NOVEL METHOD OF PREPARATION OF BLUE CRUDE COPPER PHTHALOCYANINE HAVING THE GREENISH SHADE

NURUL FARHANA BINTI ALIAS

Report submitted in partial fulfilment of the requirements for the award of Bachelor of Applied Science (Honor) in Industrial Chemistry

Faculty of Industrial Sciences & Technology
UNIVERSITI MALAYSIA PAHANG

JANUARY 2012

ABSTRACT

Copper Phthalocyanine (CuPc) is a blue pigment. CuPc is the most stable pigment towards light, temperature and chemical. Hence, combined with its attractive colors, this pigment is widely used in many applications such as in water-based and solvent-based paints and inks including automotive paints, textiles and plastics with the temperature of operation up to 350°C. In this work the greenish shade of Blue Crude CuPc which is required in the industries is obtained by adding a portion of Sodium Hydroxide (NaOH) in the preparation of Blue Crude CuPc. Crude also have been synthesized by using copper (I) ascorbic because the emission of ascorbic acid to the crude preparation produce a very green shade of the CuPc crude as well as the α-pigment CuPc. Characterization by using Fourier Transform Infrared spectroscopy (FTIR) was done to prove the presence of hydroxyl group. Then α-pigment was conducted to prove that synthesis greenish blue crude is better than doing colour mixing of pigment. Eventhough β-pigment should be done to show better greenish blue pigment but since it is not accessible to the kneader, it was replaced with α-pigmentation. Meanwhile the colour presence was tested by using chromameter. This instrument will automatically show the colour and shade of the sample without taking long time. However, black and white calibration should be done before used.

ABSTRAK

Kuprum Ftalosianina (CuPc) adalah pigmen biru. CuPc ialah pigmen yang paling stabil terhadap tindak balas cahaya, suhu dan tindak balas kimia. Dengan menggabungkan dengan pimen lain, pigmen ini digunakan dengan meluas dalam pelbagai aplikasi seperti dalam cat berasaskan air dan minyak serta cat kenderaan, tekstil dan plastik dengan suhu operasi sehingga 350°C. Dalam kajian ini, warna biru kehijauan CuPc mentah yang mana diperlukan oleh industri-industri cuba untuk dihasilkan dengan menambahkan Kalsium Hidroksida (NaOH) dalam penghasilan CuPc biru mentah. Bahan mentah CuPc dengan menggunakan kuprum (I) askorbik dihasilkan memandangkan bahan mentah yang mengandungi asid askorbik menghasilkan warna biru kehijauan yang terang. Bahan ini kemudian dianalisis dengan menggunakan Fourier Transform Infrared spectroscopy (FTIR) untuk membuktikan kehadiran kumpulan hidroksida. Kemudian α-pigmen dihasilkan untuk membuktikan bahawa, menyediakan bahan mentah berwarna biru kehijauan adalah lebih baik daripada mengadukkan pigmen-pigmen berlainan warna untuk menghasilkan pigmen biru kehijauan. Seharusnya β-pigmen dihasilkan tetapi memandangkan tiada kemudahan pengguli, jadi α-pigmen telah dihasilkan. Warna yang dihasilkan diuji dengan kromameter. Kromameter akan mengeluarkan data secara automatik tanpa mengambil masa yang lama. Walaubagaimanapun, sebelum digunakan, pengesahan warna hitam dan putih perlu dilakukan.

TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION

CHAPTER 2 LITERATURE REVIEW

CHAPTER 3 METHODOLOGY

CHAPTER 4 RESULTS AND DISCUSSION

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

α	Alpha
β	Beta
ε	Epsilon
π	Pai

LIST OF ABBREVIATIONS

CuPc	Copper Phthalocyanine
CuCl	Cuprous chloride
$CuCl_2$	Cuprum (II) chloride
Cl^-	Chlorine ion
Cu^{2+}	Copper (II) ion
FIST	Faculty of Industrial Sciences & Technology
H_2SO_4	Sulfuric acid
NaOH	Sodium hydroxide
NP-10	Nonylphenol 10
OH^-	Hydroxide ion
TiO_2	Titanium dioxide

CHAPTER 1

INTRODUCTION

1.1 Research Background

Copper Phthalocyanine (CuPc) pigments, by virtue of their exceptionally brilliant shade, high tinctorial strength, low cost and outstanding fastness properties, have been ruling the colorant industry ever since their commercial introduction in 1935. They are about to complete 70 years of meritorious service as an unchallenged leader of various types of blue and green pigments (Aravindakshan, 2005).

In the beginning of the 20th century, commercially available blue pigments consisted mainly of Ultramarine blue, Prussian blue, Indigo derivatives and some azo derivatives. Unfortunately none of these had the desired qualities demanded by the colour industry. Most of these pigments had poor chemical resistance, unsatisfactory acid and/or alkali resistance, insufficient light fastness and poor sublimation fastness. The colour chemists in those days were in need of a cheap and durable pigment that could fill the bluish region of the colour space. The discovery of copper phthalocyanine blue provided them with a satisfactory solution to their problems. Phthalocyanine pigments proved to be outstanding organic pigments because of their incredible resistance to chemical attack, good fastness to heat and light, combined with brightness and cleanliness of shade. All these properties are the qualities sought by the colour industries (Aravindakshan, 2005).

The phthalocyanine system is structurally derived from the aza-[18]-annulene series, a macrocyclic hetero system comprising 18 conjugated π-electrons (Moser and Thomas, 1963). Two well-known derivatives of this parent structure, which is commonly referred to as porphine, are the iron (III) complex of haemoglobin and the magnesium complex of chlorophyll.

Both satisfy the (4n+2) π electron rule and thus form planar aromatic systems. Copper Phthalocyanine Blue is the copper (II) complex of tetraazatetrabenzoporphine (Herbst and Hunger, 2004). The molecule has a completely conjugated structure that exhibits exceptional stability. From the planar structure of the molecule one can see how effectively the metal atom is protected within the interior of the molecule. The central metal atom is covalently bonded with two nitrogens of the porphine ring and also has co-ordinate linkage with two other nitrogens of the same ring. The other factors that contribute to the stability of phthalocyanines are the symmetry of the molecule and the lack of any dipole moment.

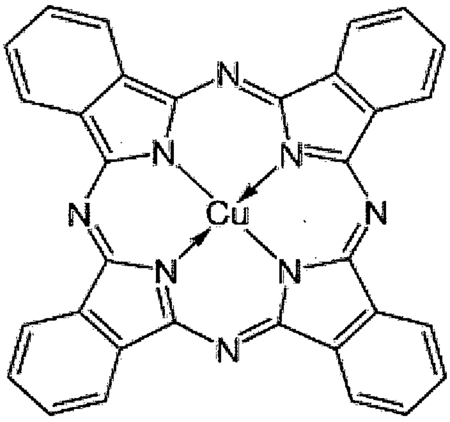

Figure 1.1: Structure of Copper Phthalocyanine ($C_{32}H_{16}CuN_8$)

A variety of peripheral substitution is possible on a phthalocyanine ring. Numerous copper phthalocyanine analogues have been reported, in which the isoindole unit has been replaced with various other heterocyclic rings. Now it is known that the phthalocyanine macrocycle can complex with cations derived from over 70 different elements. The phthalocyanine complex of Cu^{2+} ion is so strong that destruction of the macrocycle is required to remove the Cu^{2+} cation from its central cavity.

Phthalocyanines were initially produced only as pigments. At present, Phthalocyanine Blue and Phthalocyanine Green are among the most important organic pigments in the market and are sold in large volume.

1.2 Problem Statements

Any creation must have its weaknesses. Copper Phthalocyanine blue exists in three forms which are α, β and ε Copper phthalocyanine. Therefore, α-CuPc is reddish blue and ε-CuPc is most reddish CuPc but very unstable while β-CuPc is the greenish blue. The β-CuPc is mainly used in printing ink and industry still need greener shade of β-CuPc (Kunjappu, 2000).

There are four problems involves in the production of CuPc. The two of them is already solved by ump researchers which is 99% yield of crude α and β CuPc is obtained from the reaction, so no much waste produced. The other two problems are to produce the more reddish shade and the more greenish shade of CuPc.

Usually to obtain the greenish shade required, the industry often do colour mixing with other suitable pigment and for this very often troublesome and costly plus the resulting colour matched product have different flow. This is due to the increase in viscosity and other problems. Therefore, it is desired to have greener shade of CuPc compared to standard CuPc to overcome this problem.

In the synthesis of blue copper phthalocyanine, copper (I) chloride can be use in replacing copper (II) chloride. In the other word, replacing with copper (II) chloride will highly cost in production. In simple word, industries does not need highly cost in production.

Since UMP's laboratory does not have kneader in order to make β-CuPc. So, we will replace with α-pigmentation. That means α-CuPc will be obtain by using the greenish shade of blue crude copper phthalocyanine. This pigmentation only needs simple method.

1.3 The Objective of the Research

The objective of this work is to obtain the greenish shade of Blue Crude Copper Phthalocyanine which is required in the industries.

1.4 Scopes of Works

Based on the objectives, the work carried out in this project should be:

i. To conduct the synthesis of standard blue crude copper phthalocyanine.

ii. To conduct the synthesis of greenish shade of blue crude copper phthalocyanine by adding 1%, 5%, 10% and 15% sodium hydroxide (NaOH) into the standard reaction of blue crude copper phthalocyanine.

iii. To synthesis α-pigment of the crude that have been synthesized as a raw materials in order to obtain the better greenish shade present.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter reviews the current development on Copper Phthalocyanine Blue. Besides that, a brief summary about the experimental method in preparation of crude copper phthalocyanine by using phthalic anhydride and urea was also discussed. Excellent general chemical and physical properties, combined with good economy, make them the largest fraction of organic pigments in the market today (Herbst and Hunger, 2004).

There are several benefits in choosing Copper Phthalocyanine Blue than other blue pigments. Copper Phthalocyanine Blue is cheaper than other blue pigment. Besides, CuPc is more stable toward temperature and insoluble in solvent and has no tendency to migrate in the materials. Not only that, CuPc having high tinting strength and can be test by using titanium dioxide (TiO_2). When the CuPc is tested by using (TiO_2), the colour turned to blue pale while the other blue pigments become whitish.

2.2 Manufacturing Copper Phthalocyanine Blue

In 1937, Du Pont started producing Copper Phthalocyanine Blue in the USA after it had previously been launched in Great Britain and Germany. After that, this production was followed by the other companies. The application for Copper Phthalocyanine Blue patent was no longer open after it had been described by de Diesbach and von der Weid in 1927.

Nevertheless, yet a great many synthetic methods for this important compound were patented by other scientists and researchers. Copper phthalocyanine blue can be prepared from:

i. Phthalonitrile or substituted phthalonitriles and metals and/or metallic salts.
ii. Phthalic anhydride, phthalic acid, phthalic esters, diammonium phthalate, phthalamide or phthalamide and urea, metal salt and a catalyst.
iii. O-cyanobenzamide and a metal or metallic salt.

However, only two techniques have gained commercial importance. The phthalonitrile process was developed in England and Germany is particularly important in Germany while the phthalic anhydride/urea process has stimulated more interest in Great Britain and the USA. The technical importance of phthalonitrile process is only second to the phthalic anhydride/urea technique, of which two varieties are commercially used. BASF is the primary European user of the phthalonitrile method. Knowledge of the most important types of copper phthalocyanine pigments is useful for the understanding of the process concepts underlying pigment manufacture.

Heading the list are the α-modification and β-modification of unsubstituted Copper Phthalocyanine Blue. The α-modification exhibits an unstabilized and a stabilized form as to change of crystal modification. Likewise, halogenated copper phthalocyanine green pigments also have a major impact on the market.

2.3 Properties of Materials in Production of CuPc

Each material that use in production of blue copper phthalocyanine give important role in order to obtain the colour. If any materials that need in production are missed during the process, the crude will not be obtained.

2.3.1 Phthalic Anhydride as a Starting Material

Phthalic anhydride is prepared by oxidizing o-xylene. The oxidation can be performed either in the gas phase with vanadium pentoxide as a catalyst or in the liquid phase with dissolved manganese, molybdenum or cobalt salts as catalysts. Gas-phase oxidation is the favoured technique that has been chosen at this present time.

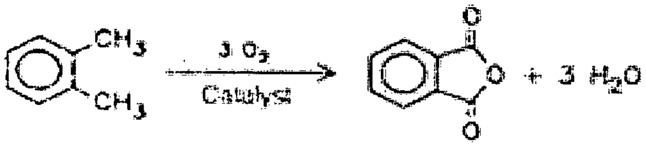

Figure 2.1: Synthesis of phthalic anhydride

A third cption involves oxidizing naphthalene, possibly with vanadium pentoxide as a catalyst. Phthalic anhydride is a significant commercial product. Its main area of application is in synthetic resins and plasticizers. The production capacity worldwide was about 3.62 million/tans in 1997.

2.3.2 Copper Chloride as a Side Material

Copper forms compounds in the oxidation states of +1 (cuprous) and +2 (cupric) which trivalent copper survives no more than a few seconds in an aqueous solution. The relatively small change in electrochemical potential between the cuprous and cupric ions in solution gives the usefulness of copper compounds in chemical reactions. Cuprous Chloride or Copper Chloride ($CuCl$ or Cu_2Cl_2) also known as resin of copper green, tetrahedral crystals which is insoluble in water. CuCl used as crude for phthalocyanine blue pigments.

2.3.3 Ammonium Molybdate as a Catalyst

Suitable catalysts used in the process of the invention which called ammonium molybdenate. Ammonium molybdate is an odorless crystalline compound ranging in color from white to yellow-green. It also called molybdic acid hexammonium salt tetrahydrate, ammonium molybdate tetrahydrate and ammonium heptamolybdate tetrahydrate. In chemistry an ammonium molybdate is a compound containing an oxoanion with molybdenum in its highest oxidation state of 6. Ammonium molybdate can form a very large range of such oxoanions which can be discrete structures or polymeric extended structures, although the latter are only found in the solid state.

2.3.4 Alkyl Benzene Solvent as a Medium

The choice of the solvent is very important, as it plays a significant role in the generation of impurities. More particularly, it relates to a process for producing copper phthalocyanine having high quality and high tinting strength, without producing a toxic by-product by an advantageous industrial operation, which comprises reaction a phthalic anhydride with a copper compound and urea in the presence of a catalyst in a specific Alkyl Benzene. It has been known that in the conventional industrial process for producing the copper, the yield of the copper phthalocyanine is highly affected depending upon the selected reaction solvent, and also the tinting strength and the hue are highly affected depending upon the selected reaction solvent. It has been also known that in the physical properties of the optimum reaction solvent, the boiling point at the atmospheric pressure should be in a range of 160°C to 250°C and the difference between the initial boiling point and the dry point should be less than 10°C and the thermal stability should be high.

2.4 Phthalic Anhydride/Urea Process

Likewise, this process may also be carried out either as a solvent-free (baking) method or in the presence of solvents (Bayer, 1972). Although initially performed as a solvent-free technique, it is the solvent version that currently dominates the fields of copper phthalocyanine production from phthalic anhydride and urea. It should be mentioned, however, that this trend has been reversed in the very recent past and that solvent-free methods are gaining interest, especially for ecological reasons.

2.4.1 Baking process

Baking process is the first commercial copper phthalocyanine synthesis that involved melting phthalic anhydride with urea at 150°C in the present of boric acid. Copper (II) chloride was then added and the temperature increased to approximately 200°C until the copper phthalocyanine production was completed. The reaction mixture was cooled and the crude product milled. After being washed, first with dilute sodium hydroxide solution and then with dilute sulfuric acid, the material was filtered off and dried. The crude copper phthalocyanine obtained was then dissolved in sulfuric acid and precipitated in ice water ("acid pasting") in order to afford a form which could be used as a pigment. In subsequent years, boric acid in its role as a catalyst largely gave way to various metallic salts. Best results were achieved with molybdenum trioxide and primarily with ammonium molybdate, both of which are currently used. It thus became possible to increase the yield from approximately 50% to more than 90% of the theory (Herbst and Hunger, 2004). Copper (II) chloride may also be replaced by copper (I) chloride, copper carbonate or most commonly copper sulphate.

The baking process has remained much the same until the present day, at a stoichiometric ratio of 1:4, phthalic anhydride or phthalic acid reacts with an ammonia releasing compound.

The reaction may also start from other suitable materials such as phthalic acid derivatives, including phthalic acid esters, phthalic acid diamide or phthalamide. Appropriate ammonia releasing agents include urea and its derivatives such as biuret, guanidine and dicyanodiamide. The fact that a certain amount of urea decomposes to form side products makes it necessary to use excess urea. Approximately 0.2 to 0.5, preferably 0.25 equivalents of copper salt should be added for each mole of phthalic anhydride. 0.1 to 0.4 mole of molybdenum salt per mole of phthalic anhydride is sufficient. The reaction temperature is between 200°C to 300°C.

The baking process, particularly the batch variety presents a number of serious disadvantages. Not only do the reaction produce solid urea decomposition products but it also release large amounts of ammonia and ammonium salts which escape by sublimation. The foam which is thus formed makes for a porous reaction mixture, which in turn even prevents heat conduction. Moreover, the reaction mixtures tend to adhere to the surface of the reaction vessel and the stirring unit, phenomena which adds to the complexity of the problem.

At least some of these disadvantages may be overcome by vigorous stirring or milling during the reaction. Baking by batch process has recently been described which involves heating the reaction components in layers on metal sheets. However, such processes require precise control. If a copper phthalocyanine complex is prepared by batch process in a ball or a pin-type mill, the reaction mixture must be allowed to cool before it is discharged. Reaction times of originally 5 to 45 minutes thus create cycle lasting up to 3 hours, a duration which is highly uneconomical.

Continuous baking processes may be conducted, for instance, by treating the reaction mixture in a heated cylinder with a screw drive. The desired thin film, however, can only be produced in large elaborate reaction units, a requirement which makes its manufacture expensive. The same is true for performing the baking process in heated rotating drums. A certain amount of product (namely, the amount that is produced in two hours) must already be present as the starting materials are added in order to prevent the materials from sticking to the unit. Long reaction times and unprofitable filling levels produce a space/time yield which is unattractive for industrial purposes.

On the other hand, economically advantageous routes by continuous baking process have also been described in recent years. The processes are carried out in self-cleaning mixing apparatus such as double screw extruders. More recent patents literature claims yields as high as 80% (Herbst and Hunger, 2004).

Invariably, the primary product is a crude copper phthalocyanine blue with insufficient properties. It is boiled with dilute hydrochloric acid or aqueous alkali and then rinsed with hot water to remove acid or base before it can be finished. The crude produced would produce cheaper pigment due to lower quality as it is dirty.

2.4.2 Solvent method

There is somewhat less of a demand on the reaction equipment if phthalic anhydride and urea react in an organic solvent. In principle, the presence of a solvent makes almost no differences to the synthesis by baking process. Using suitable inert high-boiling solvents such as kerosene, trichlorobenzene or nitrobenzene obviates many of the difficulties connected with the reaction mixtures obtained in the baking process. Solvents make it much easier to adequately mix the components and to ensure even heat transfer.

Long reaction times, however, remain somewhat of a problem, although suitable temperature control during condensation makes it possible to produce the complex in almost quantitative yield.

The solvent is removed from the solid product by filtration or centrifugation to afford crude Copper Phthalocyanine Blue of a quality that makes intermediate purification unnecessary. In contrast to the product obtained by the baking process, this material is pure enough to be used directly for further pigment manufacture. Crude Copper Phthalocyanine Blue, on the other hand, which evolves as the solvent is removed by distillation, contains so many impurities that it must be boiled before being utilized further.