Cobalt
Lithium	Barium						Nickel
Sodium	Magnesium						Paladium
Potassium	Zinc						Platinum
Copper	Cadmium						
Silver	Mercury						

British Patent 389,942 - Issued 3/20/1923
Thorp, Linstead and Thomas, to Scottish Dyes Ltd.,(ICI)
Abstract - Method of making phthalocyanines by heating ortho cyano benzamide with a metal or metal compound. This patent is of interest at this time because of a disclaimer to the use of aluminum, aluminum oxide, titanium oxide, manganese oxide and mercury. It is interesting to note that this disclaimer is not found in the equivalent U.S. Patent 2,000,051.

British Patent 410,814 - Issued 5/16/34
To Heilbron, Irving, Linstead & Thorp
Abstract - O-Arylene dicyanides, as phthalonitrile, are heated with a metal or metal compound, particularly copper, and copper salts. The reaction may take certain place in the presence of high boiling solvents. In addition to metal-free phthalocyanine, compounds are disclosed with copper, magnesium, tin, cobalt, nickel, aluminum, barium, antimony and molybdenum.

British Patent 441,332 - Issued 1/13/36
To Linstead & Dent of I.C.I.
Abstract - Lead phthalocyanine, a brilliant green, is formed by heating phthalonitrile with Litharge, metallic lead or lead carbonate.

British Patent 453,767 - Issued 9/14/36 to I.G.
See also German 658,019, French 799,901, Swiss 189,650
(None of these in the Newark files)
Abstract - 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 is inert and is used as a diluent. Example 3 discloses the reaction between phthalonitrile, couprous chloride and alumina and lists barium sulfate and titanium dioxide as equivalents to alumina. Note also the following quotation from page 3, line 55 - "When using inert substances which are insoluble in water, it is preferable to select those which can serve as substrata for lake dyestuff as for example barium sulfate or alumina. In this case an after-treatment of the dyestuff formed on the substratum is no longer necessary".

British Patent 508,583 - Issued 7/4/39
To Interchemical Corporation
Abstract - Phthalonitrile and metals or metal compounds are caused to react at temperatures below 250°C in the presence of aliphatic di or trihydric alcohols or alcohol poly ethers. An example shows the reaction between phthalonitrile and powdered copper taking place in the presence of ethylene glycol at 137°C. It is stated that the pigment is obtained in 80% yields and needs no conditioning before use.

U.S. Patent 2,116,602 - Issued 5/10/38
To Heilbron, Irving & Linstead of I.C.I.
Abstract - Metal-free phthalocyanines are formed by heating phthalonitrile with alkali metals of compounds, ammonia or tertiary organic bases.

U.S. Patent 2,124,419 - Issued 7/19/38
To Heilbron, Irving & Linstead of I.C.I.
Abstract - Phthalonitrile is heated with iron, nickel or cobalt or a salt thereof, preferably at a temperature between 230-240°C.

U.S. Patent 2,129,013 - Issued 9/6/38
To Linstead & Dent of I.C.I.
Abstract - Copper monochloro phthalocyanine is obtained by heating phthalonitrile and cupric chloride ($CuCl_2$) at a temperature above 200°C. The use of cuprous chloride (Cu_2Cl_2) is also disclosed but not claimed.

U.S. Patent 2,138,413 - Issued 11/29/38
To Turek of Interchemical
Abstract - See British 508,583 above.

U.S. Patent 2,153,300 - Issued 4/4/39
To Dahlen & Dietrich of DuPont
Abstract - The violently exothermic reaction between phthalonitrile and copper or copper salts (or other metal salts) is controlled by adding the reactant portionwise to an apparatus such as a rotary baker at such a rate as to control the temperature. This patent discloses as prior art thereto the use of inert solid diluent such as "sodium chloride or silicon dioxide".

U.S. Patent 2,155,038 - Issued 4/18/39
To Davies, Wyler, Barret & Linstead of I.C.I.
Abstract - The preparation of Vanadyl phthalocyanine is described including the method of heating phthalonitrile and vanadium pentoxide at a temperature of 240-250°C for one-half hour.

U.S. Patent 2,160,837 - Issued 6/6/39
To Dietrich of DuPont
Abstract - A reaction between phthalonitrile and metallic copper is controlled by initiating it at a temperature of 160-170°C through the presence of catalytic quantities of chlorides of ansoteric metals and ammonia, such as NH, Cl, $SnCl_2$, $SnCl_4$, $SbCl_3$, $AlCl_3$ and Cu_2Cl_2.

U.S. Patent 2,166,213 - Issued 7/18/39
To Heilbron, Irving & Linstead of I.C.I.
Abstract - Copper phthalocyanine is made by heating together phthalonitrile and a copper producing agent at a temperature between 180-250°C, preferably about 220°C. It is disclosed that the process may be carried on in the presence of non-basic, high boiling solvents.

U.S. Patent 2,202,632 - Issued 5/28/40
To Heilbron, Irving & Linstead of I.C.I.
Abstract - O-arylene dicyanides are heated at a temperature between 150-400°C in the presence of a metal compound of a metal of the second group of the periodic table. Specific disclosures include Ca, CaO, BaO, $BaCl_2$, Mg, MgO, zinc dust, $ZnCl_2$, Cd, CdO and Be. There is one claim to zinc phthalocyanine and another claim to the use of an oxide of a metal of the second group.

U.S. Patent 2,242,301 - Issued 5/20/41
To Heilbron, Irving & Linstead of I.C.I.
Abstract - Phthalocyanine coloring matters are made by heating phthalonitrile with a cupiferous reagent in an inert non-basic medium such as a neutral organic solvent.

The above references are considered those most pertinent to the subject under consideration at this time. However, the following patents also cover modifications of the reaction between phthalonitrile and various metallic salts and are deemed of sufficient interest to be included herewith for purposes of record.

U.S. Patent 2,153,620 - Issued 4/11/39
To Heilbron, Irving & Linstead of I.C.I.
Abstract - Metal-free phthalocyanine may be prepared by heating phthalonitrile either in an atmosphere of ammonia or simply under pressure.

U.S. Patent 2,154,912 - Issued 4/18/39
To Muehlbauer & Niemann of General Aniline
Abstract - Phthalocyanine dyestuffs may be prepared by heating phthalonitrile with metallic cyanamides including alkali or alkaline earth cyanamides and lead cyanamide.

U.S. Patent 2,245,098 - Issued 6/10/41
To Turek of Interchemical
Abstract - Phthalonitrile vapors are reacted with the polished surface of a metal body and the pigment removed therefrom. Suitable apparatus for continuous operation is described.

U.S. Patent 2,276,598 - Issued 3/17/42
To Stocker & Bucher of Society of Chemical Industry, Basle.
Abstract - The efficiency of the reaction between phthalonitrile and metal compounds in the presence of indifferent liquid organic diluents can be improved by adding small amounts of alkali or alkaline earth compounds such as the hydroxide, oxide, carbonate, phosphate, tetrachlorate, silicate, or salts of organic acids such as the acetate.

U.S. Patent 2,302,612 - Issued 11/17/42
To Lacey of American Cyanamid
Abstract - Chlorine-free copper phthalocyanine may be prepared by reacting phthalonitrile with cupric chloride ($CuCl_2$) in the presence of a substantially inert organic diluent (nitro benzene) and in the presence of anhydrous ammonia.

U.S. Patent 2,318,783 - Issued 5/11/43
To King, Foote & Felch of American Cyanamid
Abstract - Chlorine-free copper phthalocyanine may be prepared by reacting phthalonitrile with anhydrous $CuSO_4$ in the presence of nitro benzene and in the presence of anhydrous ammonia, the reaction being carried out in an autoclave under pressure.

U.S. Patent, 2,318,787 - Issued 5/11/43
To Lacey of American Cyanamid
Abstract - Chlorine-free copper phthalocyanine may be prepared by reacting phthalonitrile with cupric sulfate in the substantial absence of water, in the presence of an inert organic liquid diluent (nitro benzene) and in the presence of ammonia.

British Patent 457,526 - Issued 11/30/36 to I.G.
Abstract - Phthalonitrile is heated with or without metal compounds in the presence of an amide such as formamide. Compounds of a large number of metals are listed.

British Patent 458,754 - Issued 12/21/36 to I.G.
Abstract - Phthalonitrile and copper salts are heated in the presence of tertiary bases such as pyridine under special conditions of pressure and concentration.

British Patent 459,780 - Issued 1/11/37 to I.G.
Abstract - Phthalonitrile is heated with metallic compounds in the presence of tertiary bases and a high boiling diluent other than a tertiary base. A typical reaction mixture is that including phthalonitrile cuprous chloride, pyridine and nitro benzene.

British Patent 460,594 - Issued 2/1/37
To Lowe of I.C.I.
Abstract - Metal-free phthalocyanine can be made by heating phthalonitrile with an ethanolamine.

British Patent 462,239 - Issued 3/1/37 to I.G.
Abstract - Phthalonitrile may be heated with metal amide or cyanamide and high molecular weight alcohols or mercaptan. Solvents or diluents such as high boiling liquids may be present.

British Patent 482,387 - Issued 3/29/38 to I.G.
Abstract - Phthalonitrile may be heated with metal compounds in the presence of diluents, free from nitrogen and hydroxyl groups, and under pressure.