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DEPARTMENT OF CHEMICAL TECHNOLOGY

TITLE: PAINT FORMULATION BASED ON DEODORIZER DISTILLATE BASED ALKYD RESIN AND METALLOPHTHALOCYANINES

BY

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DEDICATION.

This research is dedicated with gratitude to my mother and my brother for their sacrifices and support and also to my uncle John Moto for his steadfast encouragement in recent times and to the Almighty God.

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I would like to thank my supervisor and mentor Dr M. Shumba, for guiding me intellectually during the course of the project. It has been a pleasure and a blessing to have been one of his students. I would also like to thank Mr V. Chitsa, who provided me with advice and insight throughout my studies. I am also grateful to Dulux Limited Zimbabwe for providing me with the materials and reagents that I used in the experiments and also to Mr A. Zireva for carrying out quality control tests on resin. I am also greatly indebted to my colleagues Irvin Nhutsve, Tererai Tafireyi, Julius Maringo, Wilfred Sithole, Nyaradzai Dondo and Kudzanai Makanyanga for their extensive support throughout my studies, may God bless them abundantly. Sincere gratitude also goes to my family, friends and the Moto Trust Fund for their unwavering support. I would also like to thank the MSU Chemical Technology laboratory staff for their contributions in making this research possible. Last but not least I want to thank Almighty God for making everything possible.

ABSTRACT.

A novel study was carried on paint formulation based on alkyd resin and metallopthalocyanines. Alkyd Resin was synthesised using deodorizer distillate, which is a source of fatty acids that are included in the resin formulation. The distillate is generally cheaper as compared to soya bean oil that is being used at the moment. It is a by-product produced during the deodorization process of edible oil refineries. The resin reaction was stopped at an acid value of 9.6 mg of potassium hydroxide per gram of alkyd resin. Metallopthalocyanes, Copper(II)Phthalocyanine and Cobalt(II)Phthalocyanine were synthesised as pigments in paint formulation. All the synthesised products were characterised using Fourier Transform Infrared spectroscopy (FT-IR), Ultraviolet visible spectroscopy (UV-Vis) and thermal gravimetric analysis (TGA). The synthesised alkyd resin was linked covalently with cobalt(II)tetraamino phthalocyanine and non-covalently with copper(II) phthalocyanine. The pigments were dispersed in the resin with the aid of a solvent xylene in order to produce two paints based on the two different metallophthalocyanines. The formulated paint products were exposed to sunlight in solution form for photo degradation studies. The wavelength of highest absorbance was found to be 680 nm and no new bands were observed signifying the stability of the formulated paints.

DECLARATION

I, Anesuishe Nago R141342y, hereby declare that I am the sole author of this dissertation. I authorize Midlands State University to lend this dissertation to other institutions or individuals for the purpose of scholarly research.

Signature ………………………………

Date ………………………………….

APPROVAL

This dissertation entitled “Paint formulation based on deodorizer distillate based alkyd resin and metallophthalocyanines” by Anesuishe Nago meets the regulations governing the award of the degree of Chemical Technology Honours of Midlands State University, and is approved for its contribution to knowledge and literal presentation.

Supervisor…………………………...

Date…………………………………

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ABBREVIATIONS.

CuPc – Copper(II)Phthalocyanine.

CoTAPc - Cobalt(II)Tetraamino Phthalocyanine.

UV-Vis – Ultraviolet Visible Spectroscopy.

FTIR – Fourier Transform Infrared.

TGA – Thermal Gravimetric Analysis.

DSC – Differential Scanning Calorimetry.

DMF- Dimethyl Formamide.

CHAPTER 1.

1.0 Introduction.

This chapter serves to provide a detailed outline of background of research, aims and objectives on Metallophthalocyanines and alkyd resins. It will also show information on problem statement and justification of the study.

1.1 Background.

Alkyd resins are one of the raw materials that are used during the production of oil based paints[1]. They are included in the formulation as binders and they normally have the greatest percentage in most of the oil based formulations [2]. Alkyd Resins are polyester-based materials that are normally modified with oil or fatty acids. Alkyd resins are used mostly in the paint industry because they have a generally low cost and versatility [3]. They are a major binder in enamels and vanishes [2]. These enamels and vanishes are used as surface coatings on substrates such as walls, wood, breeks and steel structures. Due to their appearance they produce a gloss finish to substrates. There are however other binders that are used in the paint industry such as latex resins but these are expensive compared to alkyd resins. Alkyd resin is synthesised by mainly alcohols and acids which gives rise to the term alkyd [4]. Alkyd resins are synthesised from three basic components polybasic acids, polyols and fatty acids. They contribute to coating flexibility, adhesion, durability, and gloss. The popularity of alkyd resins as vehicle for coatings is largely due to their unique properties such as film hardness, durability gloss and gloss retention, resistance to abrasion [5].

The alkyd resins are synthesised by a polymerisation method, polymerisation is one of the most important industrial processes. The alkyd resins contribute about 70% to the conventional binders used in surface coating according to previous research [6]. There are two main types of alkyd resins which are long and medium oil alkyd resins.

Long oil length alkyds are prepared mainly from drying and semi drying oils, pentaerythriol acts as the polyol [7]. The most commonly used medium oil is linseed oil. Alkyd resins can be analysed using different analytical techniques such as FTIR spectroscopy, DSC and UV-Vis spectroscopy. Thermal stability is also systematically determined on alkyd resins. There are different sources of fatty acids that can be used for alkyd resin synthesis such as soya bean oil, sunflower oil and crude oil [6].

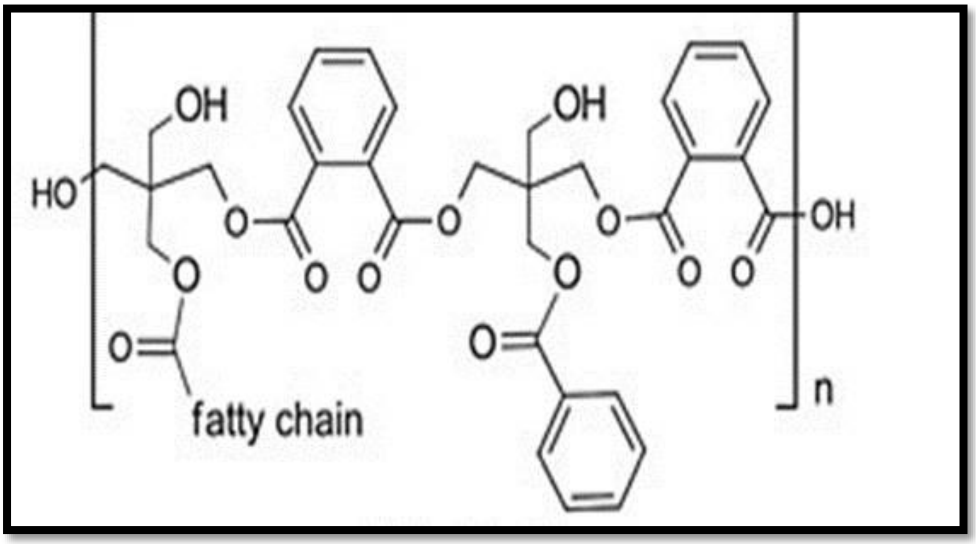

Figure 1. 1 alkyd resin [2].

Deodorizer distillate is a cheaper source of fatty acids; it is produced as a by-product in vegetable oil refineries. It is specially generated from the deodorisation process. Fatty acids are important in the alkyd resin preparation process as they act as precursors of the main structure.

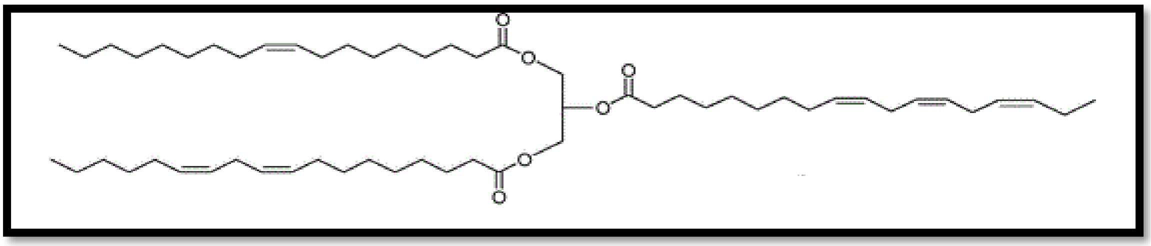

Figure 1. 2 Deodorizer distillate [8].

1.1.2 Metallophthalocyanines.

Phthalocyanines are used as pigments in the ink and paint industry. They are also used for other purposes such as in catalysis. Copper phthalocyanine is a blue pigment, it is a metallophthalocyanine. Many metallophthalocyanine functional derivatives with substituents in the benzene rings have been synthesized and isolated in individual form, and their structure and spectral properties were investigated [7]. Phthalocyanines are used in the paint industry due to their extremely high thermal stability, inertness to acids and alkalis, insolubility in most solvents, high dyeing power, and colour intensity [8]. Cobalt(II)Tetraamino phthalocyanine is also another metallophthalocyanine that is green in colour and can used in the paint industry as a pigment and also to add other good properties to the coating. The synthesised phthalocyanines are characterised using FTIR spectroscopy, UV-Vis spectroscopy and TGA for thermal stability. Phthalocyanines will be used for checking the stability of the resin [7].

1.2 Aim.

To utilise deodorizer distillate in making cheaper alkyd resin, also introducing metallophthalocyanines as a pigments in alkyd resin based paints.

1.3 Objectives.

- To synthesis and characterise CuPc and CoTAPc using FTIR spectroscopy, UV-VIS spectroscopy and TGA.
- To synthesis alkyd resin using deodorizer distillate and characterise using FTIR spectroscopy and UV-VIS spectroscopy.
- To carry out quality control tests of colour, viscosity and solids on the final product.
- To formulate a paint based on metallophthalocyanines and the synthesised resin.
- To carry out degradation studies on the formulated paints.

1.4 Problem Statement.

Alkyd resin is currently being produced at Dulux in Zimbabwe, with most paint companies importing the resin from other countries. The resin imports are expensive therefore it is important to produce our resin to reduce such expenses. The quality of alkyd resin has also deteriorated in terms of colour at the Dulux Resin plant. This is due to failure to monitor the temperatures during the alkyd resin manufacturing process. The process is also not time effective taking longer periods of time than those anticipated, resin imports are expensive causing the final product price to rise. It is also important to utilise deodorizer distillate which is a cheaper by product of soya bean oil manufacture and this can act as a fatty acid source. The use of the deodorizer distillate will result in the production of a low cost resin as the resin formulation contains a greater percentage of fatty acids. The use of by products for raw material manufacture will also reduce the consumption of edible oils by industries and increase the quantity of these edible oils to the local and international market. This will also reduce the use of land for growing plants for oil production which can be used for other purposes that benefit the economy. Currently normal dyes are being used for tinting purposes in the paint industry and these include azo dyes and inorganic dyes. These dyes are used in large quantities as their tinting strength is generally low and they also suffer heat resistance and stability in high temperatures.

1.5 Justification.

The current process is producing resin that is not meeting the quality requirements of the paint industries as most of the resins are in the dark range, beyond 8 on the gardener scale. This is because the method is overheating the system. The production process is also slow and the resin that is being imported is expensive. Some of the resins that are being important are too viscous and this causes the solid content to be decrease when they are thinned.

For paint manufacturing process it is important that the resin have a viscosity of 67-70 Ku for it to be workable. Phthalocyanines are very good pigments that have great tinting strength than most colorants. As a result of the greater tinting strength it is wise to introduce the use of metallophthalocyanines as pigments as they will be used in smaller amounts as compared to colorants. The metallophthalocyanines also have other important properties that can be added to those of the coating such as heat resistance, chemical resistance and durability.

1.6 Scope.

The research is aimed at producing a cheaper resin made from cheaper raw materials. This will be achieving by the use of deodorizer distillate which is a cheaper source of fatty acids. It is also aimed at finding optimum temperature and time needed to produce a pale coloured resin in the shortest time possible. This will be achieved through experimental investigation and literature review. The introduction of metallophthalocyanines is also aimed at reducing the amount of pigments that are used for tinting purposes due to the greater tinting strength of metallophthalocyanines.

CHAPTER 2.

LITERATURE REVIEW.

2.0 Introduction.

This chapter gives a detailed outline of copper (II) phthalocyanine, cobalt (II) tetraamino phthalocyanine, alkyd resin, deodorizer distillate and the characterisation techniques that are carried out after synthesis. It will also outline the paint formulation based on CuPc and CoTAPc also quality control techniques that are carried out on alkyd resin. Degradation studies on the formulated paints will also be carried out.

2.1 Copper (II) Phthalocyanine.

Phthalocyanines are conjugated and they are generally aromatic and symmetrical macro cyclic molecules. The phthalocyanines have an 18π electron system containing four isoindole groups. The groups are linked by four nitrogen atoms. The phthalocyanines compounds are generally structurally similar to naturally occurring porphyrins but have extended conjugation engendered by benzene rings, hence have improved chemical and thermal stability [9]. The structure of phthalocyanines is similar to chlorophyll which is the green pigment in plants, but however the central hydrogen atom has been replaced by many metals to form metal phthalocyanines. The colour of the phthalocyanine is determined by the central metal [10]. The metallophthalocyanines have greater tinting strength as compared to normal azodyes that are used in the paint industry and the can be employed for tinting purposes in the paint industry. Copper(II)phthalocyanine is a blue pigment due to its tinting ability it is used in the paint and ink industry for purposes of colour. It is also used due to its great stability properties [11]. The Copper(II)Phthalocyanine does not decompose in acidic solution and it is insoluble in water which makes it a good pigment for various applications.

Copper (II) phthalocyanine is usually achieved in high yields by cyclotetramerisation of phthalic anhydride in the present of a metal salt at high temperatures [12]. Copper (II) Phthalocyanine can be used in the paint industry due to its thermal stability and also due to the ability to produce colour even in small amounts to large amounts of extenders. The phthalocyanine molecule consists of four isoindole units (C_8H_7N) connected by four nitrogen atoms as shown in figure 2.1. The central cavity of phthalocyanine macrocycle allows the formation of metal complexes such as copper (II) phthalocyanine [13].

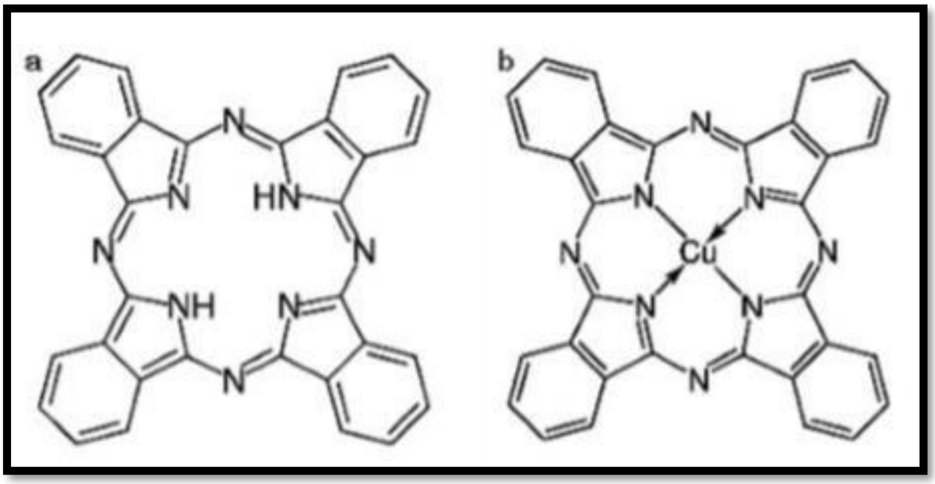

Figure 2.1 (a) Metal free Phthalocyanine b) Copper(II)Phthalocyanine [12].

Phthalocyanines have found application as semiconducting oligomers and also as model systems [9]. Copper(II)phthalocyanine is also a typical p-type organic semiconductor and its application has be found in the organic field effect transistors, organic light emitting diodes, and solar cells [14]. Phthalocyanines have a great property similar to that of absorption pigments which possess very high surface energy. The metallophthalocyanines have a tendency to self-agglomerate this causes the formation of coarser particles in paint formulations which can be reduced in size by means of dispersion using equipment such as the ball mill.

Copper(II)phthalocyanine has great thermal stability and can reach temperatures up to 550 °C before sublimation starts to occur, this is also because it does not have a decomposition temperature but decomposes at elevated temperatures [11]. The chemical properties of phthalocyanines depend on the nature of the central atom such as copper or cobalt [12]. Phthalocyanines are stable to atmospheric oxygen up to approximately 100 °C. In the paint industry, copper (II) phthalocyanine is generally preferred due to excellent colour properties, excellent resistance to heat and light, acid and alkali, and are extremely insoluble in most solvents [15]. They also very cheap as compared to most organic pigments. The pigmentary properties of copper (II) Phthalocyanine change with time in organic media due to change in crystal structure [12]. Copper (II) Phthalocyanine has been widely used in the paint and dye industry because it has 40 times greater tinting strength than ultramarine blue and 4 times greater tinting strength than iron blue. The copper (II) phthalocyanine is generally inert in acidic and alkali conditions. There are also other application of copper (II) phthalocyanines, they are used as catalysts different cases [16]. Copper (II) phthalocyanine has been used for catalysis purposes in the activation of molecular hydrogen. The results showed that copper (II) phthalocyanine can catalyse atomic interchange between molecular hydrogen and water vapour and catalyse formation of water from hydrogen and oxygen. Copper (II) phthalocyanine can be added to rubber with no effect on the aging properties of the rubber.

2.2 Synthesis of copper (II) phthalocyanine.

Phthalocyanine are planar 18 p-electron heterocyclic aromatic system with alternating nitrogen-carbon atom ring structure derived from porphyrin [12]. Several metals can be introduced on the centre of phthalocyanines and this result in modified properties and also in different colours being produced. The synthesis of metal phthalocyanines is usually achieved in high yields by cyclotetramerization of phthalonitrile, diiminoisoindoline, phthalic anhydride or phthalimide in the presence of a metal salt at high temperatures [9].

There are many precursors that can be used during the synthesis of phthalocyanine complexes, the precursors are shown in figure 2.2 below. Copper (II) phthalocyanine is synthesised by heating an intimate mixture of urea, phthalic anhydride, copper chloride, and catalyst together [17].

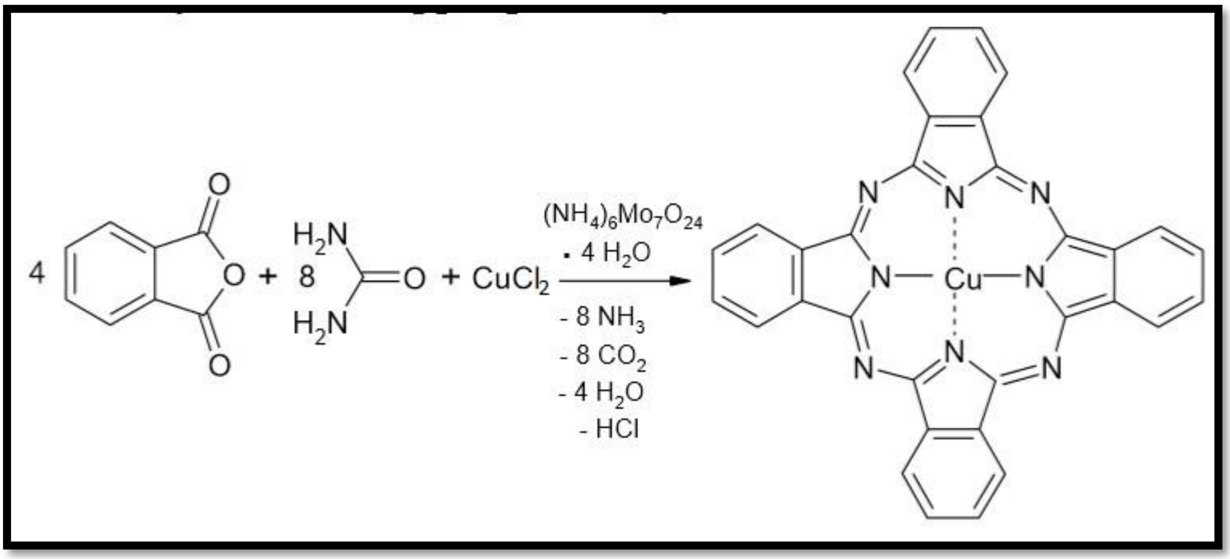

Figure 2.2 Synthesis of Copper (II) Phthalocyanine.

2.3. Cobalt (II) Tetraamino Phthalocyanine.

Phthalocyanines have good properties which include excellent stability to heat, light, and harsh chemical environments similar to CuPc. CoTAPc phthalocyanine is a metallophthalocyanine. This phthalocyanine can be regarded as a transition metal phthalocyanine due to the central cobalt transition metal and it is a versatile class of organic macrocycles with 18π electrons. These phthalocyanines are greatly used in electrocatalysis suitable for fabrication of electrochemical sensors and due to its tinting strength it can be used in the paint industry for tinting purposes. The phthalocyanine has also great tinting strength as compared to most organinc pigments they can be used in the paint industry for tinting automotive and industrial paints.

They can also add good properties to the coating such as thermal stability, durability and chemical resistance. The properties are very important especially when formulating industrial coatings.

CoTAPc is functionalised phthalocyanine that can be covalently bonded to carboxylic groups to form strong bonds that cannot be easily broken as shown in figure 2.3. The bonding is regarded as the coordination between π electron species [18,19].

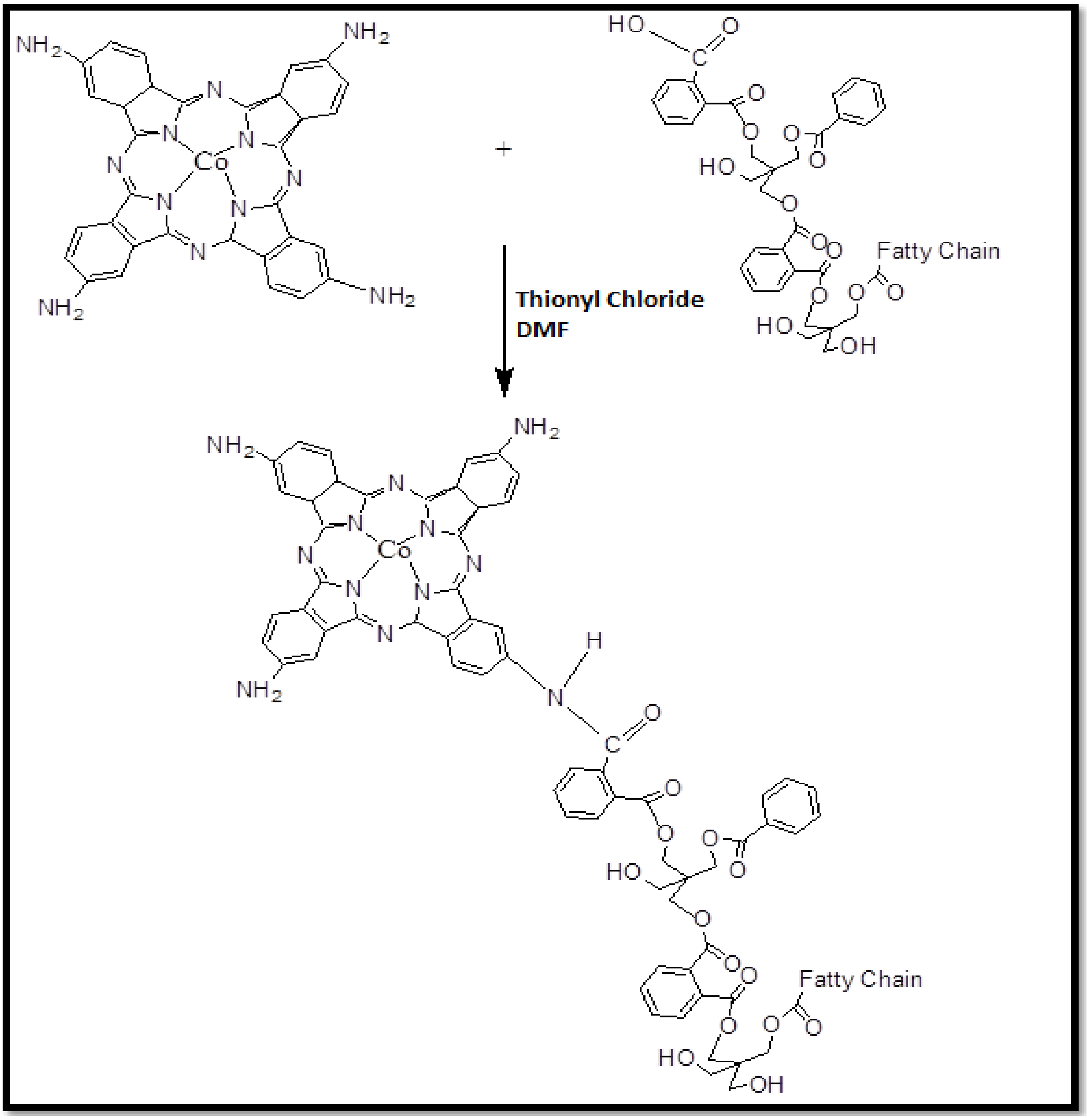

Figure 2.3 Conjugation of CoTAPc to Alkyd Resin [20].

2.4. Methods of Characterising Metallophthalocyanines.

2.4.1. Analysis by UV-VIS spectroscopy.

Phthalocyanine compounds are analysed using different techniques such as UV-Vis spectroscopy. The spectrum produced provides information on the phthalocyanine compounds, the bands that are expected to be present on the spectrum of the metal phthalocyanine are (i) the Q-band (very intense absorption band, found in the region of 660 – 1000 nm), (ii) the vibronic bands (close to the foot and the blue end of the Q-band), (iii) the charge transfer band (a result of electron transfer between the ligand (L) and the metal (M) centre), can be either M → L or L → M and is blue shifted relative to the Q and vibronic bands and the B or Soret band (a result of the superimposition of two bands, B1 and B2, giving rise to the weak band around 350 nm). Copper(II)phthalocyanines are characterized by single and split Q-bands. For the analysis of phthalocyanines DMF is used as the organic solvent since the phthalocyanines do not dissolve in water [14].

2.4.2 Analysis by FTIR Spectroscopy.

Synthesised metallophthalocyanine compounds are also characterised using FTIR spectrometry. The FTIR spectrometry gives information about the vibrational bands and the environments to which different groups are positioned. The IR spectra reveal identifiable specific absorption bands of the compounds structure such as C-N stretch and C-C stretching, C-C main ring deformation and vibrations outside the ring-plane.

2.4.3 Thermal Gravimetric Analysis.

TGA measures the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time, in an atmosphere of nitrogen, helium, air, other gas, or in vacuum. Thermal analysis gives information about changes in material properties as function of temperature [21]. This method can be used to determine the stability of a compound.

Thermal gravimetric analysis can also be used for the analysis of melting points. Generally phthalocyanine molecules do not have a sharp melting point. Phthalocyanine compounds are stable up to 410 ^{o}C[11].

2.5 Alkyd Resins and their function.

Alkyd resins are polyesters that are made by condensation polymerisation of a dicarboxylic acid or its anhydride and a polyol. The term condensation is used to characterise any reaction in which two molecules undergo addition accompanied by the loss of a small molecule such as water, carbon dioxide or nitrogen gas [22]. Alkyd resin are widely used in the paint industry as they act as binders in paint formulations. Alkyd resin still alkyd resins still remain a mainstay for a number of applications due to their balance of economies and performance. The Resin is used in the paint industry also because they contribute to coating flexibility, adhesion, durability, and gloss. They are mainly used in oil or solvent based paints for making enamels and vanishes [23]. Paints may possibly is described as a colloidal combination of chemical ingredients, when diffused on a surface in a thin layer they form a dense, consistent and adherent layer [2]. The resin has the ability to hold the pigment particles together and also aid in sticking properties as the paint sticks to the substrate. The resin is made by polycondensation, in poly condensation polymerisation of alkyd resin the carboxylic acid and alcohol are di-functional groups that is they contain two functional groups.

The alkyd resin is currently being made by acid anhydrides such as phthalic anhydride with polyols like glycerine and are modified with unsaturated fatty acids to give them air drying properties which is very important during the process of paint application [22].

2.5.1 Raw Materials for Alkyd resin preparation.

Alkyd is prepared by the reaction of a polybasic acid, polyols, fatty acids and an organic solvent. Xylene is one of the major solvents that are used during the process of alkyd resin manufacture for thinning purposes. The gaseous nitrogen is also used as a purging gas [24].

2.5.2 Polybasic Acids.

Phthalic Anhydride is the most widely used polybasic acid in the process of alkyd resin preparation. In some cases, other polybasic acids are used in cases when tougher, faster drying and more chemical and heat resistant coating is required to be formulated.

The polybasic acids that can enhance such properties are isophthalic acid and orthophthalic acid. The polybasic acids lead to higher molecular weights and high viscosities due to the carboxyl groups that make the formation of intramolecular cyclic esters. Maleic anhydride is a polybasic acid that can be used in small amounts but due its cost most industries do not use it. Maleic anhydride forms Diels-Alders adducts with unsaturated acids in dry oils [5].

2.5.3 Polyols.

The polyols are compounds that contain more than two hydroxyl alcohol groups. There are many polyols that are used in alkyd resin preparation, glycerol being the most used. The other polyols that are used in alkyd resin manufacture are ethylene glycol, propylene glycol and diethylene glycol, these are diols [25]. The polyols are responsible for determining the degree of branching of the alkyd resin. The flexibility of the resin is influenced by the distance between the hydroxyl groups [5].

2.5.4 Fatty Acids.

The fatty acids and oils that are used for resin manufacture range from vegetable oils, animal oils and fish oils to a lesser extent. There are other synthetic substances such as benzoic acid and these can provide greater hardness and improve gloss retention.

The drying properties of alkyd resin determines the degree of unsaturation. The most widely used fatty acid source is soya bean oil. The position of the double bond is important, with conjugated bonds being much more reactive in autoxidation than non-conjugated. Deodorizer distillate is also another potential source of fatty acids [8]. The distillate is a by-product of edible oil manufacture produced during the deodorization process. Deodorization is a step of soya bean oil refine that removes volatile compounds responsible for oil undesirable taste, producing soya bean oil. The distillate contains fatty acids that can be utilised for resin manufacture but however further distillation and filtration is required to produce a clear resin [26].

2.6 Methods for making alkyd resins.

Alkyd resins are mainly prepared using 2 methods and these methods are either the fusion method or the solvent method. The fusion method is the older process that was used for making alkyd resin. The process is used for alkyds of an oil length of 60 % or more. The reaction is carried out at a temperature of 220 to 250 °C, and nitrogen is used as the inert gas sparge. The gas is used for removal of the reaction water, also causes some loss of volatile polyols and of phthalic anhydride [27].

In the solvent method, the esterification is performed in the presence of a small quantity of solvent such as xylene. The process is carried out under continuous azeotropic distillation of the solvent. The xylene and water vapour mixture is condensed, the water is separated, and the organic distillate is returned to the reactor. The reaction temperature is governed by the refluxing temperature that, in turn, depends on the amount of xylene used, 5% being a normal value. According to research, the solvent method offers better control of the resin composition, as there is virtually no loss of raw materials by volatilization or sublimation. The solvent process is divided into 2 stages that is alcoholises and esterification [27].

2.6.1 Alcoholises Stage.

This process should be carried in an environment free of oxygen because the presence of oxygen tends to oxidise the fatty acids causing darkening of the product. The first stage consists of reacting the vegetable oil or a fatty acid with a polyalcohol like pentaerithrol as shown in fig 2.4. The reaction can be speeded up by the addition of a catalyst which is can be base like lithium hydroxide or sodium hydroxide with the reaction temperature maintained at 200^{o}C. The products of this stage are monoglycerides. Completion of this stage is tested by mixing the sample with methanol which is twice its volume, if the monoglyceride sample is soluble in the methanol then the stage is complete [24].

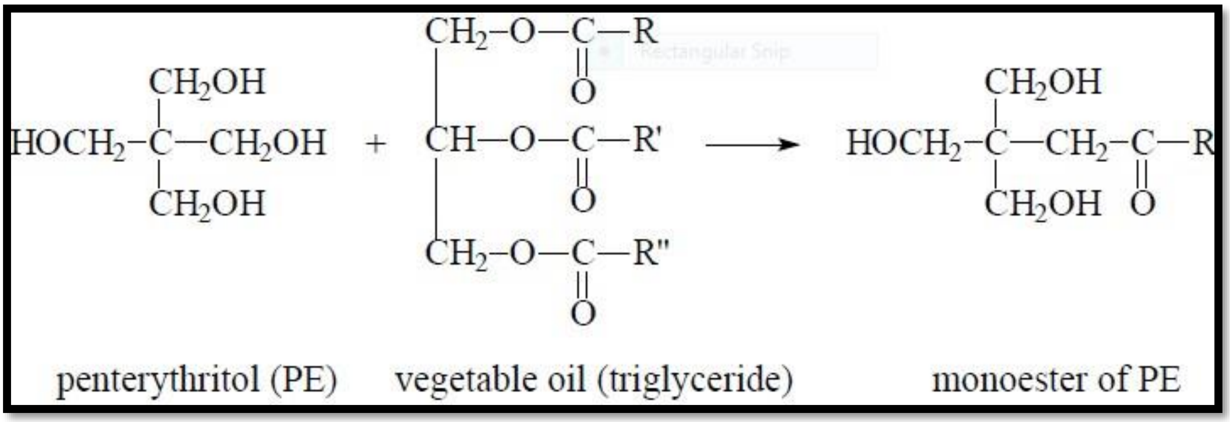

Figure 2.4 Alcoholises [21,26].

2.6.2 Esterification.

The second stage is esterification. A dicarboxylic acid or its anhydride is added to the monoglycerides as shown in figure 2.5. The reaction is carried out at 220 ^{o}C. Esterification is controlled by acid number and it is stopped when it reaches the acid desired value. This acid value is determined by titration with potassium hydroxide using phenolphthalein indicator. This reaction is not supposed to go to completion because towards end point of reaction the product tends jell and this is undesirable. The alcoholises process is economical and good in cases where end product control is not as important.

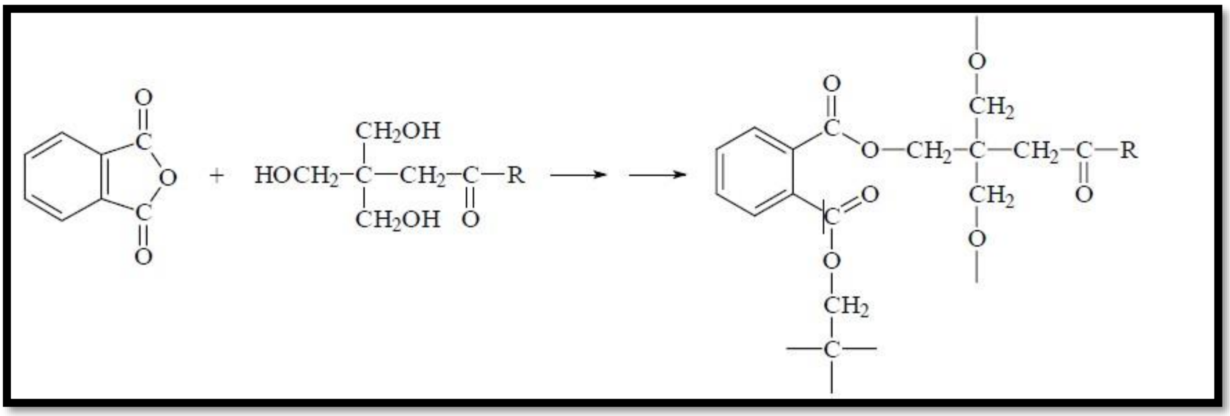

Figure 2. 5 Esterification [22].

2.7 Gelation point.

For all the methods of preparing alkyd resins, the reaction is not supposed to go up to completion because completion of the reaction of the reaction would mean that there is gelation which is a non-reversible reaction. The gel is difficult to clean and to take out of the reacting vessel. The reaction progression is measured by acid value which is determined by titrating with potassium hydroxide. The reaction should be terminated at an acid value of about 4-8 [23].

2.7.1 Acid number.

The acid number is an indication of the free acidity present in the non-volatile portion of alkyd resin. It is expressed in mg of KOH required to reach pH neutrality in 1 g of alkyd resin.

Acid value=(MV*)/W where M is molarity in moles/dm^3, V is the volume of alkali used. W is the weight of the sample of oil used [28].

2.7.2. Sparging

This process is done with either nitrogen or carbon dioxide sparging effectiveness is dependent on the rate of blow and the fineness with which the gas is dispersed as it courses upward through the reaction mixture. For alcoholysis, a blow rate between 0.01 and 0.02 ft3/min/gal is satisfactory.

Sparging is continued throughout the reaction, including the up heat and any thinning. For esterification, a rate of 0.01 to 0.04 ft3/min/gal is satisfactory with the faster blow rate applying to the beginning and the slower to the end [29].

Gas dispersion is conventionally accomplished by introducing the gas into the reaction mix through many fine holes (facing downward to ensure drainage) drilled in a perforated tubular ring assembly which is spread out over the bottom of the alkyd kettle [4].

2.7.3. Darkening of alkyd resin

During the process of resin synthesis high temperatures are required to speed up the process of making alkyd resin but however these high temperatures often lead to undesired darkening of the alkyd resin.

This is due to oxidation which is superimposed at the high temperatures if the reacting system contains some air within it. The double bonds of unsaturated acids react with oxygen. Linolenic acid oxidation depends on the presence of oxidising agents, antioxidants, temperature and the dissolved oxygen. Oleic acid, as a monounsaturated acid, can be oxidised only at elevated temperatures, while polyunsaturated acids such as linolenic and linoleic acids undergo rapid oxidation even at room temperature due to the double bonds [30].

2.7.4 Colour of alkyd resin.

When light passes through a substance it is reflected, refracted or absorbed. The colour that we see is that of the part of the light spectrum that are not absorbed. The ideal resin that is expected is pale, without visible browning. The grade of resin falls as colour gets darker. A challenge that alkyd resin producers face is how to make bio based alkyd with lower colour. Even though most alkyd resins when fully formulated into paints are highly pigmented, the lower the initial colour, and more importantly, the colour stability of the resin over time, the better the overall colour fastness of the final paint.

The sources of colour and colour shifts in alkyd paints and resins are complex, but the common causes are the aromatic content due to the phthalates and the degree of unsaturation present in the fatty acid drying oils [31].

2.7.5 Factors affecting colour of alkyd resin.

The colour of alkyd resin is dependant in the particle size of the particulates, non-volatile matter of the alkyd resin and their distribution. The non-volatile matter is the substance that remain on the substrate after application which is mainly the polymer particles as well as unused catalyst. The light absorption is inversely proportional to the particle size d because the number of particles per unit volume is proportional to d^{-3} and the cross section of the particles is proportional to d^2. Light scattering by a particle depends on its size relative to the wavelength of the light. The optimum scattering size depends on its concentration but in general it is about half of the wavelength. The gloss also affects how we perceive the colour of the alkyd resin. Gloss gets better if oils of high unsaturation are used like tall oil and linseed oil. The increase in rigidity of the networks formed due to high unsaturation lowers the degrees of freedom of atomic vibrations in polymer chains. It in turn lowers the absorption of light by polymer chains and thus a larger fraction of light reflects back from the surface [32].

2.8 Factors affecting polycondensation process.

2.8.1 Temperature.

The rate of reaction is affected by reaction temperature. Time is also an important factor since the reaction proceeds to near completion even at room temperature with sufficient time. For this type of reaction, energy is needed to break bonds. The reaction needs high temperatures but however, these temperatures can cause darkening of the resin if not monitored. The darkening is also due to oxidation especially in cases where oxygen is present in the reaction [33].

2.8.2 Purity.

An alkyd raw material may be supplied in one or more grades of purity. Purer raw materials reduce the probability of errors in the production process.

2.8.3 Contaminants.

Trace amounts of foreign material may affect the alkyd reaction. Contaminants result in side reactions which reduce the yield of the reaction. Soaps and fatty acids present in crude glycerol sources cause the incorporation of carboxylates and fatty acids to carboxyl and hydroxyl groups of polyester backbone respectively. The use of contaminated crude glycerol as a replacement of pure glycerol in bio polyester synthesis is not recommended given the heterogeneous nature of the feedstock which induces variability in the biomaterials synthesized. For example, synthetic glycerol under certain conditions may act different than glycerol from natural sources [31].

2.8.4 Order of Reagent Addition.

The order of addition is very important for the reaction of resin preparation to occur. The improved physical properties of the resin are obtained when the polymer structure is predominantly linear and of high molecular weight, and this can be obtained by adding the raw materials in the correct order. The most used process to facilitate correct order is the step by step esterification of fatty acids. Certain significant differences are observed for alkyds that are identical from a chemical composition standpoint but that differ in properties and performance depending on whether they are made by the alcoholysis or the fatty acid procedure. An explanation for this difference is afforded by considering the differential rates of reaction between -OH and -COOH groups, depending on their specific location on the parent molecule. In the fatty acid preparation method, where there is a free-for-all competition among the -COOH groups (all added at the beginning). The fatty acid -COOH groups lag behind in joining primary -OH groups and hence must settle for connections with secondary -OH groups.

In the monoglyceride method, where the competition is rigged, the fatty acid -COOH groups are deliberately reacted with the primary groups of glycerol before any phthalic anhydride is added, and the di-acid -COOH groups are placed at a competitive disadvantage and are therefore forced to settle for a reaction with leftover -OH groups [33].

2.9 Analysis of Alkyd Resin.

Alkyd resin is characterised using FTIR spectroscopy. A long- oil alkyd resin can be identified by its characteristic FTIR spectrum, containing a broad hydroxyl group peak at 3440cm^{-1} (broad rounded peak), (C-H) CH_2 asymmetric and symmetric stretching and bending peaks at 2,925, 2,855, and 1,465 cm^{-1} respectively, and a strong C=O stretching peak around 1,726 cm^{-1} and C- O and fingerprint peaks at 1,256 cm^{-1} (strong, likely due to esters) and 1,120 cm^{-1}. The aromatic rings in the polyester backbone can be identified by the sharp doublet aromatic stretching peaks at 1,600 and 1,580 cm^{-1}, the strong unsaturated ring in-p lane deformation peak at 1,071 cm^{-1} [34].

2.9.1 Mixing of Resin and Phthalocyanine.

Paint is basically made up of four components and these include a binder, pigment, solvent and additives. The additives help to give the paint special properties such as heat and uv resistance. Alkyd resin and copper phthalocynine can be manually mixed with the resin acting as the binder and the copper(II)phthalocyanine acting as the binder. The stability of the resin can then be determined by its ability to hold the pigment suspended in it without it settling to the bottom. This ability will also determine how efficient the mixture will adhere to any substrate that is suitable for application. The mixing of the resin and the CuPc is known as non-covalent linking since the phthalocyanine is non functionalised. The Alkyd Resin can be linked with the CoTAPc. This type of linking is regarded as covalent linking. This is due to the bonding of the amine groups on the phthalocyanine and the carboxylic groups that are present on the resin.

The use of thionyl chloride can be employed to activate the carboxylic groups that are present on the resin [20].

2.10 Quality Control test carried out on Alkyd Resin.

The synthesised alkyd Resin is characterised for bonds using FTIR spectroscopy. DSC is also used to test the stability of the resin. The resin and copper(ii)phthalocyanine mixture is also tested for accelerated stability test at 80^{o}C in an oven over night. Further quality control tests are also carried out on resin and these include:

2.10.1 Colour.

Colour of the synthesised resin should be pale below 7 on the colour Gardner scale. Colour of the alkyd polymer is dependant in the particle size of the particulates, non-volatile matter of the alkyd resin and their distribution. The non-volatile matter is mainly the polymer particles as well as unused catalyst. The light absorption is inversely proportional to the particle size because the number of particles per unit volume is proportional to d-3 and the cross section of the particles is proportional to d2. Light scattering by a particle depends on its size relative to the wavelength of the light. The optimum scattering size depends on its concentration but in general it is about half of the wavelength.

The gloss also affects how we perceive the colour of the alkyd resin. Gloss gets better if oils of high unsaturation are used like tall oil and linseed oil.

The increase in rigidity of the networks formed due to high unsaturation lowers the degrees of freedom of atomic vibrations in polymer chains. It in turn lowers the absorption of light by polymer chains and thus a larger fraction of light reflects back from the surface.

2.10.2 Darkening of alkyd resin.

High temperatures are required to speed up the process of making alkyd resin but however these high temperatures often lead to undesired darkening of the alkyd resin.

This is due to oxidation which is superimposed at the high temperatures if the reacting system contains some air within it. The double bonds of unsaturated acids react with oxygen.

2.10.3 Solids.

The solid content of the alkyd resin should be similar to that of long oil therefore it should be greater than 60 per cent [35].

2.10.4 Air Drying.

The long oil should give a generally slow drying due to more thermosetting of long oil alkyds, the drying time is 16hours for hard drying.

2.10.5 Gloss.

As oil length increases, initial gloss of film increases due to better orientation of oil and fatty acids, Therefore the gloss reading on a gloss meter should be above 90% on 800 head.

2.11 Paint Formulation.

Paint consists of four main components. These components include the binder (resin), pigment, solvent and the additives. The paint formulation should contain all these components in order to have a good coating with good characteristics.

The purpose of the pigment in the paint formulation is to enhance colour while the binder helps to hold the pigments particles close together. When the paint is formulated, allowance is made for some fundamental physical parameters that greatly influence the technological properties of a coating.

The pigment to binder ratio and the pigment to volume concentration are important parameters in paint formulation. These are important so that we can determine the non-volatile (solids) that remain on the substrate after application.

The pigment volume concentration is the ratio of the pigment volume to the total volume of the solid coating. The pigment volume is the sum of pigment and filler volumes [36,28].

$$\text{PVC} = \frac{Vp+Vf}{Vp+Vf+VB} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1).$$

Vp: Volume of Pigments.

VF: Volume of the fillers.

VB: Volume of dried film of the binder.

The volumes are calculated as the quotient of mass(m) and density(p)

$$V=\frac{m}{P}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2).$$

2.12 Paint Degradation Studies.

Degradation studies are aimed at monitoring the resistance of the paint to the effect of sunlight. The degradation that is normally prone to occur is photo degradation. This type of degradation is the alteration of the paint material by light. In most cases the degradation is a combined action of sunlight and air. These parameters cause hydrolysis and oxidation which result in the formation of new compounds that produce different UV-VIS spectra when the paint is analysed. Change in the appearance of painted surfaces can be the result of the formation of a compound on the paint surface that is different in colour from that of the original or it can be due to fading or darkening. Darkening is often easily visible to the naked eye and can have a profoundly negative impact on the value and possibly on the interpretation of the painted object.

A darkened appearance over time is one of the most common symptoms of aging of painted surfaces [37].

Visually the degradation can be observed as change in colour when the paint is applied on the substrate. On solid substrates the studies can be analysed using colour readings by the use of a colorimeter [38].

2.13 Reaction kinetics for poly-condensation.

The alkyd making process can be viewed as a two-stage reaction regardless of whatever method is used to make the alkyd resin. The first stage is the monoglyceride process in which the triglycerides are converted into monoglycerides. The second stage is the transesterification stage in which the monoglycerides and the fatty acid react to give the polyester. The transesterification stage is the slowest and this makes it the rate determining step.

It is assumed that reactivity of the functional groups is independent of the length of the chain that they are attached to. Reaction rate is followed by determining the concentrations of the functional groups as a function of time. Rate determining step is the nucleophilic addition step. With continual removal of water, the reaction can as well be assumed reversible.

Case 1: Polymerization without Added Strong Acid: Consider esterification as the formation of a polyester from a glycol and a dibasic acid. The progress of reaction is easily followed by titrating the unreacted carboxyl groups in samples removed from the reaction mixture. This poly-esterification and other simple esterification are acid-catalysed. In the absence of an added strong acid, a second molecule of the acid being esterified acts as the catalyst. The rate of poly-esterification process can therefore be written:

$$-\frac{d[COOH]}{dt} = k[OH][COOH]^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (3)$$

Where concentrations are expressed as equivalents of the functional groups. The equation assumes that the rate constant k is independent of molecular size of reacting species and is the same for all functional groups. If the concentration, C, of the unreacted carboxyl and hydroxyl groups at time t are equal, Equation 1 may be rewritten as:

$-\frac{dc}{dt} = kc^3$

On integration, this yields the third-order reaction expression

$2kt = \frac{1}{c^2} - constant$……………………….*(4).*

Now introducing the extent of reaction, p, defined as the fraction of the functional group that has reacted at time t. That is

$P = \frac{C_0 - C}{C_0}$………………………………………*(5).*

where Co= initial concentration of one of the reactants.

$C = C_O(1 - P)$…………………………..*(6).*

Substituting yields

$2{C_O}^2kt = \frac{1}{(1-P)^2} - 1$……………………..*(7).*

Polymerization with Added Strong Acid:

The kinetic expression can be greatly simplified if the poly-esterification is carried out in the presence of a small amount of strong acid, e.g.-toluene sulfonic acid. With the catalyst concentration kept constant throughout the process, the rate expression becomes

$-\frac{dc}{dt} = \acute{k}\, c^2$……………………………*(8).*

Where k' = k [catalyst] and where the alcohol and carboxylic acid concentrations are kept constant. Integrating this second-order rate equation and inserting the extent of reaction, p, we have:

$C_0 k' t = \frac{1}{1-p} - 1$………………….(9).

CHAPTER 3.

MATERIALS AND METHODS.

3.0 Introduction.

This chapter gives a detailed overview of the reagents that were used in all steps of experimental procedures, along with detailed steps that were done during the course of the project. It will also show the equipment and reagents that were used in the project.

3.1 Reagents and Chemicals.

The chemicals that were used in this study were of pure analytical grade and used directly without further purification. Deodorizer distillate was obtained from Zimgold (Harare, Zimbabwe. Potassium hydroxide (KOH) and sulphuric acid ($H_2SO_{4)}$ were obtained from Springfield (Johannesburg, South Africa). Methyl red and Iodine solution were obtained from Sigma Aldrich (Johannesburg, South Africa). Methanol CH_3OH, hydrochloric acid (HCl), copper (II) chloride and sodium hydroxide (NaOH) were obtained from Associated Chemical Enterprise (Southdale, Johannesburg, South Africa). Urea (mp 132.5-134.5 °C) and ammonium heptamolybdate were manufactured by Sigma Aldrich (Johannesburg, South Africa). Phthalic anhydride (mp 129-132 °C) (18.0 mmol, ethanol (bp 78 °C), pentaerithrol, organic solvent xylene and phthalic anhydride were provided by Dulux Limited Zimbabwe from its suppliers AI Davis. Nitrophthalic acid was manufactured by skylabs. Cobalt sulphate, ammonium chloride and nitrobenzene were obtained from Associated Chemical Enterprise (Southdale, Johannesburg, South Africa).

3.2 Equipment.

A digital analytical balance (G and G of model JJ224BC) was used for weighing. An ultra-sonicator model KQ250B from China Corp was used during the course of the research.

UV- Vis spectrophotometer model from Shimadzu, Japan was used for analysis of synthesised CuPc, CoTAPc,covalently linked CoTAPc with alkyd resin and non-covalently linked CuPc with alkyd resin. Thermal analysis was done using TGA 550 and DSC 25 manufactured by tain instruments.

3.3 Synthesis of Metallophthalocyanines.

Copper(II)phthalocyanine [10,39] and Cobalt(II)tetraamino phthalocyanine [19] were synthesised as reported before.

3.4 Purification of Deodorizer distillate.

The deodorizer distillate was purified by column chromatography. The column was packed with dried silica gel (100 g) using petroleum ether. Deodorizer distillate (100 g) was mixed with hexane (500 mL) and transferred to the column and allowed to percolate as the fraction was being collected. A second solvent system consisting of a mixture of two solvents, (3:1 of ethanol in hexane) was poured onto the column and allowed to pass through the column to obtain the second fraction which was the purified deodorizer distillate [4].

3.5 Synthesis of Alkyd Resin.

3.5.1 Stage 1 alcoholises.

The deodorizer distillate 66.5 g (0.2277 moles) and pentaerithrol 12.9 g (0.0358 g) were weighed separately using an analytical balance and dissolved in 12ml of xylene. The resultant was mixture was refluxed for 30 min with stirring under nitrogen as shown in fig 2.4. A sample was withdrawn from the reacting vessel and the methanol test was carried out at 10 minute intervals to check if alcoholises took place [5]. The sample that was withdrawn was taken and mixed with methanol in the ratio methanol 1: sample 3. Under stirring the mixture is checked for any visible cloudiness or lack of homogeneity. Alcoholises was confirmed by the homogeneity of the resultant solution [6].

3.5.2 Modification by Esterification.

An analytical balance was used to weigh 26.9 g (0.1816 moles) of phthalic anhydride which was ground to a fine powder. The weighed sample was mixed with the product from stage one as shown in figure 2.5. This mixture was put in a three necked 100ml round bottomed flask equipped with a reflux condenser and it was heated to 100^{o}C. The mixture was stirred using a magnetic stirrer. After 6 minutes a sample was withdrawn and acid value and viscosity were measured. Nitrogen gas was used as a purging gas and it was collected using a balloon and introduced through the third neck of the round bottomed flask [7].

3.5.3 Determination of acid value.

A mass of 3 g of the alkyd resin sample was weighed. The 3 g sample were dissolved into 50 ml of methanol. The mixture was mixed well. The 3 drops of phenolphthalein indicator were added. Titration was carried out against 1molar potassium hydroxide. End point was indicated by a permanent pale pink colour. The acid value was calculated by calculating the mass of potassium hydroxide used in milligrams per gram of the sample [35].

3.5.4 Testing for Solids.

Analytical balance was used to weigh resin samples into small metal crucibles. The crucibles containing the resin were placed in the oven that was set at 60^{o}C. The samples stayed in the oven for 2 hours. After 2 hours they were removed and they were cooled in a desiccator containing silica. The sample remaining masses of the resin were weighed using an analytical balance and the masses resembled the solid percentage [5].

3.5.5 Testing for Colour.

The synthesised resin was placed into a Gardner tube. The tube was then compared to the resin colour standards on the Gardner scale and the colour range was noted. The expected maximum colour range [35].

3.5.6 Testing for Drying.

The synthesised resin was tested for drying, a drawdown of 75 microns was done using a doctor gauge on a glass panel. The glass panel was left in the constant temperature room at a temperature of 25 °C [5].

3.6 Paint Formulation Covalent Linking of CoTAPc and Alkyd Resin.

The synthesised CoTAPc (0.5 g, 70.43 mmol) was activated in the presence of thionylchloride (1.1g, 7 mmol) and Dimethyl formamide DMF (0.8 g, 7 mmol) before 1mg of Alkyd Resin was added and the solution was left stirring for 48hours. The resultant mixture was washed with THF, to remove unbound CoTAPc, and Thionylchloride. The product was then dried overnight at 70 °C in an oven [20].

3.7 Paint Formulation using CuPc and Alkyd Resin.

The paint was formulated using copper phthalocyanine (pigment), alkyd resin (binder) and xylene (solvent). A ratio of 2.1 was used for mixing alkyd resin and CuPc respectively with addition of xylene. This was based on the solid content of alkyd resin that was found to be 61.3 %. [28,19].

3.8 Characterisation using FT-IR Spectrometry.

3.8.1 Analysis of Metallophthalocyanines.

The synthesised copper(II)phthalocyanine and cobalt(II)tetraamino phthalocyanine were characterized by FTIR spectrophotometer model. A mass of 0.01g of samples were mixed with 1g KBr in pistol and mortar to form a pellet and this was characterized within the range 400-4000cm^{-1} for both the two metallophthalocyanines [11].

3.8.2 Analysis of Alkyd Resin.

The synthesised alkyd resin was analysed using FTIR spectroscopy. The sample of resin was poured on both sides of a KBr disk. The disk was placed into the instrument in a position that allowed light to pass through. The sample was then analysed. [8].

3.9 Analysis by UV-Vis spectrometry.

3.9.1 Analysis of Metallophthalocyanines.

After synthesis the synthesised copper(II)phthalocyanine and cobalt(II)tetraamino phthalocyanine was analysed using uv-vis spectroscopy. A concentration of 1µM was prepared in 50 ml volumetric flask. The metallophthalocyanines were dissolved in dimethyl formamide which acted as the solvent and also as the blank during the analysis by uv-vis. The samples and the blank were placed in plastic cuverts and analysed in the wavelength range of 300-800 nm [15].

3.9.2 Analysis of Alkyd Resin.

The synthesised Alkyd resin was analysed using UV-Vis spectroscopy in dimethyl formamide. The DMF solvent was used because xylene acts of plastic curverts that were available. The resin was analysed using uv-vis in the range of 300 nm up to 800 nm. A concentration of 1 µm was prepared in dimethyl formamide. The solvent was also used as the blank during the analysis procedure.

3.10 Analysis by TGA (Thermogravimetric Analysis.)

The synthesised copper phthalocyanine was analysed by TGA. Before the sample was placed into the instrument, nitrogen was turned on then the instrument was turned on later. The sample holding pan was tared after the program was run. The ambient temperature of 500 ^{o}C was set. The sample was then placed on the pan and analysed for 30 minutes.

The results were produced as a graph. The same procedure was used to analyse the covalently linked CoTAPc and Resin and also for the analyses of the non-covalently linked CuPc and Alkyd Resin.

3.11 Analysis by DSC.

The synthesised resin was analysed by DSC. The sample holder was weigh using the analytical balance and a small amount of the resin was added to the sample holder. The sample was covered and tightly closed. The crucible containing the sample was placed in the DSC cell and analysed [5].

3.12 Degradation Studies.

The paint mixture of CuPc and Alkyd resin was put in a glass vial. The vial was closed and it was exposed to sunlight for 48 hours before analysis by UV-VIS Spectrophotometer. The samples were analysed in the range from 300 nm to 800 nm. A solution of 1 µM was made with DMF, taking the paint sample from the bulk after each period of exposure. This test was done to test the resistance of the paint to light degradation.

CHAPTER 4.

RESULTS AND DISCUSSION.

4.0 INTRODUCTION.

The chapter presents results obtained experimentally. Bands appearing in the FT-IR spectrum were assigned to various functional groups. Thermal gravimetric analysis was used for thermal stability analysis of the synthesised products. UV-Vis spectroscopy was used for the analysis of the synthesis CuPc, CoTAPc and alkyd resin it was also used for degradation studies on the formulated paints.

4.1 Characterisation by FT-IR.

4.1.1 IR Spectroscopy of the Synthesised Copper(II)Phthalocyanine.

The synthesised Copper Phthalocyanine was characterised by the FT-IR in the range of 400 cm^{-1} to $4000cm^{-1}$. Figure 4.1 shows the FT-IR spectra of Copper(II)phthalocyanine. The spectra showed a broad band at 3437.33 cm^{-1} in the high frequency region, this band corresponds to the vibrational bending and the stretching frequency of OH bond. This shows the presence and incorporation of the water and ethanol molecules in the copper phthalocyanines as these two solvents were used during washing. A sharp band was observed at a wavelength of 1633.08 cm^{-1}. The band resembles the presence of N-H bend of primary amines, these are present on the structure of copper(ii)phthalocyanine [40]. A sharp small band was observed at a frequency of 1391,94 cm^{-1}. This band is due to the presence of a C-H rock due to the presence of alkanes [41]. The band is generally small because the bulk of the product has conjugated alkenes also showing that FT-IR can be used for quantitative purposes. A peak was also observed on the frequency of 1107,06 cm^{-1} which resembles C-N stretch in aliphatic amines. The band is a bit longer which means that there is more than C-N group on the same environment.

Two bands were observed with frequency of 898.65 cm^{-1} and 720.72 cm^{-1}. The bands resembles the presence of =C-H bend resembles the presence of alkenes [12].

4.1.2 FT-IR of Alkyd Resin.

The synthesised alkyd resin was characterised by the FT-IR in the range of 400 cm^{-1} to 4000 cm^{-1}. Fig 4.1 shows the FT-IR spectra of Alkyd resin. The resin was analysed on a KBr disk. A broad band was observed at a frequency of 3532.71 cm^{-1}. This band corresponds to the presence of O-H of the free pentaerithrol and the residue moisture. The hydroxyl group of the alkyds are expected to enhance the adhesion of the blends of the resin, the band corresponds to the expected peak of 3018 cm^{-1} [24]. There was also another broad peak that was observed at a frequency of 2829.06 cm^{-1}. The peak resembles the presence of C-H stretch in an aromatic [8]. This band is due to the stretching of the double bonds which is sp^2 these are expected to be observed around 3006 cm^{-1} which is the same range with the obtained band. The band confirmed the presence of aromatic rings on the structure of the alkyd resin which are expected. Also C-H stretching of sp^3 was observed at region 2829,06 cm^{-1}. Another band was observed with a frequency of 1695.13 cm^{-1} this band was the appearance of the characteristic of strong band of ester group of –C=O stretching [23]. The weak absorption bands at 1581.11 cm-1 arising from C=C are due to the aromatic rings in phthalic anhydride. Bands observed at 1459 cm^{-1} are for C-H stretching aromatic and aliphatic. Band in the aromatic region at 752 cm^{-1} confirms the esterification reaction of the alkyd resin. All these characteristic absorption bands support the structure of alkyd resin [27]

4.1.3 FT-IR of Cobalt (II) tetra amine phthalocyanine.

An FTIR spectrum for CoTAPc was obtained in the range of 400 cm^{-1} to 4000 cm^{-1} as shown in fig 4.1. A sharp band was observed at a wavelength of 1142.49 cm^{-1} This band resembles the presence of C-C, showing the presence of carbon ring structures that are expected in phthalocyanine compounds [28].

The FTIR spectra showed a broad band at 3438 cm^{-1} in the high frequency area which corresponds to the vibrational bending and the stretching frequency of O-H bond. This suggest the incorporation of water molecules into the phthalocyanine. It also helps to confirm the hydrophobic nature of the phthalocyanine molecule. The absence of the C-N triple bond shows the success of synthesis of Pcs upon their tetramerization reactions but however a C-N single bond was observed at the wavenumber of 1522.08 cm^{-1}. This shows the presence of aliphatic amines in the structure. Aromatic C-H stretching vibration of the compound was observed around 895 cm^{-1} [29].

The spectra of the phthalocyanine reviewed a band at about 682 cm^{-1} this confirms the presence of cobalt in the structure [15]. A peak was observed at a wavenumber of 1611.58 cm^{-1} this resembles the presence of N-H. All these characterised bonds show the success of synthesis.

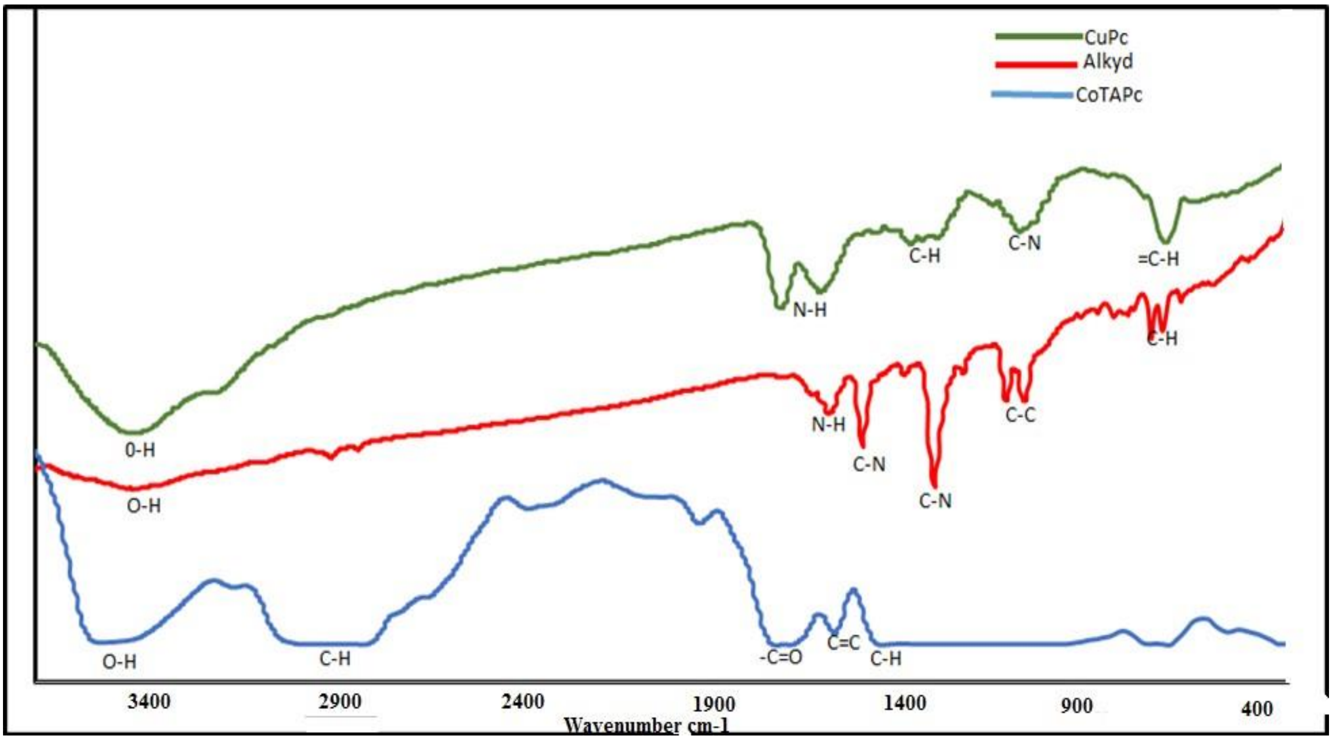

Figure 4.1 FT-IR of Alkyd resin, CoTAPc and CuPc.

4.2 UV-VIS Spectroscopy Analysis.

4.2.1 Ultraviolet Visible Spectroscopy of Copper(II)phthalocyanine.

Phthalocyanines exhibit uv-vis spectra with two strong absorption regions around 300-400 nm which is the B band and absorption around the region 600-700 nm which is the Q band [42]. The synthesised copper(ii)phthalocyanines was analysed by uv-vis spectroscopy as shown in figure 4.2 . Phthalocyanine molecules absorb light in the visible spectrum (400–700 nm), they have at least one chromophore (colour-bearing group) and also they have a conjugated system, i.e. a structure with alternating double and single bonds, A solution of 1 micro molar of the copper(ii)phthalocyanine was made using Dimethylformamide(DMF) [43]. The solution was sonicated for 30 minutes and it was analysed using uv-vis with DMF being used as a blank. A band was observed at 360 nm. The band resembles a B band. The B band arises from deeper π levels LUMO transitions which are occur in the uv region between 300 and 400 nm. Another band was observed at 680 nm which is a Q Band [15]. The Q band is associated with the π-π* transition from the highest occupied molecular orbital HOMO to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring [44]. There was also splitting of the Q band as another shoulder was observed at 620 nm. Broadening was also observed and this could have been due to low symmetry or aggregation [16,45].

4.2.2 Analysis of Cobalt (II) tetra amine phthalocyanine by UV-VIS.

The CoTAPc was analysed using uv-vis spectroscopy as shown in figure 4.2. The spectra showed a band of absorbance at 360 nm. This band is due to the conjugated double bonds that are present in the synthesised compound. The band is known as the Soret band and it is attributed to the transitions from deeper pi levels to the lowest unoccupied molecular orbital, this is regarded as an electron dipole movement that allows π-π* transitions [11]. It also results from the transitions from a2u to eg and also b2u to e.g. This is due to the alternating double bonds in the phthalocyanine structure.

The Q band is also observed and it is split to wavelengths of 620nm and 680 nm. The band of highest absorbance is that of 680 nm. The peak is attributed to the S0 TO S1 transitions [22]. This peak arises due to the transitions from aiu to eg. There are other factors that are known to affect the uv-vis spectra of phthalocyanine molecules and these include metalation, nature of ring substituents, solvent effects and symmetry (mono, di, tri, tetra or octa-substitution). The charge transfer band observed between 450 nm and 500 nm is due to the charge transfer from the ligand to the metal.

4.2.3 Analysis of Alkyd Resin Using UV-VIS.

The Alkyd resin was analysed using UV-VIS spectroscopy and DMF was used as the solvent and also as the blank. The resin was analysed in the range from 300 nm to 800 nm which was the same range that was used to analyse the metallophthalocyanine compounds as shown in fig 4.2. The UV-VIS results showed a band of high absorbance at 320 nm this band is due to the π-π^* transitions. Low absorbances were observed in the blue range but however slight increase in absorbance was observed in the red region which attributes to the gold colour of alkyd resin [27].

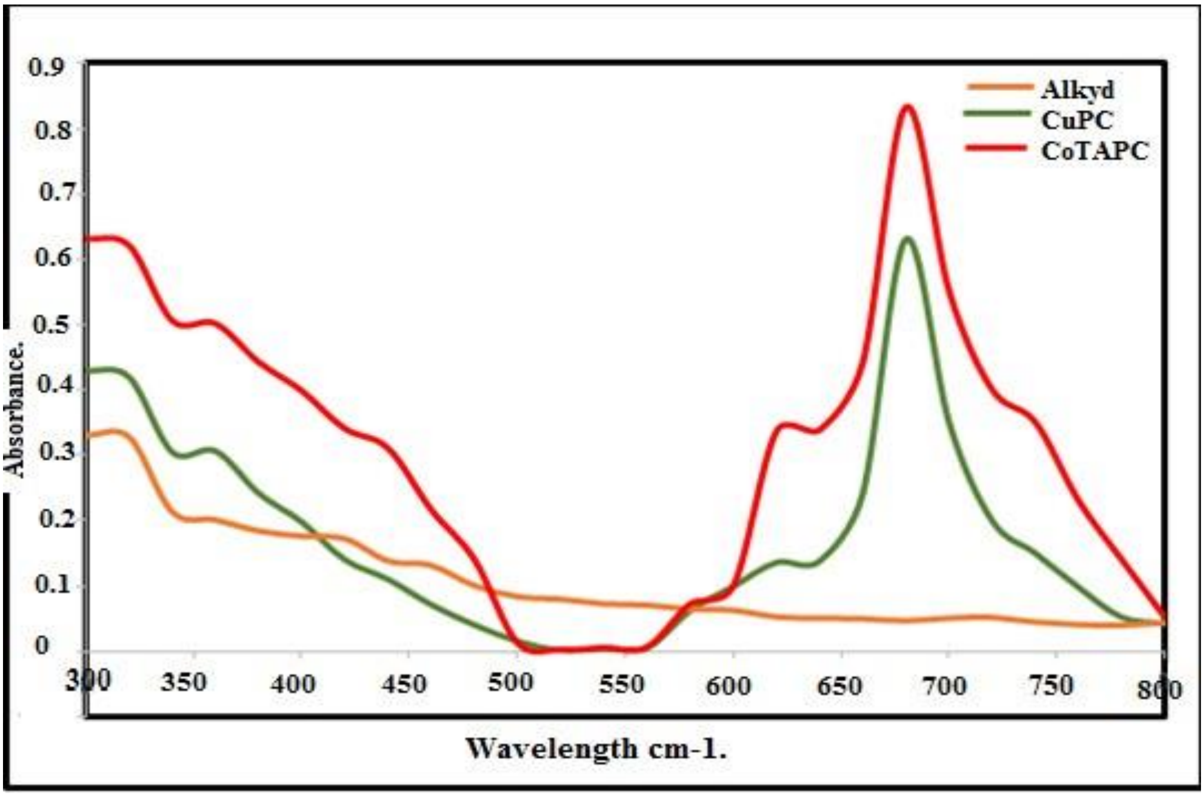

Figure 4.2 Ultraviolet visible spectra of CuPc, CoTAPc and Alkyd Resin.

4.3 Thermal Gravimetric Analysis.

4.3.1 TGA of Copper(II)phthalocyanine.

Thermogravimetric analysis (TGA) was used to determine the copper(II)phthalocyanine's thermal stability and its fraction to volatile components by means of monitoring the weight change that occurred as the sample was being heated [10]. The TGA was used so as to observe if copper(ii)phthalocyanine is stable at curing temperature. The results showed a decrease of weight at temperatures below 200 ^oC as shown in figure 4.3. This attributed to water loss resulting in the decrease in weight. After the water was lost the stability of the solid copper(II)phthalocyanine was observed up to 350 ^oC. The degradation was not observed since the curing temperature was not able to produce the degradation [46,47].

4.3.2 TGA of CuPc and Alkyd Resin.

The formulated paint of CuPc and Alkyd was analysed using TGA. The technique was used to monitor the degradation as a function of weight loss. A slight decrease in weight was observed at 130 ^{o}C this decrease is due to the loss of low molecular weight solvent xylene that was used as the thinning solvent. The temperature was increased gradually and a significant percentage weight loss was observed at 340 ^{o}C this is due to the decomposition of the phthalocyanine compound. Further analysis was carried out and this was done in order to determine the decomposition of the alkyd resin the decomposition was observed at 430 ^{o}C where the weight loss was observed. Generally the TGA showed the percentage weight loss of the solvent, CuPc and Alkyd Resin [47].

4.3.3 TGA of CoTAPc and Alkyd Resin.

The formulated paint that contained the covalently linked alkyd resin and CoTAPc was also analysed by thermal gravimetric analysis. The result from the analysis showed a slight decrease in percentage loss at 158 ^{o}C due to the loss of the solvent DMF. Further analysis was done on the product and decomposition was observed at 300 ^{o}C. This is due to the decomposition of CoTAPc, another decomposition was observed at 340^{o}C due to the decomposition of alkyd Resin [20].

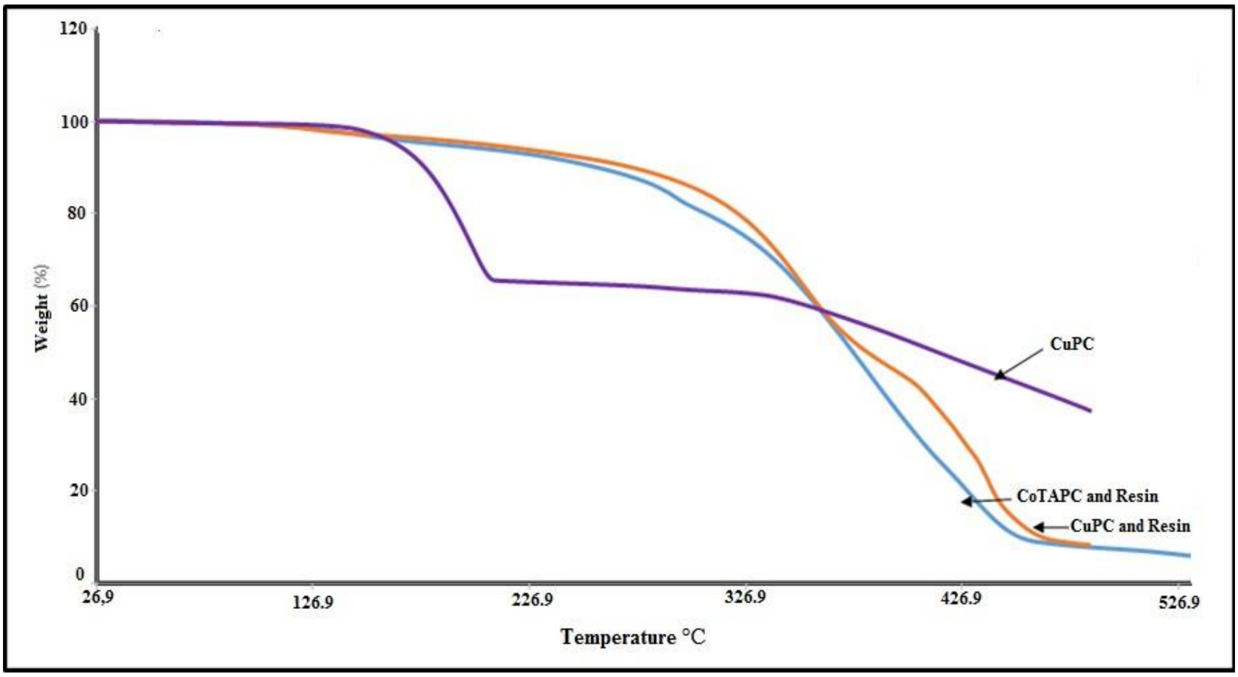

Figure 4.3 TGA of CuPc, CuPc with alkyd resin and CoTAPc with Alkyd Resin.

4.3.4 DSC of Alkyd Resin.

Differential Scanning Calorimetry was used for the thermal analysis to investigate how the synthesised alkyd resin was transformed by temperature as shown in figure 4.4. The variations in the heat capacity of the alkyd resin sample were observed as alterations in the heat flow. The obtained information allowed to reveal the melting point of the alkyd resin. The endothermic peak was observed at 130 ^{o}C this peak resembles the melting point of the alkyd resin [27]. The glass transition temperature was observed at 50 ^{o}C in the endothermic region, but however the decrease in the heat flow was not properly visible. The degree of crystallisation was not observed because the curing temperature was set at 150 ^{o}C. However, a slight rise in heat flow was observed at 140 ^{o}C [2].

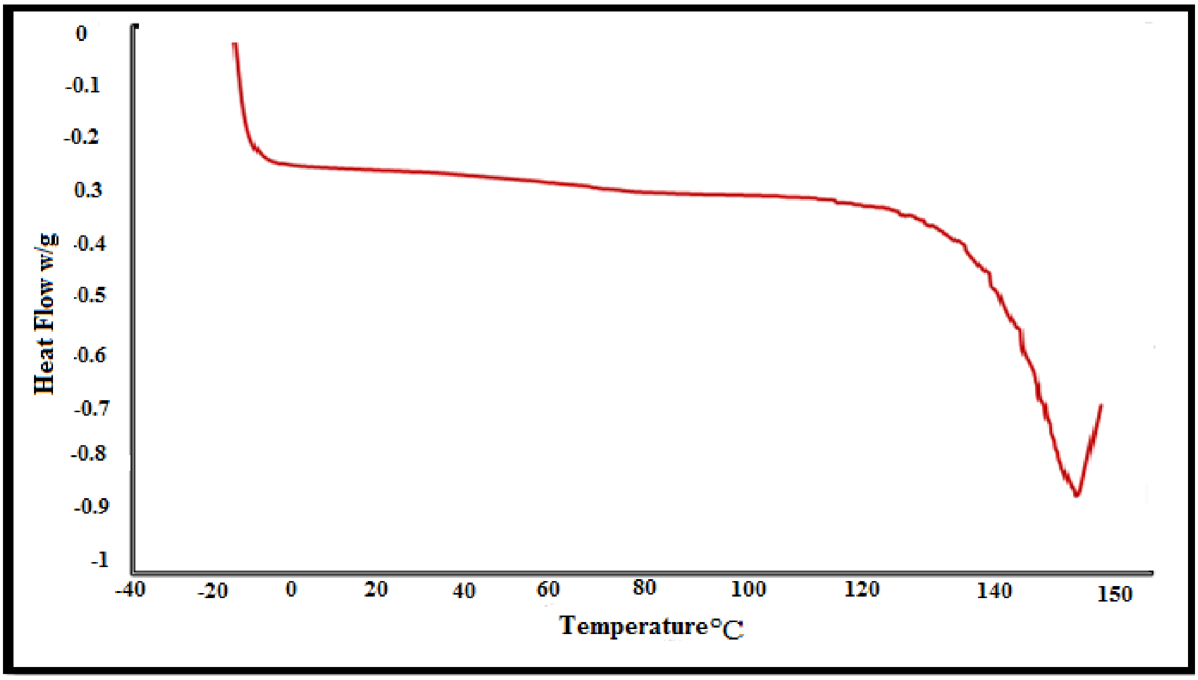

Figure 4.4 DSC Alkyd Resin.

4.4 Acid Value.

The acid value was determined after every 6 minutes during the course of the reaction as shown in figure 4.5. The procedure was carried out until the acid value was below 15[48]. The acid value dropped to 9.6 mg of KOH per gram of resin after 78 minutes which is generally faster than the time which is taken at the plant which ranged between 90-100 minutes. This is because the laboratory set up is easier to control due to size as compared to the industrial plant setup [34].

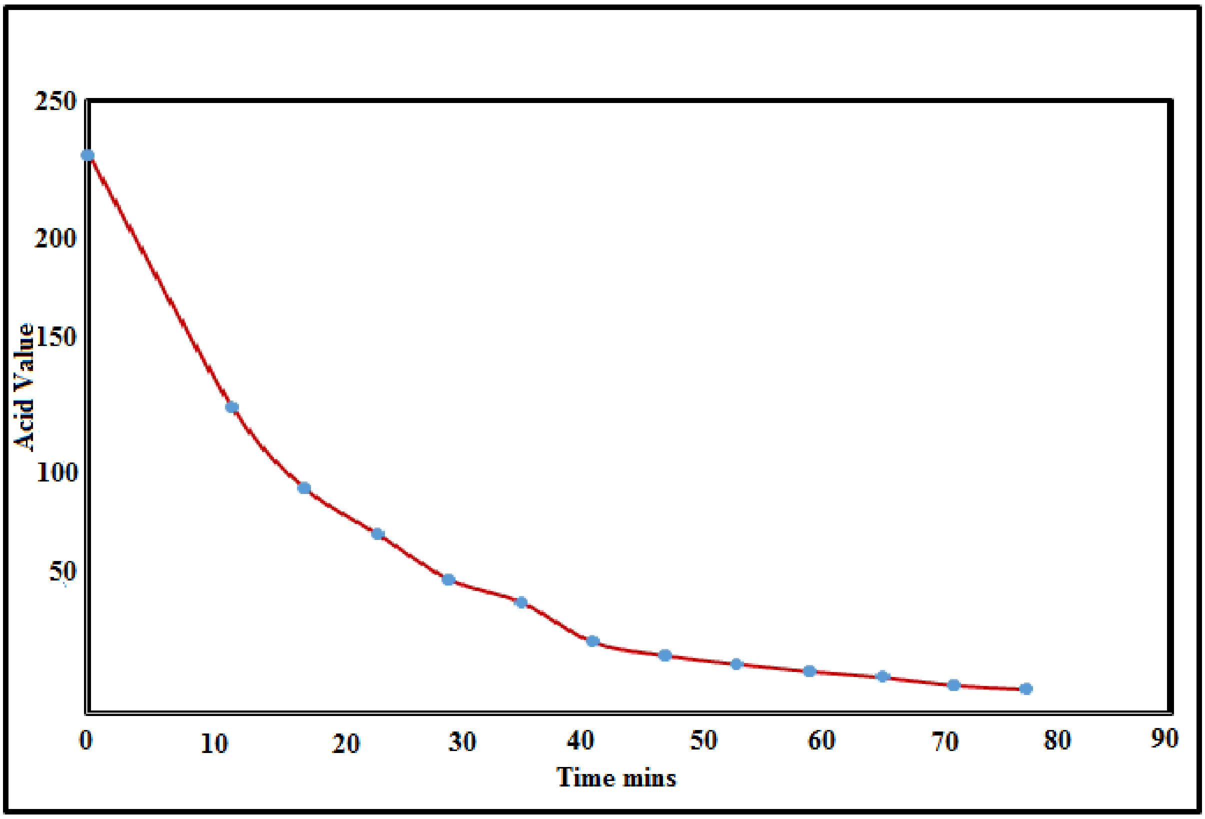

Figure 4.5 Acid Value.

4.4.2 Yield.

$$\text{Yield}=\frac{\mathit{Actual\ yield}}{\mathit{Theoratical\ Yield}}$$

Theoretical yield= Input – Water

$$\text{Water of Reaction} = \frac{\mathit{Acid\ Quantity}}{\mathit{Molecular\ Weight}}\, x\ 18$$

Water of Reaction = 0.1816 x 18

= 3.2688g

Theoretical Yield = 106.3 – 3.2688

= 103.0312.

Assumption all the water was vapoured out.

Percentage Yield = $\frac{86.2}{103.0312} x100$

$= 83.7\%$

The decrease in the yield could have been caused by the loss of raw materials during the heating process. The prolonged heating time could also result in side reactions occurring negatively effecting on the yield of the alkyd resin product.

4.5 Quality Control Test.

4.5.1 Colour of Alkyd Resin.

The colour of the synthesised alkyd resin was analysed visually using a Gardner scale. The standards that were used were Akzonobel Dulux standards. The expected colour range is a maximum of 6-7 on the Gardner scale, with anything lower than that being highly accepted. The synthesised alkyd resin was placed in the Gardner tube and was found to lie in the range of 4-5. The result proved that the alkyd resin can be used even for the production of white paints along with white pigments such as titanium dioxide and also it works with other coloured pigments such copper(ii)phthalocyanines [34].

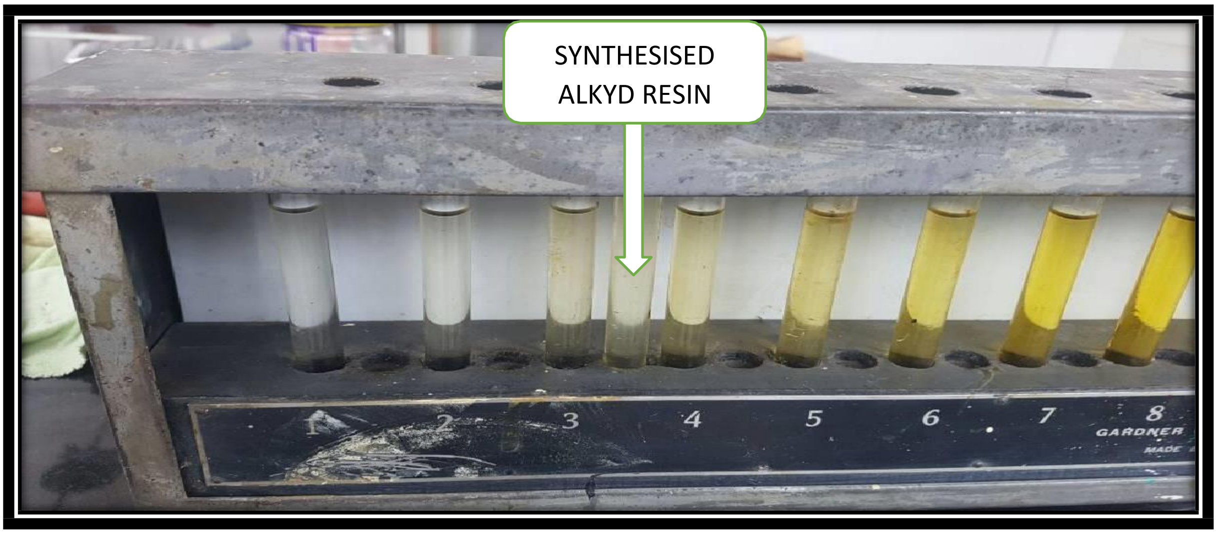

Figure: 4.6 Colour of Alkyd Resin.

4.5.2 Solids of Alkyd Resin.

The synthesised alkyd resin was analysed for solids. The weighed masses of the resin were place in an over at 60 ^oC in metal crucibles. The samples were withdrawn after 2 hours and then cooled. The weight of the remaining solids was used to calculate the solids of the resin. The solids were found the 61.3 %. The percentage solids were found to be in the range expected by paint standards of 59-61 % solids. The percentage solids resemble the amount of solids that remain on the substrate after the paint dries. It also shows that the resin has 38.7 % volatiles [8,35].

4.6 Paint Formulation.

The paint was formulated using both CuPc and CoTAPc in Alkyd Resin. The formulated paint was subjected to sunlight for degradation studies. The studies were carried out using UV-VIS. The analysis was done after each period of exposure.

4.7 Degradation Studies.

4.7.1 Degradation Studies of CuPc and Alkyd Resin.

The formulated paint was exposed to sunlight for the 3 days before analysis by UV-VIS. From the studies 5 spectras were obtained shown in figure 4.7. The solution was taken from the bulk and a dissolved in DMF. The general increase in absorbance was observed. This was attributed due to the solvent loss that resulted in increase in concentration. The solvent was lost on exposure to light since the studies were done on the paint in solution form. The normalisation of the graphs was done in order to compare the spectra if there were any new peaks that were observed. The new peaks are attributed to the formation of new compounds after the exposure to sunlight. The Q band was observed around 680 nm in all cases of the exposure and this peak is attributed to the transition from S0 to S1. The Soret band also maintained its position around 300-400 nm and this shows that the conjugated double bonds are still present in the structure which are alternating single and double bonds the peak results from transitions from π-π^*.

4.8.2 Degradation Studies of CoTAPc and Alkyd Resin.

The covalently linked CoTAPc and Alkyd Resin was analysed using UV-VIS to monitor the degradation after exposure to sunlight. The analysis was done after 3 days of exposure. There was a slight increase in absorbance due to the slight loss in solvent as shown in figure 4.8. The general trend in the peaks was maintained and this was due to absence of new compounds formed. The soret band and the Q band were observed at 300-400 nm and 680 nm respectively. The Soret band is due to the π-π*. The degradation studies were carried out in solution form which is the less stable form of the paint as compared to the solid form. The solution has advantages since the slight changes in structure can be monitored [49].

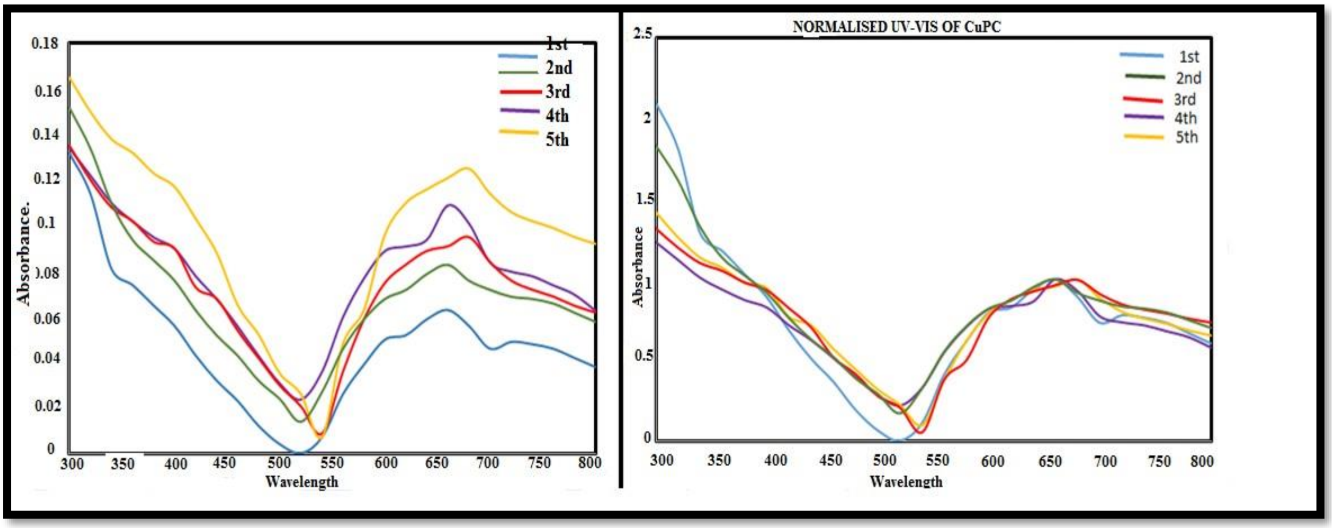

Figure 4.7 Degradation Studies of CuPc and Alkyd Resin and Normalised spectra.

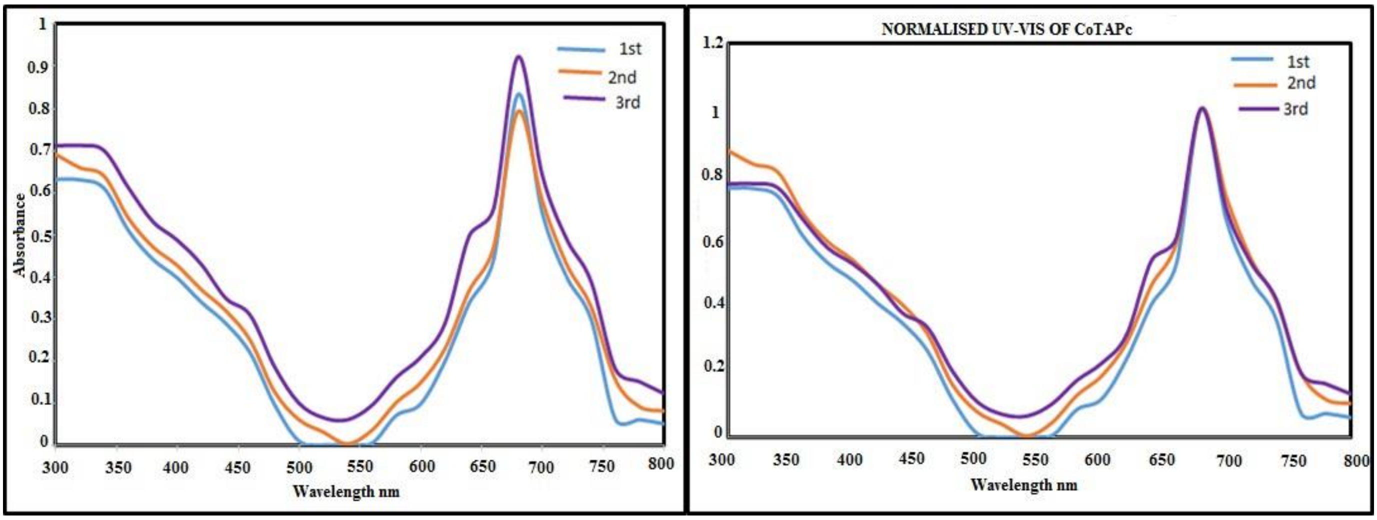

Figure 4.8 Degradation Studies of CoTAPc and Alkyd Resin.

CHAPTER 5.

CONCLUSION AND RECOMMENDATIONS.

5.1 Conclusion.

Two paints have been prepared using deodorizer based alkyd resin and two different metallophthalocyanes. The alkyd resin which was synthesised using the solvent method was linked non covalently to the synthesised copper(II)phthalocyanine which is not functionalised. Covalent linking was used to link the synthesised cobalt(II)tetraamino phthalocyanine which is functionalised to the deodorizer based alkyd resin with the aid of thionyl chloride. The synthesised phthalocyanine molecules copper(II)phthalocyanine and cobalt(II)phthalocyanine had blue and green colours respectively, this was further confirmed by the UV-Vis spectroscopy. All the synthesised products were characterised using FT-IR and UV-Vis spectroscopy. Quality control tests were also carried out at Dulux Limited for analysis of the alkyd resin. The formulated paints were exposed to sunlight for photo degradation studies that were carried out using UV-Vis Spectroscopy.

5.2 Recommendations.

According to the quality control tests that were carried out at Dulux Limited the synthesised resin in the required specifications, but however the drying time was longer than anticipated. The expected drying time was 4 hours but however the resin dried at 5 hours 50 minutes. This result shows the importance of driers as additives to reduce the resin drying time. The metallophthalocyanines and the alkyd resin showed good stability to thermal decomposition. This shows that the formulated paints can be used in the formulation of industrial coatings but however the paint cannot be applied in areas that exceed 300 ^oC to avoid degradation of the paint.

The degradation studies also showed the importance UV-Vis stabilizers in small quantities because the paint showed good stability on exposure to sunlight. The stabilizers are important to avoid photo degradation.

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APPENDIX

APPENDIX A: MATERIALS

List A1: Apparatus used for the study.

Beakers, volumetric flasks, spatula, sample bottles, funnels, weighing crucibles, Erlenmeyer flask, Buchner funnel, water bath, hot plate, measuring cylinders and syringes.

Table A.1: Reagents and chemicals.

NAME	**CHEMICAL FORMULAE**	**MANUFACTURER**	**MASS/ VOL**
Phthalic Anhydride.	$C_8H_4O_3$	A.I Davis	10.5 g
Urea	CH_4N_2O	Sigma Aldrich	47.9 g
Ammonium Molybdate	$(NH_4)_2MoO_4$	Sigma Aldrich	1.25 g
Copper(II)chloride.	$CuCl_2$	A.C.E	12.6 g
Ethanol.	C_2H_5OH	Skylabs	300.0 ml
Sodium Hydroxide.	NaOH	A.C.E	500.0 ml
Hydrochloric acid	HCl	Skylabs	500.0 ml
Pentaerythirol	$C_5H_{12}O_4$	A.I Davis	12.9 ml
Xylene.	C_8H_{10}	A.I Davis	600 ml
Dimethyl Formamide	C_3H_7NO	A.C.E	650 ml
Methanol	CH_4O	Sigma Aldrich	10 ml
Nitrophthalic Acid.	$C_8H_5NO_6$	Skylabs	10.0 g
Cobalt Sulphate.	$CoSO_4$	A.C.E	7.5 g
Ammonium Chloride.	NH_4Cl	A.C.E	5.0 g
Nitrobenzene.	$C_6H_5NO_2$	A.C.E	15.0 ml

Pottasium Hydroxide	KOH	Springfield	80.0 ml
Sulphuric Acid	H_2SO_4	Springfield	65.0 ml
Distilled Water	H_20	Msu labs	-

Table A.2: Instrumentation

NAME.	**MODEL.**	**MANUFACTURER.**	**USE.**
Analytical balance.	GA-110	OHAUS	WEIGHING
Ftir Spectroscopy	Nocolet 6700	Thermoscientific	Characterisation
TGA/ DSC	TGA 550 DSC 25	Tain instruments.	Characterisation
UV-Vis	UV-1700	Shimadzu	Characterisation

Cleaning of glassware.

Glassware was cleaned using liquid soap detergent and was then rinsed using distilled water. Organic stains on glassware were cleaned using aqua-regia, a 3:1 mixture of concentrated HCl and HNO_3 acids.