

**DEVELOPMENT OF NEW ORGANIC WOOD
PAINTS WITH LIGNIN AS ADDITIVE**

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**DEVELOPMENT OF NEW ORGANIC WOOD
PAINTS WITH LIGNIN AS ADDITIVE**

by

ASNIZA BINTI MUSTAPHA

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LIST OF ABBREVIATIONS

AQ	Anthraquinone
AD	Air Dry
BP	Boiling Point
C	Control
CA	Contact Angle
CCA	Copper Chrome Arsenic
DMF	<i>N,N</i> -Dimethylformamide
EFB	Empty Fruit Bunch Fiber
EMC	Equilibrium Moisture Content
FT-IR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
LA	Aromatic Lignin-based Paint
LB	Heterocyclic Lignin-based Paint
MA	Maleic Anhydride
MC	Moisture Content
NMR	Nuclear Magnetic Resonance Spectroscopy
NA	Aromatic Non-Lignin Paint
NB	Heterocyclic Non-Lignin Paint
OD	Oven Dry
OL	Oil Length
OPB	Oil Palm Biomass
PA	Phthalic Anhydride
PAP	<i>p</i> -Aminophenol

PF	Phenol-Formaldehyde
PVC	Pigment Volume Concentration
RT	Room Temperature
SEM	Scanning Electron Micrograph
UV/Vis	Ultraviolet/Visible Spectrophotometer

PEMBANGUNAN CAT ORGANIK BARU UNTUK KAYU MENGGUNAKAN LIGNIN SEBAGAI ADITIF

ABSTRAK

Lignin telah digunakan sebagai aditif dalam penyediaan cat organik baru. Soda lignin diekstraks daripada likor hitam yang diperolehi melalui pemulpaan soda-AQ (anthraquinon) gentian tandan buah kelapa sawit kosong (EFB) secara pemendakan asid sulfurik berkepekatan 20%. Dua jenis pigmen azo iaitu fenil-azo-2-naftol dan 4-Hidroksifenilazo-3-N-(4-hidroksifenil)maleimida disintesis melalui tindak balas gandingan azo. Pigmen azo aromatik iaitu fenil-azo-2-naftol dihasilkan daripada tindak balas garam diazonium (fenildiazonium klorida) dengan 2-naftol tulen sebagai agen gandingan manakala agen gandingan heterosiklik baru iaitu, N-(4-hidroksi-fenil)maleimida disintesis melalui tindak balas antara maleik anhidrida dan *p*-aminofenol dengan kehadiran di-fosforus pentoksida (P_2O_5) sebagai pemangkin. Agen gandingan tersebut kemudian melalui tindak balas dengan amina aromatik (*p*-aminofenol) untuk menghasilkan pigmen azo heterosiklik baru iaitu, 4-Hidroksifenilazo-3-N-(4-hidroksifenil)maleimida. Resin alkid yang bertindak sebagai pengikat dihasilkan daripada tindak balas antara minyak soya, ftalik anhidrida dan gliserol melalui kaedah alkoholisis. Ciri-ciri dan struktur sebatian-sebatian ini dikenalpasti dengan menggunakan Spektroskopi Inframerah (FT-IR), analisis elemen (CHN), Spektroskopi Resonans Magnetik Nuklear (1H -NMR, ^{13}C -NMR), Spektroskopi Ultraungu/Nampak (UV/Vis) dan analisa sinar-X kristal tunggal. Perbandingan sifat antara cat organik yang berasaskan lignin dan tidak berasaskan lignin bagi kedua-dua sistem heterosiklik dan aromatik kemudian

dijalankan melalui ujian-ujian fizikal dan mekanikal untuk mengenalpasti prestasi setiap sistem. Ujian sebelum aplikasi cat ke atas substrat meliputi ujian kelikatan, kandungan bahan terlarut, kadar penyebaran, kilauan, ujian kelegapan dan ujian tempoh pengeringan permukaan manakala ujian kelekatan, mikrograf elektron imbasan, sudut sentuh, kadar penyerapan air dan ketahanan cuaca ditentukan selepas aplikasi cat pada substrat. Selain itu, ujian kekerasan dan kelenturan cat juga dikaji dengan menggunakan pendulum, kekerasan pensil dan impak hentaman. Keputusan ujian menunjukkan bahawa darjah penyebaran kesemua sistem cat sesuai untuk digunakan sebagai cat asas atau cat primer. Kajian ke atas panel kayu membuktikan bahawa penggunaan lignin sebagai aditif memberi kesan positif terhadap tempoh pengeringan, kelekatan, serta sifat penyebaran dan daya penutupan cat. Di samping dapat mengurangkan kadar penyerapan air, kehadiran lignin di dalam cat juga memberi ketahanan yang baik kepada panel kayu apabila didedahkan kepada persekitaran luar. Selain itu, cat berasaskan lignin juga menunjukkan keputusan yang lebih baik berbanding cat yang tidak berasaskan lignin bagi kedua-dua ujian kekerasan dan ujian kelenturan.

DEVELOPMENT OF NEW ORGANIC WOOD PAINTS WITH LIGNIN AS ADDITIVE

ABSTRACT

Lignin has been used as additive in preparation of the new organic paints. Soda lignin was extracted from black liquor of soda-AQ (anthraquinone) pulping of oil palm empty fruit bunch (EFB) fibers by 20% sulfuric acid precipitation. Two different types of azo pigment namely, phenyl-azo-2-naphthol and 4-Hydroxyphenylazo-3-N-(4-hydroxyphenyl)maleimide were synthesized by azo coupling reaction. Phenyl-azo-2-naphthol which was represented as aromatic azo pigment was produced from the reaction of diazonium salt (phenyldiazonium chloride) with pure 2-naphthol as the coupling agent whereas a new heterocyclic coupling agent namely, *N*-(4-hydroxy-phenyl)maleimide was synthesized by the reaction of maleic anhydride and *p*-aminophenol in the presence of di-phosphorus pentoxide (P₂O₅) as a catalyst. The coupling agent was then undergone a reaction with aromatic amine (*p*-aminophenol) to produce a new heterocyclic azo pigment, 4-Hydroxyphenylazo-3-N-(4-hydroxyphenyl)maleimide. Alkyd resin, as the binder was obtained from the reaction of soya oil, phthalic anhydride and glycerol by alcoholysis process. The characteristics and structural features of these compounds were confirmed by Fourier Transform Infrared Spectroscopy (FT-IR), CHN elemental analysis, Nuclear Magnetic Resonance Spectroscopy (¹H-NMR, ¹³C-NMR), Ultraviolet/Visible (UV/Vis) Spectroscopy, and single crystal X-ray analysis. A comparison study between lignin-based paint and non-lignin paint films on wood for both aromatic and heterocyclic system was then performed through paint testing

to examine their physical and mechanical performance. Testing prior to application includes viscosity, solid content, degree of dispersion, gloss, opacity and surface drying time whereas adhesion, SEM, contact angle, water absorption and weathering were determined after application of the paints on the substrates. Furthermore, the hardness and flexibility of the paints were also studied by pendulum hardness, pencil hardness and impact test, respectively. Results indicated that the degree of dispersion of all paint systems were suitable for use as an undercoat or primer. Studies on wooden test panels proved that the incorporation of lignin as additive led to significant improvements in the drying time, adhesion, as well as better hiding and obliteration. Notably, the presence of lignin in the paint has reduced the water uptake of wood substrates in total immersion tests and also possessed good resistance when exposed to outdoor. In addition, the lignin-based paints also showed superior results than that of lignin-free paints for both hardness and flexibility tests.

CHAPTER 1

INTRODUCTION

1.0 General

Wood is a hard, fibrous tissue that built up from cellulose, hemicelluloses and lignin. It is widely applied for millennia as industrial raw material for many purposes, primarily as a fuel, construction production and decoration purposes (Briffa *et al.*, 2008; Ontario, 1993). Wood is our most important raw material not only because it is versatile, but also because it is a renewable natural resource. Through careful planning and use, forests will provide a perpetual supply of wood. Besides their durability, versatility and aesthetical value, wood is an extremely variety material with a wide range of physical and mechanical properties than those of competitive materials such as steel, concrete, or plastic (Jerrold, 1994; Wagner, 2004). It possesses timeless beauty and lovely works of wooden decor by displaying the elegance and appearance of the color, grain and the texture. Thus, with these many encouraging properties as well as being renewable, it is extensively used for literally hundreds of products (Bowyer *et al.*, 2003; Pandey, 1999; Williams, 2004).

However, the biodegradable property, sensitivity to moisture and light, deteriorates on continued exposure to mild conditions as well as microorganism attack such as fungus and insects are the major drawback in the use of wood materials for construction and decorative applications (Goodell, 2008; Highley, 2004; Schultz and Nicholas, 2002). Exhibits hygroscopic property, wood can absorb and desorbs water quickly, causing swelling and shrinking thus lead to dimensional changes (Rowell *et al.*, 2008). In addition, enzymatic decomposition of cellulose and hemicelluloses in wood is restrain by lignin, which acts as the physical barrier can be

destroyed mechanically by insects and marine borers and biochemically by bacteria, white-, brown- and soft-rot fungi (Kirk and Cowling, 1984). Fungi cause serious strength loss, whereas bacteria affect wood permeability by altering the wood structure to predispose wood to fungal attack (Clausen, 1996).

Thus, there are a number of different coatings and preservatives that formulated by tremendous researchers around the world in order to prolong the service life of wood. Wood usually coated or painted by various decorative and protective finishes to provide desired aesthetical properties like color and gloss but is mostly a vital importance in the protection of the wood materials against environmental influences like moisture, radiation, biological deterioration or damage from mechanical or chemical origin (Ahola, 1991; Meijer, 2001; Schaller and Roger, 2007; Schurr, 1976). On the other hand, wood is generally treated by chemical preservatives such as water-borne preservatives and oil-borne preservatives for example, copper-chrome-arsenic (CCA), boric acid and linseed oil. However, the chemical preservatives are commonly said to raise problems to the environment in terms of human health and the environment itself. For example, CCA, which is widely used to prevent decay by fungus and insects (Kartal and Clausen, 2001; Yamamoto and Hong, 1988) is proved to be harmful to human being as it do leach out and gather on the ground underneath or transferred by direct hand contact. Besides, improper disposal of treated wood also contribute to hazardous problem as the burning CCA-treated wood will release a large amount of arsenic into the air. It also caused fatalities in plants, animals (Patricia *et al.*, 2008) and serious poisoning in human (Mandal and Suzuki, 2002) either by direct or indirect breathing of the wood ash. Furthermore, there is a possibility that the harmful preservatives being absorbed into the soil and contaminate the underground water source that flow to

dwelling (Dickey, 2010; Grant and Dobbs, 1977; Kartal *et al.*, 2007; Kazi and Cooper, 2002; Mohan *et al.*, 2007; Robinson *et al.*, 2006).

In the case of paint, additives are commonly added to improve performance, processing and productivity. Types of additives include surfactant, catalyst, thickener, stabilizer, emulsifier, UV stabilizers, biocides, and the like (Kumar and Kumar, 2009) as for example, titanium dioxide (Colling and Dunderdale, 1981; Krebs, 2006; Stevens *et al.*, 1998; Topuz *et al.*, 2011) and zinc oxide (Guedri *et al.*, 2004; Moustaghfir *et al.*, 2004). Apart from this, ecological concerns have generated increasing interest in products based on renewable resources. Thus, natural fibers and biodegradable polymers such as lignin are considered to be environmentally desirable alternatives to artificial materials. Lignins in particular possess highly reactive locations that can be extensively modified through various chemical, physical and/or enzymatic reactions (Gosselink *et al.*, 2004). They are proved to be versatile additives for many industries where their uses have been expanded to hundreds of applications in agricultural, ecological, food and even health applications (Antonsson *et al.*, 2008; Canetti and Bertini, 2007; Ghosh *et al.*, 1999; Gosselink *et al.*, 2004; Lora and Glasser, 2002; Mishra *et al.*, 2007; Mozaffar *et al.*, 2004; Patricia *et al.*, 2002; Samuelson, 2001; Suhas and Ribeiro, 2006; Vinardell *et al.*, 2008).

However, to date, few reports describing the addition of soda lignin in paint have been found in the literature. As the easy and cheapest lignin resources are from oil palm biomass (OPB), large amounts of lignin is easily available as the oil palm empty fruit bunch (EFB) fibers are abundant in Malaysia where there are over 300 crude palm oil mills that generate more than 30 million tons of the lignocellulosic biomass annually (Mohamed and Lee, 2006; MPOB, 2009). Thus, fragmented and

derivated forms of lignin can be generated in vast quantities from spent liquors as a by-product of EFB fibers pulping. Due to the increasing competition between different building materials, it is important that the durability of wood be extended. Also, it is necessary to determine the performance of new paint formulations due to the length of service-life trials. Therefore, the aim of this research project was to examine the effect of soda lignin in wood paint formulations, with the expectation that its inclusion would improve the properties of the paints.

1.1 Objectives

The above aims are achieved through fulfilling the objectives as follows:

1. To synthesize and characterize aromatic azo-pigment and a new heterocyclic azo-pigment.
2. To prepare new organic paints based-lignin and non-lignin.
3. To investigate the influence of lignin on the physical and mechanical properties of the paints.
4. To study the SEM of the paint based-lignin and non-lignin.

1.2 Thesis Layout

This thesis consists of seven chapters. Chapter 1 is the introduction, which covers the progress and inherent issues, problem statement, research goals and scope of this research. Chapter 2 explains the literature survey, whereas Chapter 3 details out the research methodology. Furthermore, Chapter 4 presents the structural elucidation of the synthesized materials by various spectroscopic techniques. Subsequently, the paint analyses for both physical and mechanical properties are discussed in Chapter 5 and 6, respectively. Lastly, Chapter 7 concludes this research and lists out suggestions for further investigation.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

There are four major components of paint formulation which are binder, pigment, solvent and additive. The formulation of paint is largely dictated by the intended application. Thus, paint systems for timber, metals, masonry, etc., may differ markedly from each other, and coatings designed primarily to protect can be formulated on different principles from those that apply to coatings whose function is largely cosmetics. Therefore, this chapter covers the fundamental of the paint formulation as well as general properties of paint system that found in the literature.

2.1 Lignin

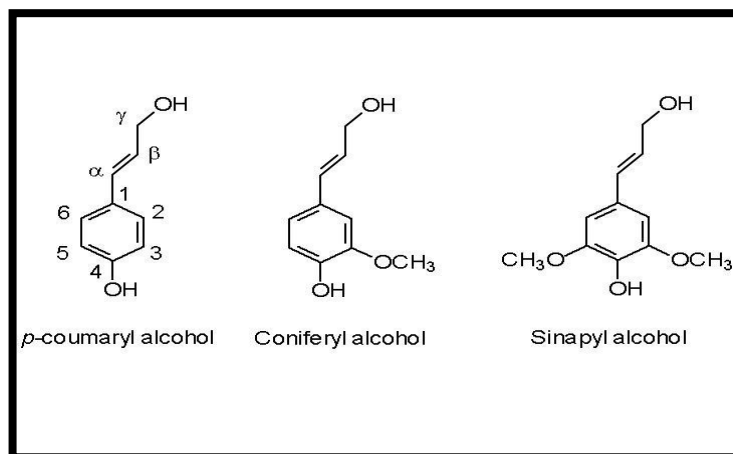
Lignin is a brown colored complex aromatic chemical compound most commonly derived from wood and an integral part of the cell walls of plants (Lebo *et al.*, 2001). The term was introduced in 1819 by de Candolle and is derived from the Latin word *lignum*, meaning wood (Sjostrom, 1993). It is the most abundant organic polymer on Earth after cellulose, employing 30% of non-fossil organic carbon (Boerjan *et al.*, 2003) and constituting from a quarter to a third of the dry mass of wood. Lignin fills the spaces in the cell wall between cellulose, hemicelluloses and pectin components, especially in tracheid, sclereid and xylem. It is covalently linked to hemicellulose and thereby cross-links different plant polysaccharides, conferring mechanical strength to the cell wall and by extension the plant as a whole (Chabannes *et al.*, 2001). The amount of lignin in plant varies widely, and is

normally in the range of 20% - 30% by weight.

According to Merdy *et al.*, (2002), lignin is natural polymer that is biologically produced through random polymerization process. Its structure is not fully known which makes it difficult to study. It is linked through carbon-carbon (C-C) and ether (C-O-C) bonds to form macromolecule lignin (Fengel and Wenger, 1989; Roger, 1984; Sarkanen and Ludwig, 1971; Sjostrom, 1981). This macromolecule is highly ramified and forms a three-dimensional structure, which depends not only on the type but also on the growing condition of plant (Lara *et al.*, 2003).

2.1.1 Structure of Lignin

The elucidation of its chemical structure has been a formidable task, requiring almost 140 years of effort by some of the world's finest natural products chemists. The compound has several unusual properties as a biopolymer, not least its heterogeneity in lacking a defined primary structure. It has been recognized for over 50 years as an amorphous, three-dimensional, aromatic polymer composed of oxidative coupling of three major C₆-C₃ phenylpropanoid units. It is formed at the sites of lignification in plants by enzyme-mediated polymerization of three substituted cinnamyl alcohols: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol as shown in Scheme 2.1 (Sarkanen and Ludwig, 1971; Suhas and Ribeiro, 2006).



Scheme 2.1: Structure of the three lignin precursors

These are incorporated into lignin in the form of the phenylpropanoids *p*-hydroxyphenyl (H), guaiacyl (G), and syringal (S), respectively. Gymnosperms have lignin that consists almost entirely of G with small quantities of H. That of dicotyledonic angiosperms is more often than not a mixture of G and S (with very little H), and monocotyledonic lignin is a mixture of all the three. Many grasses have mostly G, while some palms have mainly S. All lignins contain small amounts of incomplete or modified monolignols, and other monomers are prominent in non-woody plants (Belgacem *et al.*, 2003; Roger, 1984; Sjostrom, 1981).

The lignin composition will be different not only between plants of different genetic origin, but also between different tissues of an individual plant. In softwood lignin, the structural elements are predominantly derived, for more than 95%, from coniferyl alcohol. In hardwoods, various ratios of coniferyl/sinapyl alcohols have been observed, whereas in lignin derived from cereal straws and grasses, the presence of coumaryl alcohol is typical (Lin, 1992). Wood tissues have quite high lignin contents since they are composed to a large extent of tracheids, vessels and fibers (Freudenberg and Neish, 1968). Hence, lignin is a large, cross-linked, and

racemic macromolecule with molecular masses over the range of 8000-11,000. Figure 2.1 shows the molecular weight distribution of the lignin fraction, which is isolated from the black liquor of the fiber pulping at pH 2.0 after isolation of the polysaccharide degradation products (RunCang *et al.*, 1998).

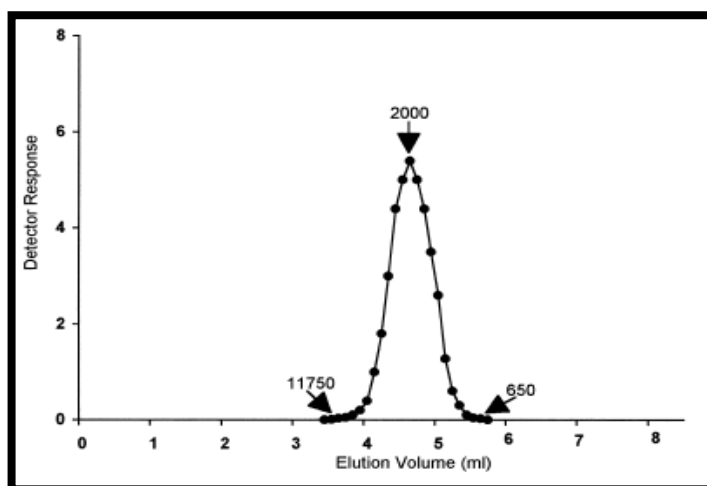
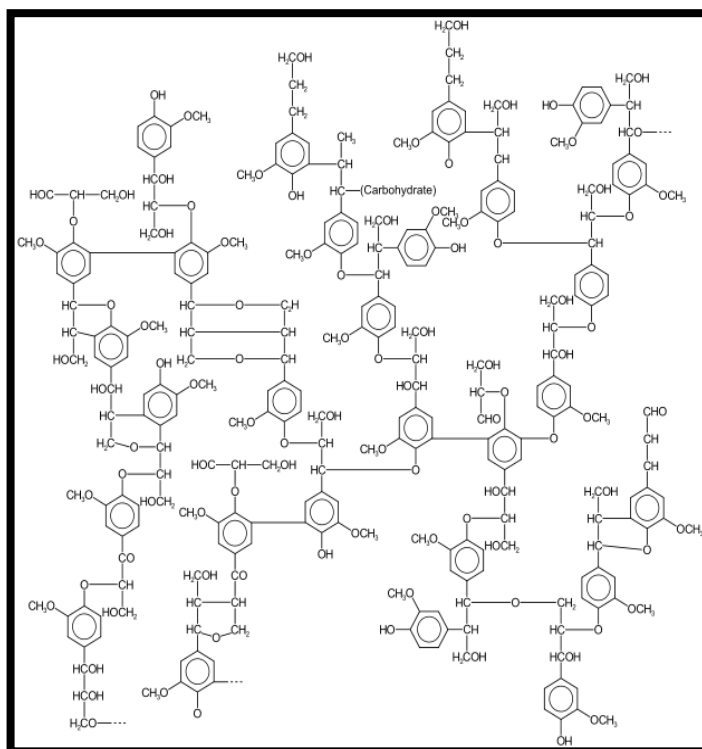


Figure 2.1: Gel Permeation Chromatography (GPC) molecular weight distribution of lignin fraction

Since lignins are very complex natural polymers with many random couplings, their exact chemical structure is not known although in present time there are many researches and analyses of data about the composition of lignin functional group (Gosselink *et al.*, 2004). However, this information still can not be summarized into simple formula because there are so many differences in between wood species and even in the same cell wall. It is unusual compared to other abundant natural polymers due to the low degree of order and the high degree of heterogeneity in its structure (Vinardell *et al.*, 2008). Scheme 2.2 shows an example of the possible lignin macromolecule structure.



Scheme 2.2: Lignin macromolecule

These aromatic biodegradable macromolecules perform a multiple function that is essential to the life of the plant by decreasing the permeation of water across the cell walls in the conducting xylem tissues. Lignin plays an important role in the intricate internal transport of water, nutrients and metabolites. Despite of this, in the admixture with hemicellulose, it forms the cementing material for cellulose fibrils and gives strength and rigidity to the structure elements of the plants (Mohamad Ibrahim *et al.*, 2004; Rohella *et al.*, 1996) and, in woody parts, act as permanent bonding agents between cells generating a composite structure outstandingly resistant towards impact, compression and bending. Besides, lignified tissues effectively resist attacks by pathogens, insect and other microorganisms by impeding the degradation of wall polysaccharides (Hatfield, 2005). In addition, the ability of lignin to strengthen and reduce the wettability of cellulose walls is considered to be essential for large erect terrestrial plants (Freudenberg and Neish, 1968).

2.1.2 Isolation of Lignin

In the last decades, new delignification processes have been developed which produce low-molecular weights lignins, soluble in common solvents. Among these processes, the most prominent are the organosolv and steam explosion refineries to remove lignins from plants (Goyal and Lora, 1991; Pye and Lora, 1991; Sederoff *et al.*, 1999). Commercial lignin is currently produced as a co-product of the pulp and paper industry, which separated from fibers by a chemical pulping process. Kraft lignins (also called sulfate lignins) are obtained from the kraft pulping process. The usefulness of commercial lignosulfonates product comes from their dispersing, binding, complexing and emulsifying properties. Industry first began to use lignins in the 1880s when lignosulfonates were used in leather tanning and dye baths. Since then, lignosulfonates have even found applications in food products, serving as emulsifiers in animal feed and as raw material in the production of vanillin.

2.1.3 Utilization of Lignin

Lignin by-products possess highly reactive locations that can be extensively modified through various chemical, physical and/or enzymatic reactions (Gosselink *et al.*, 2004). They are non-toxic and extremely versatile, inexpensive and available in large amounts. Differences in raw material, pulping and isolation conditions result in a highly heterogeneous macromolecular structure due to variations in lignin composition, molecular size, cross-linking and functional groups (Antonsson *et al.*, 2008; Rohella *et al.*, 1996). Lignins make versatile additives for many industries. It has the right chemistry to be used in making coatings and composites because they have small particle size, hydrophobic and have the ability to form stable mixtures. Their uses have been expanded to hundreds of applications in agricultural,

ecological, food and even health applications (Mozaffar *et al.*, 2004; Patricia *et al.*, 2002; Suhas and Ribeiro, 2006).

Many different formulation approaches have been explored in lignin-based thermoplastics (Canetti and Bertini, 2007; Ghosh *et al.*, 1999; Mishra *et al.*, 2007; Oliveira and Glasser, 1994) as well as in thermosetting resin (Lora and Glasser, 2002). For example, replacement of phenol by lignin into phenol-formaldehyde (PF) resin has been one of the primary areas of research in lignin utilization (Hse and Hong, 1989) due to the similarity between of the structure of lignin and phenol (Khan and Ashraf, 2007; Park *et al.*, 2008; Vazquez *et al.*, 1997). In other case, soda bagasse lignin used as a thermosetting adhesive gave acceptable adhesion of particleboard along with better mechanical and swelling properties (Haars *et al.*, 1989; Olivares *et al.*, 1988; Pizzi *et al.*, 1989).

This aromatic biodegradable macromolecules also been demonstrated as antioxidants, where it acts as free radical scavengers (Dizhbite *et al.*, 2004; Pan *et al.*, 2006; Vinardell *et al.*, 2007). Studies by Barclay *et al.*, (1997), Lu *et al.*, (1998), Satoh *et al.*, (1999), Schmidt *et al.*, (1995) and Triboulot *et al.*, (2000) have revealed the efficacy of lignins and some lignin related monomeric and dimeric compounds as antioxidants in different materials (rubber, wood, thermomechanical pulp), as well as medicines and dietary products.

In coating applications, it has been reported that lignin can be used in anti-corrosive coatings (Samuelson, 2001) and also in paper coating applications due to its hydrophobic properties (Antonsson *et al.*, 2008; Kolattukudy, 2002). It is also claimed that enzymes (e.g. peroxidases) and lignin derivatives (e.g. liginosulfonate) can be used for the protection or treatment of lignocellulosics, wood or paper-based products (Bolle and Aehle, 2001). Organosolv-derived lignins are also being

examined due to their superior solubility and thermal properties than that of sulphite or kraft lignins (Park *et al.*, 2008). It can be used as a filler in inks, varnishes, paints and vegetable oils (Belgacem *et al.*, 2003; Issam *et al.*, 2010; Nada *et al.*, 2000). Paints can be prepared through the enzymatic polymerization of lignin-based compositions (Bolle and Aehle, 2000).

Furthermore, lignin in particular has potential as a complexing and sorption agent (Digabel and Averous, 2006; Embree *et al.*, 2001; Lalvani *et al.*, 2000). Other applications include its use as stabilizers for oil in water emulsion, stabilizers for fire fighting foams, dye levelers, extenders in rubber compounding, briquette binders, dispersants in oil well drilling operations (Hoyt and Goheen, 1971), an additive in controlled release pesticides (Allan *et al.*, 1971), an additive in ion exchange resins (Nimz *et al.*, 1981; Psotta *et al.*, 1983) as well as soil stabilizer (Pearl, 1982).

2.1.4 Source of Lignin

The lignin which plays a part of additive in this paint manufacturing was obtained from the extraction of soda black liquor of oil palm empty fruit bunch (EFB) fibers. Section 2.1.4.1 and 2.1.4.2 ahead will discuss about the oil palm tree and EFB, respectively.

2.1.4.1 Oil Palm

Oil palm, *Elaeis guineensis*, originates from West Africa and was introduced into Southeast Asian countries in particular Malaysia and Indonesia for its oil-producing fruits. Malaysia is the world's second largest exporter of palm oil where it able to produce 17.7 million tons of palm oil on 4,500,000 hectares of land in 2008

(MPOB, 2008; MPOIP, 2009). As a source of palm oil, oil palm is one of the most important tree species in Southeast Asian countries such as Malaysia. The increasing in oil palm plantation areas has resulting in substantial residues within the replantation and harvesting sites (Sreekala *et al.*, 1997). Large quantities of this waste are left in the field as underutilized resources. It is estimated that overall, the oil palm industry generates at least 30 million tons of lignocellulosic biomass per year in the form of trunks, fronds, empty fruit bunches, and leaves (Abdul Khalil *et al.*, 2006; Sumathi *et al.*, 2008). These resources are not yet used effectively for instance, open burning and land filling is the common practices used to eliminate the oil palm residues.

The tree can reach to the height of 60-80 ft in nature, but is rarely more than 20 or 30 ft in cultivation. Trunks are stout, straight, about 1-2 ft in diameter, and grow about 1.5 to 3 ft per year. Its leaves are up to 25 ft in length, with leaflets numbering 200-300 per leaf, about 3-4 ft long and 1.5-2.0 inch wide, with entire margins. Leaf bases are persistent for years, and prominent leaf scars are arranged spirally on the trunk of mature palms where bases have fallen. Wild palms are said to reach 200 years of age, but cultivated palms are removed after about 25 years, when they reach about 30 ft in height since this presents difficulty in harvest. During replanting, an average of 7.45 tons per hectare of fibrous derivative of oil palm is generated. All these fibrous derivatives of oil palm can be fractionated, isolate and purify to obtain value added products. Extensive research has provided us with an alternative way of optimizing the usage of oil palm residues fiber based into value-added product.

For example, oil palm fiber is now considered to be one of the most promising non-wood lignocellulosic raw materials for the preparation of various

types of cost-effective and environment-friendly composite materials due to the rich in carbohydrates in the form of starch and sugar and containing cellulose, hemicelluloses and lignin (Murai *et al.*, 2009; Sulaiman *et al.*, 2009). Tanaka *et al.*, (2002) proposed an alternative form of utilization of empty fruit bunch in the production of cellulose pulp, or dissolving pulp which is used as raw materials of cellulose derivatives or regenerated cellulose.

2.1.4.2 Oil Palm Empty Fruit Bunch (EFB)

The oil palm industry produces not only crude palm oil as the main product, but also generates a huge amount of biomass in the form of trunks, fronds and empty fruit bunches (EFB) fibers. It is the part where the oil palm fruit attached. The fruit bunch is made up of a main stalk and numerous spikelets with sharp spines at their tips. The freshly sterilized EFB contain 65% water, 30% dry matter and 2-5% of crude palm oil. It has natural polymer, which is called lignocelluloses. EFB consisting of vascular bundles in which built of parenchyma tissues are similar to that found in the trunks and fronds. The vascular bundles of empty fruit bunches are quite springy and flexible. The main constituents of the lignocellulose are cellulose (45%), hemicellulose (32.8%) and lignin (20.5%) (Ridzuan *et al.*, 2002). The EFB fiber lignins can be considered as structurally more complex than wood lignins from the point of view that they are composed of syringyl and guaiacyl propane units together with small amounts of *p*-hydroxyphenylpropane units. It contains about 17.2% lignin, which is relatively low compare to hardwood or softwood (Sun *et al.*, 1999). Characteristically, EFB fibers are clean, biodegradable and compatible than many other fibers from other wood species.

EFB also contains natural hard fibers, which are 0.82 mm in length. It was identified as the first of the series of standards on oil palm fibres because of logistic reasons. The EFB has the highest fiber yield and is the only material commercially utilized for fiber extraction but there are good potentials for the exploitation of the other two materials. The choice and selection of fiber length is very much dependent on the nature of the manufactured product. However, moisture content will have a detrimental effect on the oil palm residues. Degradation and infection will easily take place thus leading to deterioration in the properties of the fibers. A maximum moisture content of 15% (on wet basis) was set to prevent degradation happening. This value is comparable to the moisture content for all wood-based fibers. Besides, impurities have been identified as a critical element in producing high quality fibers. Impurities by definition mean the calyxes, spikes, aggregates or fiber strands, any dust or fine particles and parenchyma of EFB. Since it is practically impossible to have fiber free impurities, the maximum level of impurities allowed for in the standard is at 15%. Presence of a significant percentage of residual oil in EFB possess a major problem in that it will react with the moisture content hence giving rise to rancidity and ultimately fungal growth. The control limit for oil content shall not exceed 3%. Other inherent characteristics are such as the salt content, odor and mass (Hussain *et al.*, 2006).

However, this fibrous wood-like residue has not yet been effectively utilized. It is estimated that at least 7.45 tons per hectare of fibrous derivative of oil palm is generated yearly. At present, only a small percentage of this is used for generation of power, dumping at plantation sites or processed to produce fibers for mattress, mulching mat and medium density fiberboard. There are huge amounts of EFB left to decay or dumped into landfills. They are seldom burnt as fuel as the shell and fruit

fiber is sufficient for the oil palm mill (Alam *et al.*, 2007; Ellis and Paszner, 1994; Husin *et al.*, 1985; Ibrahim, 1999).

2.2 Paint

Paint can be defined as any liquid, liquefiable, or mastic composition which after application to a substrate in a thin layer is converted to an opaque solid film. It is pigmented surface coating that is designed to fulfill a protective, decorative or to add functionality to a substrate.

Protective value of paint is crucial on either interior or exterior surfaces but the outdoor part demand the paint more because it is expose to the outdoor environment. The exterior part of paint must provide protection from moisture, temperature changes, UV radiant, atmospheric pollutant and microbial growth that can degrade wood and even metal surface. The protective function of paints includes protection of surfaces from air, water, microorganisms, and chemicals where it is applied to improve properties of the substrate such as appearance, adhesion, wettability as well as mechanical properties through better hardness, abrasion resistance, corrosion resistance, wear resistance, scratch resistance and so on. Regarding the protective function, paint promotes safety in several ways in our daily lifestyle for example, coating on electrical parts for excluding moisture and electrical insulation, coating on the interior metal lining of metal cans or drums to prevent corrosion from food or chemicals, fire-retardant paints to protect combustible surfaces, high frictions and skid-proof paints as well as coating on porous surfaces such as concrete and plaster for ease of cleaning (Fuller, 1973; Koleske, 1995; Martens, 1981; Meijer, 2001; Talbert, 2008).

Conversely, many paint systems designed to provide coatings with high

degree of decorative value often can only be used on substrates exposed to relatively mild service environments. Generally, however, a compromise can be achieved between the decorative and protective functions of a coating system. Decorative effects may be produced by color, gloss, or texture or a combination of these characteristics. A secondary decorative function is lighting as the color of the surface affects the reflectance of light or heat radiation of a surface (Boxall and Fraunhofer, 1977 & 1980). There are also luminescent paints that impart visibility in the dark as well as glow and brilliance by daylight. A wide variety of surface appearances like wood grain, hammered metal, wrinkled textures, crystalline effects, top grain leather and suede leather can be simulated by paints. Basically paint can be awarded for its multifunctional purposes but it is successfully achieved to the extent that the protective, decorative or functional coating remains bonded to the substrate and retains its essential properties. So, it selects suitable paints, which requires careful selection of proper coating system, close attention to surface preparation and skilled application (Fuller, 1973; Schweitzer, 2005).

2.3 Types of Paint

The protective coatings industry is divided into two broad categories. Trade sales or shelf goods include products sold to consumers, contractors, and professional painters for use on new construction or maintenance. This is on-site painting, and these paints are sometimes known as architectural paints. Shelf goods are usually air dry finishes. Industrial maintenance finishes, which are high-performance finishes particularly in regard to corrosion resistance, are usually included in this class. Apart from this class, waterborne paints are growing in the trade sales market due to their ease of application, which exhibits easy cleanup and minimal odor. They now

dominate the consumer market and are usually sold in the form of latex paints. Alkyd paints dominated the architectural market before latex paints were introduced. They first replaced alkyds in wall finishes; however, the new systems could not compete with alkyd paints, particularly in exterior house paints where the durable oil-based paints had good adhesion and weathering properties.

In practice, paints are applied to a very wide variety of surfaces which can differ markedly in their physical and chemical characteristics. For example, such diverse substrates as woodwork, metals, concrete and plaster are painted. Clearly these substrates may vary in their quality, that is, state of deterioration, cleanliness, surface finish, shape, accessibility, and there also may be wide differences in the severity of the service environments to which the painted surface is to be exposed.

Basically, paints may be classified on the basis of the type of pigment (e.g. red lead paint), by the resin binder (e.g. alkyd paint), or by its proposed function or service applications (e.g. water insoluble finish). The classification of paints and allied materials by their function will be of greatest value and the characteristics of the most important classes are summarized below:

I. Fillers and stoppers

These are paste-like materials, normally highly pigmented, used to fill surface imperfections (fillers) and to make good gross surface defects prior to painting operations (stoppers). A variety of non-setting materials such as mastics, sealants and putties, which are designed to stay flexible, can also be included in this class.

II. Sealers

These are low viscosity materials, not necessarily pigmented, whose primary

function are to penetrate and seal porous surfaces such as plaster, masonry and certain timbers. Certain types may also be used to seal chemically active surfaces or to consolidate friable surfaces. Sealers do not normally deposit films of high-build although in certain situations they may be used instead of conventional primers.

III. Primers

Primers are the first high-build pigmented coats applied to new surfaces or to old cleaned surfaces, prior to the application of other components of the finishing system. They are invariably specifically formulated for particular substrates, but all primers regardless of other performance criteria must possess good adhesion on the substrate.

IV. Undercoats

The undercoat is a pigmented paint applied after sealing and/or priming of a surface, but prior to the application of the finishing coats. An undercoat normally has a matt finish (so as not to impair adhesion of subsequent coats), a high pigment content (to enhance the opacity of the paint system) and a color to compliment that of the ultimate finishing coats.

V. Finishes

The finishing coat is the final coat of the paint system, formulated to provide both high durability and acceptable aesthetic value in the proposed service environment. Finishing coats are normally pigmented although unpigmented finishes may be used, particularly on certain metals and timber. Materials of the

latter class are generally termed varnishes or lacquers, and the coating system in these instances is obtained by multicoat application of unpigmented finishes. The surface appearance of pigmented finishing coats can be modified to suit most requirements in terms of color, gloss level and texture, whereas the unpigmented finishes are normally varied in terms of gloss level (Arthur, 2005; Woodbridge, 1991).

2.4 Basic Ingredients and Essential Concepts of Paint Formulation

All paints are basically similar in composition in that they contain a resinous material, pigments, solvent and certain minor of additives. The absolute amounts and relative proportions of the various ingredients play a major role in determining the performance of the resultant coating formulations although, obviously, the characteristics of the selected components must also be suitable for the coating in its service environment. In fact, the incorrect choice of only one component can reduce paint's performance even if the other additions and general formulation requirements are otherwise satisfactory. This is a frequent cause of premature paint failure in practice.

Given that the constituents selected are suitable for the end use, then the most fundamentally important characteristics of paint is its pigment volume concentration, which is the ratio of the volume of pigments and extenders to that of the non-volatile binder content of the formulation. Other formulation aspects must also be considered for instance, the solvent composition affects such properties as drying time, film formation and application characteristics. It also plays a major role in controlling and modifying the viscosity and flow characteristics of the resultant coating (Talbert, 2008).

2.4.1 Resin/Binder

In general terms, binders are a resinous material that surrounds the particles of pigment. It is the film-forming agent of paint formulation. Without it, continuous coatings would not be possible. The purpose of binder is to hold the pigment together and provide adhesion. The binder forms the tough, continuous film that will adhere tenaciously to the surface to which it is applied. Paint with little or no binder will obviously perform very poorly. The type and level of binders will have a dramatic impact on key properties of the paint film including scrub resistance, gloss and color retention, flexibility, toughness and durability (Saunders, 1988; Taylor and Marks, 1969).

Paint binders can be subdivided into two broad categories, that is, convertible and non-convertible types. Convertible paints are materials that are used in an unpolymerized or partially-polymerized state, where it will undergo polymerization reaction to form a solid film after application to the substrate. Non-convertible paints are based on polymerized binders dispersed or dissolved in a medium which evaporates to leave a coherent film on the substrate surface after the coating has been applied. Some examples of convertible binders include oils, oleoresinous varnishes, alkyd, amino, epoxy, phenolic, polyurethane and silicone resins, whereas non-convertible binders include cellulose, chlorinated rubber, acrylic and vinyl resins.

2.4.1.1 Alkyd Resin

Alkyds are network polymers which find extensive use as surface coatings and constitute the most widely used paint binders. They are synthetic polyesters, which are manufactured by the interaction of a polycarboxylic or fatty acid or its anhydride (e.g. phthalic anhydride), a polyhydric alcohol (e.g. glycerol) and a

vegetable oil or its fatty acid (Saunders, 1988). The name 'alkyd' comes from its ingredients which are alcohols and acids (Turner, 1980). This type of esterification reaction produces compound of the general class of polyesters. The key feature that distinguishes alkyds from other polyesters is the presence of monoacids (commonly fatty acid) as a major part of its composition. An alkyd is classed as a polymer formed by chemical synthesis from smaller molecules. The process where small unattached molecules are joined together by chemical reaction to form a tight network of interconnected molecules is called polymerization. Since the alkyd reaction usually releases a simple by-product molecule (commonly water) during the molecular tie-up, the process can be thought of as a compacting or condensing action. For this reason, the preparation of an alkyd is referred to as a condensation reaction and the end alkyd product as a condensation polymer (Patton, 1962; Pizzi and Mittal, 2003).

Alkyd resins fall into three broad categories, namely drying, semi-drying, and non-drying alkyds, depending on the oil used in conjunction with the alkyd resin. These categories may be subdivided further on the basis of oil length (OL), this being the amount of oil, or fatty acid, in the alkyd resin. Short-oil alkyds (up to 45% oil length) are soluble only in aromatic solvents and are cured by high temperature that is, baking and stoving. Medium-oil alkyds (45-60% OL) are soluble in aromatic or aromatic-aliphatic solvent mixtures and these can be cured by either air-drying or high temperature process. Non- and semi-drying oil alkyd resins of these oil lengths are primarily used in conjunction with other film forming resins such as amino, melamine and nitrocellulose resins. Medium-oil length alkyds are frequently used as binders in certain types of quick air-drying finishing systems. The long-oil alkyds (60-80% OL) are normally prepared from drying oils (or their fatty acids), and resins

of these oil lengths are completely soluble in aliphatic solvents. There are used primarily as binders for decorating finishing systems and film formation is normally by air drying. The OL of an alkyd resin on a charged weight basis is less than on a finished alkyd basis because of the by-product chemical losses sustained during processing. The difference is generally a matter of a few percentage points. For purpose of designing an experimental alkyd, OL is conveniently based on a charged weight rather than on a finished weight. Except to meet some specification figure, the difference between the two oil lengths is generally not too significant (Bently and Turner, 1997; Jones, 2005).

2.4.1.2 Raw Material for Alkyd Resin Manufacturing

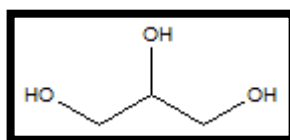
The most widely used oils for the preparation of semi-drying and drying oil modified alkyds are soya bean and linseed oil, respectively, whereas castor and coconut are used for non-drying oils. The common polycarboxylic acids and polyhydric alcohols (or polyol) used in alkyd manufacture are given in Table 2.1 (Talbert, 2008).

Table 2.1 Raw material used in alkyd resin manufacture

Polycarboxylic acids	Polyhydric alcohols	Oils
Phthalic anhydride	Glycerol	Soya bean
Isophthalic acid	Pentaerythritol	Linseed
Orthophthalic acid	Sorbitol	Castor
Maleic acid	Trimethylolthane	Coconut
Fumaric acid	Trimethylolpropane	Tung
Adipic acid	Ethylene glycol	
Sebacic acid	Propylene glycol	

2.4.1.2.1 Glycerol

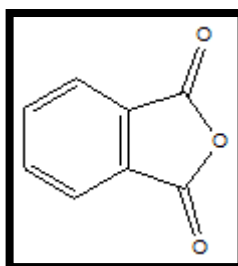
Glycerol (Scheme 2.3) is the polyhydric alcohol most widely used for the preparation of alkyd resins and is obtained both synthetically and as a by-product in the manufacture of soap. It is a colorless, viscous liquid with boiling point 290 °C. Glycerol is the preferred polyol for the preparation of alkyd resins because of its low cost and high boiling point which enables reactions to be carried out at high temperatures. Besides, glycerol-based alkyd resins have good solubility and compatibility characteristics and good film properties (Saunders, 1988).



Scheme 2.3: Structure of glycerol

2.4.1.2.2 Phthalic Anhydride

Phthalic anhydride is the difunctional acidic component most widely used for the preparation of alkyd resins. It is preferred in this application on account of its low cost and because it gives rise to resin with good solubility and compatibility characteristics as well as good film properties (Ernest, 1989). The structure of phthalic anhydride is shown in Scheme 2.4.



Scheme 2.4: Structure of phthalic anhydride