CHAPTER ONE

INTRODUCTION

1.1 Background of The Study

Volatile organic compounds (VOCs) have aroused concern in many parts of the world especially in large cities due to their negative impact on the environment.Volatile organic compounds are those organic chemicals that have a high vapour pressure at room temperature.These VOCs pose long term health effects to humans. Although most of the VOCs originate from petroleum products and internal engine exhausts, and plants, a significant amount is derived from solvent based coatings (Njuku et al 2014). Some of the VOCs from paints include; aliphatic hydrocarbons, ethyl acetate, glycol ethers, acetone, formaldehyde and methylene chloride. The routes to reduce VOC emission from coatings include the use of water-based polymers, higher solids content polymers, water reducible alkyd (Sorensen, 2008), powder coatings (Erin et al, 2016) and the use of the novel technology which disperses highly hydrophobic alkyd resin into water (Malvern, 2017).

According to Jennifer, (2018); Elioss, (2012), the European Union in their directives classified VOC emission into four categories, and also stipulated a maximuim acceptable VOC content of 30g of VOC content per liter of the total volume of paints and related coatings. This is approximately 30% by volume of the paint. The four categories of VOC emission include; Minimal VOC content for VOC content within the range of 0 - 0.29%, low VOC content for VOC content within the range of 0.30 - 7.99%, medium VOC content for VOC content within the range of 8 - 24.99%, high VOC content for VOC content within the range of 25 - 50% and very high VOC content for VOC content within the range of 50% or above.

According to the Global Air Report published by the Health Effects Institute (HEI) (Nwafor, 2018), air quality in Nigeria is among the deadliest anywhere on the earth with higher than ambient air pollution death rates as a result of VOCs emission. While developed nations have experienced success in reducing VOCs emission by introducing tougher pollution control, poorer nations have fallen behind of which Nigeria is among. Health problems including chest pain, dry throat, nausea, aggravated respiratory disease such as emphysema, bronchitis, lung damage and asthma among other respiratory problems are often associated with poor air quality. Symptoms such as irritation to the eyes, nose and throat and upper respiratory track infection such as pneumonia are also suspect. VOCs emission also increases the risk of cancer.

In Nigeria, VOCs emission is hardly listed among causes of death on death certificates in Nigeria, yet the health conditions linked to VOC exposure are often fatal. VOCs emission from indoor sources is recognised as the single largest contributor to the negative health effects of air pollution in Nigeria. Nigeria requires tougher air pollution control if it hopes to effectively combat indoor air pollution by producing safer and more environmentally friendly alternatives. Increasing public awareness of indoor air pollution and the burden of diseases that it imposes on individuals, families and society is an essential step towards making the changes that will improve public health (Nwafor, 2018).

Part of the indoor air pollutants include; paints, thinner, solvents, wood preservatives, carpets, adhesives, detergents and some cleaning agents. In developed countries, increasing concerns about the impact of chemical paints on health and the environment have led to a growing market in non-toxic paints (EPA, 2017). Toxic paints release organic compounds during manufacturing, storage, application, drying and after drying. The concentration of these compounds can remain in the air long after the activity is completed.

Waterborne coatings are non-toxic though they do not have the same advantageous rheological properties as solvent-based coatings. If not formulated correctly, they display inferior characteristics with regard to flow properties, leveling, application properties, film build and stability (TA Instruments, 2015).

This work is therefore aimed at using locally available vegetable oils in providing less toxic alkyd resin (alkyd emulsion) and washable paints with improved rheological properties.

1.2 Statement of the Problem

Toxic paints still dominate the local market, and as such, these paints are mostly used because they are cheap and readily avaliable. The few available non-toxic paints (washable paint) are sold at high price because the major raw materials are not locally sourced. The behaviours of some of the available washable paints under certain conditions are yet to be established. This research will make use of locally sourced oil to produce and study the behaviour of non-toxic washable paints.

1.3 Aim of the Study

The aim of this research is to study the kinetics and the rheological behaviour of washable paints from palm kernel and jatropha seed oils.

1.4 Research Objectives

The objectives include;

1. To determine the properties of palm kernel oil and non edible jatropha oil.
2. To determine the effect of palm kernel oil specie on the acid value and volatile organic content for alkyd resin emulsion.
3. To produce and determine the properties of the alkyd emulsion using PKO *(Eleasis guineensis dura*) specie and non edible jatropha seed oil (JSO) (*jatropha curcas)* respectively.
4. To optimize the production of alkyd resin using Box- Benkin response surface methodology.
5. To study the kinetics of polycondensation reaction for alkyd resins production from PKO *(Eleasis guineensis dura*) and (JSO) (*jatropha curcas).*
6. To produce, characterise and study the rheological properties of washable paints produced from PKO *(Eleasis guineensis dura*) and (*jatropha curcas)* oil (JSO) based alkyd emulsion respectively.
7. To study the effects of different composition of polystyrene acrylic, (JSO) (*jatropha curcas)* and PKO *(Eleasis guineensis dura*) based alkyd emulsions on the properties of washable paints.

1.5 Significance of Study

The significance of this research includes;

Paint technology is gradually evolving from the solvent and high VOC coatings to environmentally friendly systems. This has moved paint production from solvent-based system to water-based system.

The use of PKO *(Eleasis guineensis dura*) and JSO (*Jatropha curcas)* for alkyd production will push up the demand on these oils. This will inturn create employment opportunities, foreign exchange and reduce stress on Omega-3 and calcium-rich soybean oil which is also used for alkyd production.

This research will also serve as a reference for the regulation of eco-friendly paints in Nigeria as most public facilities, industries, hospitals and schools still rely on solvent based paints for their decorations.

Jatropha and palm trees produce seeds all year round unlike rubber trees which fruit seasonally. These are also locally sourced oils and therefore will be cheaper than other imported oils used in alkyd production.

1.6 Scope of the Work.

1. Production and the determination of the physiochemical properties of PKO *(Eleasis guineensis dura)* and JSO *(jatropha curcas)*
2. Esterification and emulsification of the oils into alkyd emulsion and the characterisation of the emulsions.

3. Using the emulsified resins for the production of washable paints and the studying the rheological behaviour of the paint samples.

CHAPTER TWO

LITERATURE REVIEW

2.1Emperical Studies

2.1.1 Alkyd resin.

2.1.1.1 *Water reducible alkyd (alkyd emulsion)*

Cardanyl methyl ether, cardanol acetate water-reducible resins are resins that can be diluted with water with the assistance of neutralizing agents and solvents such as glycol ethers and alcohols (Vance et al, 1991).

According to oil and colour chemists' association (1993), a water- reducible polymer is defined as a polymer that can be diluted in water with or without the assistance of co-solvents and neutralizing agents. These solutions will remain clear on further dilution with water down to relatively low levels of polymer concentration. Alkyd emulsions can be made using no, or virtually no, solvents. A frequently recommended method for producing alkyd emulsions is the inversion process in which water is added to the alkyd until a critical volume concentration of water is reached, and a phase transfer from a water-in-oil emulsion to an oil-in-water emulsion takes place (Sorensen, 2008). Alkyd emulsion is a water reducible alkyd resin and water reducible alkyds are VOC compliant. There have been several reports in literature dwelling on the production of alkyd emulsions from different oils. Sorensen (2008) used tall oil fatty acid to produce emulsifiable alkyd, Aigbodion et al (2003) used rubber seed oil to produce water-reducible alkyd, Changchun et al (2000) utilized soyabean oil in production of water-reducible binder. Their properties were also reported.

Idiaghe et al (2012) studied the physico-chemical properties of *Hura crepitans* seed oil and its modification in low volatile organic component alkyd resin preparation. The properties studied include; colour, specific gravity,% free fatty acid, acid value, saponification value and iodine value. These properties are relevant in determining the quality of the resin. His work utilized linear alkyd benzene sulphonate as an emulsifier and polyvinyl acetate in preparing a low VOC hybrid binder. The binder produced had good chemical and water resistance. The film samples reportedly were of relatively lower volatile organic compound (VOC) (between 0.2 and 0.9%) compared to their corresponding alkyd resins (about 1.3%). Aigbodion et al (2003) used melanized rubber seed oil to produce water reducible alkyd with VOC of about 10%. The binder exhibited excellent resistance to brine and water, and fair resistance to acid and alkali. It was concluded that the oil extracted from *Hura* c*repitans* seed can modify alkyd resin, making it suitable as binder for surface coating applications.

Different emulsifiers can be used in water-reducible alkyd. Ethylene glycol n-butyl ether is the glycol ether most often used in water-reducible systems due to its good solvency properties and superior coupling efficiency (Vance et al, 1991). Aigbodion et al(2003) utilized isopropyl alcohol as an emulsifier in low volatile organic component alkyd resin preparation from rubber seed oil. Sorenson (2008) used a combination of trimellitic anhydride (TMA) and monomethylether of a polyethylene glycol to internally stabilise tall oil modified alkyd emulsion.

Ibanga and Nyeneime (2014) studied the physiochemical properties of fumarized and maleinized cotton seed oil which include; colour, specific gravity, acid value, iodine value, saponification value, volatile and non volatile matter using IUPAC(1987) standard method. Different percentage of fumaric anhydride and maleic anhydride were used in treating the cotton seed oil. The results of the properties showed that fumarized and maleinized cotton seed oil can be used in production of eco-friendly alkyd resin.

Haveren et al (2007) prepared and characterized alkyd resins for high-solid paints based on sucrose and unsaturated oil. The resins produced showed a low intrinsic viscosity, making them suitable to be used in high-solid alkyd paints. Incorporation of small amounts of other diols and trifunctional components was found to improve color and coating properties.

Research on coupling ability of various solvents and solvent blends was carried out by Vance et al (1991). Primary emphasis was on glycol ether solvents and C4 alcohols. The effect of glycol ether solvents on the stability of water-reducible alkyd resins was examined. Perceived toxicity concerns with ethylene based glycol ether, have resulted in requests for propylene-based glycol ether. However, current studies indicated that ethylene -based can be used safely, commensurate with good industrial hygiene practices. The resins utilized in the study were water-reducible, chain stopped alkyds. Data which demonstrated equivalent stability behavior of propylene series glycol ethers and blends of propylene series glycol ethers and C4 alcohols to the ethylene-based/secondary butyl alcohol control blend were generated (Vance et al,1991).

Alireza et al (2013) describes the use of less valuable by-product palm stearin as a partial substituent for valuable vegetable oils to polymerize alkyd resins. A more environmental friendly, economical and lower energy consumption process; fusion process, was employed by Alireza et al (2013) in the production of alkyd resin from palm stearin.

Results indicate that the alkyd resin synthesized from the by-product palm stearin is a successful alternative to sustain and save natural resources, environment, and energy.These results in a cleaner process compared to the solvent based process which is also another technique for synthesizing alkyds. The solvent method consumes fatty acids and more energy and pollutes the air with aromatic solvents.

Alkyd resin synthesized from cashew nut shell liquid, were studied for their characteristics and evaluated for their suitability as reactive diluents in alkyd coatings (Njuku et al, 2014). These cashew nut shell based products were found to be compatible with long alkyd coatings. These diluents helped in lowering the volatile organic compounds (VOC), total time of drying and application viscosity of alkyd based coatings. Coatings formed had excellent adhesion, better drying time, and pencil hardness and are cheaper since cashew nut shell liquid (CNSL) is a renewable raw material. Volatile organic compound reduction to the extent of about 39 % compared to conventional commercial products was realized using cashew nut based reactive diluents Use of the reactive diluents developed would not only reduce direct pollution through VOCs from coatings, but also pollution generated from burning cashew nut shells, which is currently widely practiced among cashew nut processors (Njuku et al, 2014). Lane (1994) describes a method for removing the co-solvent from water-borne alkyd resins, which in turn makes possible the technology for preparing water-borne alkyd paints that have a VOC approaching zero. Simple alkyd resin based on purified isophthalic acid, linseed oil and trimethylolpropane was formulated. The alkyd was cooked to a final acid number of 9 to 10. This is a very important control parameter, and resins prepared with acid numbers lower than 9 have been observed not to form stable emulsions utilizing the technology described by (Lane,1994).

Aigbodion et al (2003) utilized maleinized rubber seed oil (MRSO) and its alkyd resin as binders in water-borne coatings. Rubber seed oil was used in the production of alkyd emulsion. Samples of the oil were initially treated with different amounts of 2%, 5%, 10%, 15% and 20% of maleic anhydride. The resultant maleinized rubber seed oil samples were used to formulate water-soluble alkyd samples. The MRSO samples were of relatively lower volatile organic compound (VOC) (between 1 and 1.5%) compared to their corresponding alkyd derivatives (about 10%).

Aigbodion et al (2003), prepared a 60% (w/w) emulsion solution with known weight of the neutralised alkyd and the melanized rubber seed oil (MRSO) samples using isopropyl alcohol. The pH was adjusted to slightly alkaline with ammonia. Water (70%, w/w) based on the weight of the alkyd was added and the solution was agitated vigorously. Cobalt and calcium drier were added to the emulsion. Each alkyd emulsion was applied on a glass plate and oven-baked for about 90 min at 100^oC. The chemical resistance of the films was determined using ASTM (D1308-57) standard test method.

2.1.1.2 *Properties of alkyd resin*

Chemical drying of alkyd resin is based on heavy metal catalyzed cross-linking of the unsaturated fatty acid moieties. Among the heavy-metal catalysts, cobalt complexes are the most effective, yet they have been proven to be carcinogenic (Griemel et al, 2013). The effects of different driers on film properties of alkyd resin was investigated by (Athawale and Chamankar,1997). The driers selected for study were calcium naphthanate and the octoates of cobalt, manganese, lead and zirconium. The following properties were studied; hardness, adhesion, flexibility, film formation, skinning tendency, resistance to water and acid media, viscosity and time of drying. It was concluded that driers not only dry coatings (paints, varnishes, resins, inks) but have significant effect on the film properties. Secondly combination of manganese, lead and zirconium can be used as the most promising drier system for better coating properties.

Aghaie et al (2011) investigated the utilization of soya bean fatty acid for synthesis of alkyd resin. The properties of the resin produced were compared with those based on other vegetable oils. Rate of decreasing of resins acid value and increasing of viscosity of resin were among the properties measured. FTIR spectroscopy, GPC method and different viscosity measurements were employed to determine the quality of the product. FTIR spectroscopy was employed for identifying the structure of resin and gel permeation chromatography (GPC) was used for determination of average molecular weight (Mn) and polydispersity (PDI).

Nway and Mya (2008) prepared oil-modified alkyd resin from dehydrated castor oil in the presence of 0.3% (wt%) NaOH catalyst. The obtained resin was characterized by Fourier Transform Infrared Spectrophotometer (FTIR). Scratch and guoge hardness, refractive index and colour were also characterised. Chemical and water resistance were also tested after the film was dried for 30mins.

The FTIR spectrum of prepared alkyd resin has aromatic ring ester band at 1730.09 cm^{-1} and straight chain ester band at 1738.64 cm^{-1}. The presence of O=C at 1125.26 cm^{-1} also indicated the presence of ester band. The appearance of CH_2 -CH- confirms the present of methyl group at 1460.43 cm-1 and 2856.67 cm-1. Scratch hardness of alkyd resin was F and gouge hardness was HB. The alkyd had a refractive index of 1.447 and yellow in colour. The resistance result of the alkyd film showed that there was no effect on alkyd film after immersion in distilled water for 18 hours. When the alkyd film was immersed in strong alkali solution, 3N NaOH, the film got whitening after immersion time for 8 hours, blistering after immersion time for 16 hours and removal after immersion time for 24 hours. These results show that the alkyd resin has high chemical resistance.

The properties of refined tobacco seed oil based alkyd resin were studied by (Mukhtar et al, 2007). The alkyd resin prepared was found to be bright and of low color with high gloss. The drying and hardness properties and adhesion were also found a bit superior to those of other alkyd resins of the same oil length. In addition, the water and acid resistance of the said alkyd were also found comparable to the other alkyds.

Omya (2005) worked on water-thinnable synthetic resins. Its features include fast drying, good hardness and high gloss. Primer formulations using the alkyd resin emulsion display remarkably good anti-corrosive properties.

The film properties of maleated alkyds and fumarized alkyds which include the film hardness, adhesion, water and alkali resistance, and thermal stability, of the two series of alkyd coatings were compared by (Gan et al 2012). In both series, alkyds with high amount of $-\mathrm{CH}=\mathrm{CH}-$ could be cured with UV within short time to produce coatings with good film properties. Although both approaches, fumarization and maleinization, serve the same purpose to increase the level of unsaturation in the alkyd, it was found that coatings produced from the two series of alkyds have different film and UV curing properties.The effects of tall oil fatty acids and hydroxylated hyper branched polyester on properties of hyper branched alkyd resins were investigated by López et al (2011) using thermogravimetric analysis, vapor pressure osmometry, differential scanning calorimetry, friction resistance, and hardness. The resins with higher modification percentage presented the best thermal and hydrolytic stability, but lower friction resistance and hardness.

Ramakant et al, (2010) synthesised water reducible alkyd using canola oil and then chemically modified with styrene and acrylamido tertiary butane sulfonic acid. The physiochemical properties were compared and the results revealed that styrene and acrylamido tertiary butane sulfonic acid grafted water reducible polymers have better thermal, chemical and coating properties than canola oil alkyd resins.

Aigbodion et al (2003) used malenized rubber seed oil and rubber seed oil respectively in the formulation of water reducible alkyd resins. The melanized rubber seed oil samples and their corresponding alkyds were evaluated for their physico-chemical properties and compared to the pure rubber seed oil. Menkiti and Onukwuli (2011) also tested the physiochemical properties of rubber seed oil based alkyd resin. The results of alkyd properties showed that the acid value, iodine value and saponification value range from 8.08 to10.60mgNaOH/g oil, 46.4 to 86.18 gI2/100g oil; and 389.90 to 531.08mg NaOH/g fat, respectively.

According to Aigbodion et al (2003), incorporation of maleic anhydride into rubber seed oil increases the acid value and saponification value but decreases the iodine value.

The samples of the melanized rubber seed oil and their alkyd derivatives were evaluated as binders in water-borne coatings. While the melanized rubber seed oil samples exhibited poor chemical resistance, the alkyds exhibited excellent resistance to acid, brine and water, and fair resistance to alkali. It was concluded that RSO treated with different amounts of maleic anhydride can be used as binder in non-polluting coating and also used to prepare alkyd resin.

Monika et al (2012) studied the morphology of film cast from multiphase polymer particle using waterborne alkyd-acrylic nanocomposite particles, it was found that phase migration leading to the formation of aggregates occurred during film formation. A coarse-grained Monte Carlo model was developed to account for the effects of polymer microstructure and particle morphology on the morphology of waterborne alkyd-acrylic film. The model was validated by comparing its predictions with the observed effects, and then used to explore combinations of polymer microstructure and particle morphology not attainable with the system used as a case study.

The morphology of the particles was found to have a greater influence than the compatibility of the phases in determining the film structure. All the films presented aggregates of alkyd resin and acrylic-rich polymer that were larger than the size of the corresponding phase in the particles, meaning that phase migration and agglomeration occurred during the film formation. Phase migration in blends of alkyd and acrylic particles was more apparent than in the hybrid particles because of the compatibilising effect of the grafted alkyd-acrylic copolymer.

The results from the hybrid systems identified three key factors that enhanced phase migration, leading to the formation of aggregates in the films. Phase migration increased as the fraction of the low molecular weight polymer (free alkyd resin) increase, it also increased as the compatibility between the phases decreased (*i.e.* a smaller fraction of grafted copolymer), and when the more mobile phase was located in the outer part of the particles. A standard canonical Monte Carlo model was developed to simulate the transformation of the particle morphology into film morphology. The simulation was able to predict the observed trends. The model was used to gain some understanding about the relative importance of the polymer compatibility and the particle morphology. The results obtained showed that the effect of the phase compatibility on film morphology was stronger than that of the particle morphology.

Alkyd resin was produced using beniseed oil as the source of glyceride oil. Beniseed oil extracted from sesame indicum seed was evaluated for its physicochemical properties. The extracted beniseed oil was converted into alkyd resin for use in surface coating. Analyses of the alkyd resin after dilution with kerosene showed the following results: Acid index 8.6mgKOH/g; %Nonvolatile matter 70.4; Color(Gardner)14-15; Viscosity 140 poises;Density0.9902g/cm3,surface dry(70% solid) within 15 mins. The alkyd resin was found suitable in paint. It was concluded that beniseed oil has shown potential as a substitute for soya bean oil due to its high oil content and the high degree of unsaturation and consequent ability to polymerization (Igbo et al, 2014).

Electrical properties of alkyd resin were studied during the formation of unmodified alkyd resins. It showed a progressive increase in electrical resistance with time, temperature of preparation being constant. No abrupt change in resistance was obtained with the heat convertible resins as they gelled. Mobility was shown to be an important factor in influencing the resistance of a resin during formation since the heat convertible resin shows a much higher resistance for a given percent esterification than does the heat non-convertible resin. It is suggested that electrical resistance may be conveniently used to study and follow resin formation. Curing the resins improves the electrical properties by allowing the chemical reactions to continue, or by driving off volatile products, or by reducing the proportion of conducting to non conducting components. Dielectric losses are greater at high temperatures than at low temperatures because of the increased conductivity of the conducting components remaining in the resins (Kienle and Race 1934).

Idiaghe et al (2012) determined the physico-chemical properties of Hura crepitan seed oil based alkyd resin in comparison with the virgin Hura Crepitan seed oil. The drying schedule and the resistance of the alkyd sample in different service media were evaluated using standard methods; ASTM D1640-69 and ASTM D1308-5-57 respectively. The drying performance of the modified alkyd was found to out stand that of unmodified alkyd.

2.1.1.3 *Kinetics of alkyd resin synthesis*

The kinetics of the preparation of alkyd resin from two triglyceride oils- melon seed and cottonseed oils were studied by Isaac and Nsi, (2015) using alcoholysis-polycondensation process. Six grades of alkyd resin were formulated to have different oil content of melon and cottonseed oils were respectively prepared. The extent of polycondensation reaction was monitored by determining the pH, acid value of an aliquot of the reacting mixture, and measuring the volume of water of esterification evolved at various intervals of time (Aigbodion et al, 2003).

The extent of the reaction and number-average degree of polymerization were calculated from end-group analysis of aliquots of the reaction mixture withdrawn at various intervals of time (Satheesh et al, 2010). The rate of water evolved during the reaction for short oil alkyd samples were in the order of 10^{-1} cm^3/min, while those of medium oil samples and long oil samples were in the order of 10^{-2} cm^3/min. The pH of the in-process samples increases with decreased in acid values. The initial reaction rates followed second order kinetics and thereafter deviations were observed (Satheesh et al, 2010). The second order rate constants for all the samples were of the order 10^{-4} g(mgKOH)$^{-1}$min^{-1}(Ibanga and Nyeneime, 2014).

The kinetics of polyesterification for the formation of jatropha oil based alkyd resins were studied by (Satheesh et al, 2010). The degree of conversion noticed from the extent of the reaction lies in the range of 49.5 % - 62.5%. The average degree of polymerisation calculated in the region of deviation from second order suggested the occurrence of chain branching at relatively shorter intervals along the polymer chain. The second order rate constants were found to be of the order of 10^{-5} g (mg KOH).

Oladipo et al (2013) did a study on kinetics of alkyd resin using Ximenia americana seed oil. Four grades of alkyds were formulated at different oil lengths. The reaction progression was followed by determining the acid value of the aliquots for the reaction mixture at various time intervals beside the volume of water evolved (Aigbodion et al, 2003). Kinetic studies showed that the reaction was second-order (Satheesh et al, 2010) with values of 3.12 x 10^{-4}, 2.44 x 10^{-4}, 2.3 x 10^{-4} and 2.28 x 10^{-4} g (mg KOH)$^{-1}$min^{-1} for samples 1, 2, 3 and 4 respectively.

According to Santosh (2006), the rate equation for acid catalyzed polyestrification reactions is given by equation (2.1)

$$-\frac{d[Acid]}{dt} = k''[\text{dicarboxylic acid}][\text{catalyst}][\text{diols}] \qquad (2.1)$$

Since concentration of catalyst remains constant, the rate law is be given by equation (2.2)

$$(-\frac{d[Acid]}{dt} = k^{''}[\text{dicarboxylic acid}][\text{diols}] \qquad (2.2)$$

when $k = k''$ [catalyst]. (2.3)

At equivalent concentrations of dicarboxylic acid and diol i.e. c, rate law equation (2.2) becomes equation (2.3)

$$-\frac{dc}{dt} = \mathrm{kc}^2 \tag{2.4}$$

where k is a second order rate constant.

Fraction of functional group that has reacted at any time is given by equation (2.5)

$$f = \frac{c_{0-c}}{c_0} \quad or\ c = c_0(1-f) \tag{2.5}$$

Reaction orders as expressed by (Santosh , 2006;Ronald et al ,1998) are given in equation 2.6 through 2.8

First order reaction is given by $$-ln\frac{Ca}{Co} = kt \tag{2.6}$$

Second order reaction is given by $$k = \frac{1}{t}\left(\frac{1}{Ca} - \frac{1}{Co}\right) \tag{2.7}$$

nth order reaction is given by $$\frac{1}{n-1}(Ca^{1-n}Cao^{1-n}) = kt \tag{2.8}$$

From (2.6), a plot of $-ln\frac{Ca}{Co}$ against t will give a straight line graph with slope k.

From (2.7), a plot of $\frac{1}{Ca}$ against t will give an intercept of (- $\frac{1}{Co}$) and slope k. If it is a straight line, the data fit the second order. If it is a curve the data do not fit a second order. From (2.8), a plot of (Ca^{1-n}) against t will give a straight line graph of slope (n-1)k and intercept of Cao^{1-n}).

Uzo et al, (2015) used the viscosity conversion relation suggested by the classical free volume theory to study the reactor kinetics based on viscosity measurement. Non linear least squares was used to fit the viscosity and conversion models. Non linear least square is the form of least squares analysis used to fit a set of observations with a model that is non-linear in unknown parameters. This is a relevant theory for constructing a mechanistic model which is a non linear in the unknown parameters. It involves iterative procedure that starts with an initial guess of the unknown parameters. This involves selecting the mechanistic models that would provide adequate fit to the experimental data.

2.1.1.4 *Synthesis of alkyd resin from different oil lenght*

Menkiti and Onukwuli (2011) investigated the potential utilization of Rubber Seed Oil (RSO) as a base oil for the production of alkyd resin using different samples (40,50,60%)of oil length. The methodology employed is the experimental frame works and procedures developed by Rubber Research Institute of Nigeria (RRIN), Iyama, Benin City, Project Research and Development Institute (PRODA), Enugu and America Standard for testing of Materials (ASTM), USA.

Alkyd properties were tested and it was concluded that the 60% of oil length is of the best drying qualities in terms of tack free conditions with respective to the oil investigated and at the conditions of the experiment .The 60% oil alkyd formation has shortest drying time in tack free condition. This was followed by 50% and 40% of alkyd resin formulations. 60% oil formulation has least cost of production since it has least quantities of material for its formulation. Processing of the alkyd resin to a low acid value of 10% gives a finished alkyd resin of excellent air drying time. Also LiOH catalyst has the most desired drying and performance effect on the produced alkyd resin sample.

Umeobika et al, (2013) also utilized rubber seed oil (RSO) in the production of two samples of alkyd resins of varying oil length, (35%) for short alkyd and 50% for medium alkyd. The rubber seed oil and its alkyd resins were all characterized and evaluated by standard methods for their physico-chemical properties, drying schedule and chemical resistance as reported by Umeobika et al, (2013). The characterization of result of the rubber seed oil samples showed that rubber seed oil can be employed in the production of alkyd resin (Umeobika et al, 2013; Menkiti and Onukwuli, 2011).

RSO gave alkyd resins whose coating properties are comparable to those of commercial alkyds, as its air-film dried within a few hours and showed good chemical resistance in various solvent media such as water, brine and water. The iodine value of the short and medium alkyds were 30.90 gI2/100g and 42.50 gI2/100g respectively which showed that the level of unsaturation of the alkyd resins increased with the proportion of the RSO used in the production. The obtained resins were also characterized by Fourier Transform Infrared Spectrophotometer (FTIR) and results showed absorptions at regions 1957cm-1 and 2644cm-1 for short and medium alkyds respectively.

Qualitative application of FTIR method is more useful for identification of products; especially identification of functional groups of organic compounds. FTIR method is the best tools for reach and investigation of chemical nano structures of alkyd resins. Translation of FTIR spectra of alkyd resins and their varnishes may help to identify and characterize rheological and mechanical properties of resins and varnishes (Ilkhani, 2012).

Six grades of alkyd resin formulated to have oil content of 40% (M1), 50% (M2), and 60% (M3) melon seed oil (MESO) and 40% (C1), 50% (C2), and 60% (C3) cottonseed oil (COSO) respectively, were prepared with phthalic anhydride, and glycerol.Molecular weight averages and polydispersity index (PDI) of the finished alkyds were determined by two different methods, Rast method and end-group analysis. The molecular weight averages and PDI vary with oil length of the alkyds. The two samples which exhibit the highest PDI are samples M2 and C2 respectively.

Molecular weight averages calculated from end-group analysis are larger than those obtained by Rast method for both MESO and COSO alkyds and seem to overestimate their molecular weights. The difference in the properties mentioned above implies the complexicity in the production of melon seed oil and castor seed oil alkyds. Correlation of PDI with the quality of the finished alkyds shows that the higher the PDI value the better the quality of the alkyd. Performance properties such as rate of drying, film hardness and resistance to chemicals were optimum at 50% oil length for both triglyceride oil alkyds (Isaac and Nsi,2015).

Four grades of alkyds were formulated at 40% (I), 50% (II), 60% (III) and 70% (IV) respectively using *Ximenia americana* seed oil lengths. Characterization of the alkyd gave iodine value of 70.1 + 0.74, 76.1 + 1.05, 81.2 + 1.0 and 86.3 + 0.8gI2100g^{-1} for samples I, II, III and IV respectively. The corresponding saponification values were 297.5 + 1.5, 332.5 + 1.2, 378 + 1.1 and 420.2 + 1.3 mg KOH g^{-1}. The 40 and 50% oil length The alkyd films with 40% and 50% oil length showed good resistance to water, acid and brine.The resistance to alkali were poor. Paints were produced and characterization based on the 40% and 50% oil length alkyd resins. The samples showed surface drying and tack-free property in less than 2 hours for 50% and 5 hours for 40% oil length (Oladipo et al, 2013).

Okon and Ibanga (2013) utilised melon seed oil in synthesis of alkyd resin. Four sets of alkyd samples formulated by varying the percentage of melon seed oil contents were synthesized. Properties of paint films which include; drying schedule, hardness, gloss, colour, and chemical resistance of the alkyds were evaluated for different oil length. Short oil alkyd of crude and refined oil possessed the best hardness, drying time and resistant to

5% brine solution. It was concluded that these properties can be compared to those of the soya alkyd paints.

Alireza et al (2013) describes the use of less valuable by-product palm stearin as a partial substituent for valuable vegetable oils to polymerize alkyd resins. This by-product and vegetable oils were used to produce four differnt alkyd resins. The reaction was monitored by measuring the viscosity of the reacting mixture and the acid values at different time interval. The performances of the synthesized resins for coating applications were determined using ASTM D 1640, 4366, 3559, 2794 and 1647.

Methyl esters of rubber seed oil (MERSO) were used in the preparation of alkyd resins by Ikhuora et al (2004). Methyl esters of rubber seed oil were obtained through the alcoholysis of RSO. Alcoholysis method was used in preparing alkyd resins of different oil lengths which include; 45 %, 50 % and 55% using methyl esters of rubber seed oil, phthalic anhydride and glycerol. The refluxing agent used was xylene while lead (II) oxide served as catalyst. The physico-chemical characteristics of the MERSO and the resins obtained were compared with the corresponding value of rubber seed oil (RSO) and its alkyd resins. Njoku and Ononogbo (1995) also used Rubber seed oil to formulate alkyd resin which was used in wood finish formulation.

Ikhuora et al (2004), after determining the acid value of the MERSO and RSO alkyd resins concluded that acid value depends on the extent as well as the rate of esterification. It was also observed that iodine value of the alkyd samples showed that the extent of unsaturation of the resins depends on the oil length. The free fatty acid (FFA) values of the resins were 1.99% for MERSO and 9.54 % for RSO. Hence methyl ester of rubber seed oil was preferred to raw RSO in the alkyd resin production. All the alkyd films were tested for chemical, brine and water resistance. The films gave better resistant to acid, water and brine compared to alkali resistant. The MERSO alkyds had a better resistance compared to the RSO alkyd resins. The hardness test was also carried out. This showed that the hardness of the films decreased with the length of oil.

Vikkasit et al (2006) in effects of oil type on the properties of short oil alkyd coating materials, prepared short-oil alkyd resins by using five different oil types which include; soybean oil, sunflower oil, corn oil, rice bran oil and dehydrated castor oil (DCO). Alkyd produced from soybean oil gave the darkest color due to oxidation reaction. The alkyd films were air dried and, it was shown that rice bran oil-based alkyd films had the longest drying time. This was attributed to the low number of double bonds and extra natural antioxidant in rice brain oil as compared to other film samples. The film test showed that DCO alkyd-based film had the poorest resistant to alkali and sea water but, shortest drying time and the greatest hardness. This was caused by the differences in the type of fatty acid and double bonds, the high amount of double bonds being in DCO.

Increase in the reaction temperature darkened the alkyd color and reduced the drying time of the coating films. Soya bean oil-based film was the best in terms of cost and technical properties.

Three medium oil alkyd resins (50% oil length) were synthesized by Ibanga and Edet, (2013) with cottonseed oil using different polybasic acids [phthalic anhydride (I), maleic anhydride (II) and succinic acid (III)]. Dilute solution viscosity measurements were carried out on the alkyd resins in acetone and in toluene. The effect of polybasic acid type on dilute solution viscosity characteristics of the alkyd samples were investigated by determining the following parameters: viscosity number (ηrv), intrinsic viscosity [η] and

Huggins constant (KH). Also, the effect of polybasic acid type on properties such as colour, solid content, specific gravity, adhesion, drying time, chemical resistance and hardness was evaluated by formulating the alkyds into white gloss paints. The [η] values of the alkyd samples in acetone were found to vary in the order: (I) > (II) > (III) in acetone and (II) > (I) > (III) in toluene. The [η] values were found to be larger in acetone than in toluene. The KH of the alkyd resins on the other hand, were found to be larger in toluene than in acetone. While succinic acid alkyd resins produce coatings with very soft film, that from phthalic and maleic anhydrides gave the best hardness and drying time. All the alkyd paint samples showed good resistant to 5% NaCl and poor resistant to 0.1 mol/dm^3 of KOH. Succinic acid alkyd paint sample showed poor resistance in distilled water. White gloss paints were formulated using standard soybean alkyd for comparison. The properties of phthalic and maleic anhydrides alkyds were compared with those of the stansadr alkyd. These were found to be comparable (Ibanga and Edet, 2013).

Physico-chemical properties of alkyd resin and palm oil blends were studied by Blaise et al,(2012). Blends of palm oil and long-oil alkyd resin were prepared and these blends contained quantities of palm oil ranging from 10% to 50%. A drying agent composed of a mixture of cobalt, calcium and lead compounds was included in each blend sample. After the preparation of the samples, their physico-chemical properties were obtained. The analysis showed that the alkyd resin blended with palm oil caused an increase in the drying time and increase in dry extract.

The blend exhibited low viscosity and density, which indicated good rheological properties. The results suggest that palm oil can be used as a blending additive for coating formulations. It was observed that the resin gloss does not change up to 20% palm oil content in the blend. Above 20% palm oil content, the gloss values decrease with a significant drop of the gloss being noticed between 20%and 30% palm oil content in the blend. Density and viscosity of the blends decreased as the palm oil content in the blend increased. Since the viscosity of the blend is also lower compared to that of the pure alkyd, it is not likely to produce a hard film, but it may be suitable for paint systems which require low viscosity. Also, it was observed that the inclusion of palm oil led to increase in the dry extract which may also affect the thickness of alkyd resin.

2.1.1.5 *Alkyd Resin from Waste Products*

In Gamze (2012), alkyd resins based on waste PET for water-reducible coating applications was presented. Simultaneous glycolysis and neutral hydrolysis of waste PET flakes obtained from grinding post-consumer bottles were carried out in the presence of xylene and an emulsifier at 170°C.

The samples were used for preparation of the water-reducible alkyd resins and compared with long oil alkyd resin. Film properties and thermal degradation stabilities of these alkyd resins were investigated. Physical properties, drying times and hardness and thermal degradation stabilities of the PET-based alkyd resin were better than these properties of the reference alkyd resin.

George et al (2005) investigated alkyd resins derived from glycolized waste poly(ethylene terephthalate. In this investigation the production of secondary value-added products, such as alkyd resins, derived from the glycolysis of (polyethylene terephthalate) (PET) was examined as an effective way for its recycling. Used PET bottles were depolymerization using diethylene glycol (DEG) at different molar ratios. Different oligomers were obtained and were also analyzed based on their average molecular weights.

Maleic anhydride, phthalic anhydride and propylene glycol were reacted with the oligomers also known as the glycolyzed PET to form unsaturated polyester resins. The reaction was carried out at ambient temperature in the presence of styrene and benzyl peroxide-amine as initiator. The curing characteristics of the resins produced were investigated with respect to the initial molar ratio of DEG/PET as well as the initial initiator concentration. The mechanical properties (tensile strength and elongation at the break point) of the resins were compared with the conventional general purpose resin and were found to be comparable.

The possibility to utilize two waste products – crude glycerol (CGly) and waste polyethylene terephthalate (PET) for production of alkyd resins was investigated. Flakes, obtained from PET beverage bottles were depolymerized with CGly- a side product by the biodiesel production.Two fractions were separated from the depolymerization product – water soluble and water insoluble (Gamze, 2012)

Two medium oil alkyd resins were obtained from water soluble and water insoluble fractions. A reference alkyd resin was synthesized from phthalic anhydride, glycerol and a mixture of sunflower oil and linseed oil. Progress of the polycondensation reaction, was monitored according to Aigbodion et al (2003). Some of their properties were comparable to that of the reference alkyd (Nikola and Donka, 2014).

Osemeahon et al (2013) in their continuous desire to find suitable methods of recycling waste, expanded polystyrene waste was converted into a paint binder using gasoline as a solvent. Some properties of the binder at different concentrations (5% - 30%)

were investigated. The melting point, refractive index, density, viscosity, turbidity and elongation at break were found to increase with increase in binder concentration. The solubility of the binder was however, found to decrease with increase in binder concentration. At a concentration of 20% w/v, the binder was found to be insoluble in water. This implies that in processing of waste polystyrene binder for emulsion paint, the concentration should be lower than 20 % w/v. This study proved that polystyrene waste can be used as a binder in emulsion paint formulation.

Ayman et al (2013) also used recycled poly ethylene terephthalate (PET) and different vegetable oils in obtaining alkyd resin. Glycolysis of PET waste using pentaerytheritol was used to produce suitable hydroxyl oligomers (GPEr) for alkyd resin. The glycolysis was carried out in the presence of manganese acetate as a catalyst and m-cresol as a solvent at 220 ^{o}C. The PET waste was used in preparing alkyd resin in the presence of phthalic anhydride, glycerin, ethylene glycol, sunflower oil and linseed oil respectively to produce PET-based alkyd resin. GPEr was used to produce the second type of alkyd resin. The reactions were carried out in the presence of butylhydroxytin oxide as a catalyst to prepare alkyd resins. Corrosion resistivity and the curing characteristics of the prepared resinwere also evaluated.

2.1.1.6 *Optimization of polyesterification of alkyd resin*

The optimization of polyesterification process of air drying alkyd resin from non-drying palm oil was studied by Uzo et al (2013). Response surface methodology (RSM) based on central composite rotatable design (CCRD) was employed for the optimization process. Thirty experiments with four process variables and five levels were carried for the optimization purposes. Self cured resin was obtained by modification of The saturated structure of palm oil was used to modifiy a self cured resin through alcoholysis and polyesterification using Phthalic anhydride. The studied process parameters were reaction temperature, reaction time and catalyst concentration. Predictive model describing the fractional conversion in terms of process variables was derived from multiple regression analysis. Optimum fractional conversion of 97.28% was predicted at reaction temperature of 240.61 °C, reaction time of 150 min and catalyst concentration of 0.03% for the process. Extent of reaction at 120 min of polycondensation of the monomers was more than 85%. Model validation experiment shows good correspondent between the actual (96.04%) and predicted (97.28%) (Uzoh et al, 2013).

Onukwuli and Obodo (2015) studied the optimization of copolymerization process of high performance styrenated resin from non-drying palm kernel oil (PKO). During the process of copolymerization, response surface methodology (RSM) based on three-level, three-factorial central composite rotatable design with categorical factor of zero was employed to optimize the process. Effects of the amount of styrene, reaction time and reaction temperature on the synthesis of styrene modified alkyd resin were investigated. The optimum conditions (reaction temperature of 150^{o}C, reaction time of 180min and styrene weight of 4.95g) and predicted fractional conversion of 83.57 % were determined by statistical analysis. Experimental conversion value of 82.52% was obtained. This agreed with that predicted by the statistical model.

The optimal composition concerning the resin neutralization, type and amounts of neutralization agents, co-solvents and water were determined by Response Surface Methodology (RSM) for the production of low VOC emission paints (Andrei et al, 2015). The resin was neutralized with a mixture of ammonia and triethylamine in 1:1.8 ratio and solubilized with butanol and butyl glycol co-solvents (2.8:1 ratio). The final product was a homogenous, viscos fluid, with 152 s flow time and 22.5% VOCs content. In the optimized drying conditions, it formed a film with a fineness of 40 µm, a semi-gloss aspect, a good adherence, an elasticity (after 7 days) of 5.5 mm and a hardness of 45, 93 and 104 s (after 24 h, 3 and 7 days respectively).

Enrigue (2007) developed a Monte Carlo model for the improvement on alkyd resin production processes. The aim was to evaluate changes in plant operating conditions. These changes will reduce the overall processing time. The study was made using FORTRAN. It was concluded that with the proposed changes, in the simulation studies, productivity could be improved to around ten percent.

2.1.1.7 *Structurally modified alkyd resin*

In synthesis and curing of alkyd enamels based on ricinoleic acid by Jovičić et al (2009), a combination of an alkyd resin with a melamine-formaldehyde resin gave a cured enamel film with the flexibility of the alkyd constituent and the high chemical resistance and hardness of the melamine resin at the same time. Two alkyds having 30 and 40 wt% of ricinoleic acid were respectively formulated using two commercial melamine resins: three isobutoxymethyl melamine-formaldehyde resin (TIMMF) and hexamethoxymethyl melamine resin (HMMMF). TIMMF resin was more reactive with synthesized alkyds than HMMMF resin.

Alkyd resin with 30 wt% of ricinoleic acid was slightly more reactive than alkyd with 40 wt% of ricinoleic acid, because it has the high contents of free hydroxyl and acid groups.

Murillo et al (2012) did a work on alkyd hyperbranched resins (AHBRs) modified with a Z-6018 silicone (a polysiloxane intermediate) and with high solid content at different molar ratio. Structural, thermal, hydrolytic, anticorrosive, and tribological properties were studied using infrared (IR) analysis, nuclear magnetic resonance (NMR), vapor pressure osmometry (VPO), thermogravimetric analysis (TGA), acid value, electrochemical impedance spectroscopy (EIS), and pin-on-disk friction.

IR and NMR provide evidence of grafting of the silicone on AHBR; the efficiency of grafting was quantified by TGA. Thermal stability was studied by acid value analysis. Corrosion resistance on steel is improved by two orders of magnitude, hence the modified materials can be used as highly effective anticorrosion coatings. At higher concentrations of silicone, dynamic friction was reduced by grafting.

Alkyd resins that are biodegradable were synthesized from glycerol and maleic anhydride. One set of glycerol-derived alkyd resin/clay nanocomposites was successfully prepared by melt blending maleic anhydride-glycerol precursors with organoclays (Lin et al, 2008). El-Shaid et al (2012) reported on the synthesis of a series of modified alkyd resins by partial replacement of phthalic anhydride with 2, 2\-di-thiosalicylic acid. The clays samples of Lin et al (2008) were pretreated with methyl tallow bis-2-hydroxylethyl ammonium chloride salt yielding a nano-composite, and some samples of the nanao-composite were further treated with the diglycidyl ether of bisphenol A (DGEBA). Resin/mica and resin/talc nanocomposites were also prepared, in the same way, to yield materials for purposes of comparison.

The properties of the resulting nanocomposites which include thermostability were investigated. X-ray scattering results and transmission electron microscopy (TEM) images clearly indicated that 30BT was further delaminated by the DGEBA, and that the clay30B and clay30BT were mostly exfoliated and finely distributed in the alkyd resin matrix. These layered silicates fillers gave remarkable improvements in thermostability and mechanical properties even at very low loadings (Lin et al,2008).

A commercial alkyd resin was blended with various mole ratios of three different resins; product of reaction between castor oil and epoxy resin (diglycidylether of bisphenol-A)(DGEBA), unsaturated resin prepared by reacting diglycidylether of bisphenol-A with maleated cyclohexanone formaldehyde resins and that prepared by reacting diglycidylether of bisphenol-A with tetrahydrophthalated cyclohexanone formaldehyde resins (Hasmukh et al, 2011).The resins were characterized and the results suggested that the films gave good surface dry and good tack-free dry properties as well as good adhesion and flexibility.

Athawale and Chamankar (1998) described the preparation and coating properties of long oil-length alkyd and ketonic (cyclohexanone formaldehyde) resin blends. It was observed that when a 30% concentration of ketonic resin was blended with the alkyd resin, a significant improvement in adhesion, hardness, gloss, storage stability, acid resistance, and drying time were achieved.

Patel et al (2012) blended castor oil with varying mole ratios of commercial epoxy resin of diglycidyl ether of bisphenol-A (*i.e*. DGEBA) using triethyl amine (TEA) as a base catalyst. The modifier used by El-Shaid et al(2012) containing aromatic ring and sulphur atom enhanced the physical, mechanical and chemical properties of the modified alkyds, especially at higher content. The antibacterial activity was also investigated and gave promising results which promoted the application of the modified alkyds and in antibacterial aspects especially at high modifier content.

Rubber seed oil alkyd was prepared by Ikhuoria et al (2011) using styrene monomer at ratios of 1:2, 1:4, 1:6, 1:8, and 1:10 at 100°C for 3 h (samples i - v) and 6 h (samples A – B). The rubber seed oil and its derived alkyds were all characterized and evaluated. The following properties; physico-chemical properties, drying schedule and chemical resistance were evaluated. The samples showed outstanding properties. Moreso, the styrenated alkyds dried faster time, even without the aid of a drier. The styrenated alkyds were also resistant to alkali, brine and acid, while the resin without styrene only showed good resistance to water and brine. At the same styrene ratio, the styrenated alkyds prepared over a period of 6 hours dried faster than those prepared in 3 hours.

Gan et al (2012) converted non-self-drying palm stearin alkyds into UV-curable resins via fumarization and maleinization. The maleated alkyds and fumarized alkyds were characterized by ^{1}H-NMR and FTIR before they were formulated into UV-curable coatings, with methyl methacrylate as the active diluents, and benzophenone as UV photoinitiator. The film properties of the alkyd coatings were compared.

Changchun et al (2000) developed a new process for synthesis of alkyd resins in which a conventional monoglyceride was reacted with a carboxy-functional acrylic copolymer. The novel products were called acrylicalkyd resins. The carboxy-functional acrylic copolymers were synthesized by solution-free radical polymerization. Gelation during alkyd resin synthesis was avoided by limiting the molecular weight of the acrylic copolymers to Mn 3500–5000 and limiting the number average functionality about 6.5–10 carboxyl groups per molecule.

2.1.1.8 *Drying performance of alkyd resin*

Ten alkyd artists' paints from the Griffin Alkyd, "fast drying oil colours" series (Winsor & Newton) were studied by Duce et al, (2014) in order to evaluate the effect of pigment-binder interactions on the stability of the alkyd resin. Four alkyd colours (red, blue, yellow and green) in two formulations based on inorganic or organic pigments together with titanium white and black formulated with carbonized bones were selected and a combined differential scanning calorimetric (DSC) and thermogravimetric (TG) approach were applied. The pure pigments and the whole paint replicas were analyzed, and the effect of natural ageing on the paints was monitored for eight months. Artificial ageing in an acetic acid atmosphere was also studied. It was found that organic and metallorganic pigments interacted the strongest with the alkyd resin, while the inorganic pigments appear to act more as dispersants. The paint was fully dried after eight months.

According to the work of Ekpunobi et al (2014), paint samples were investigated by DSC in order to evaluate the effects of several years of natural ageing on alkyd fast-drying oil colours. At the end of chemical drying, the alkyd colours seemed very stable. Artificial acid ageing was found to damage the paints, though it acted less on the resin network and, mainly on the pigment. Naphthenic acid from the used lubricating oil was recovered and converting to a heavy metallic soap drier (cobalt naphthenate) which was further used in an alkyd paint formulation. The results were compared with that of the commercial paint to ascertain its quality as regards to those sold in the market.

A commercial alkyd resin was blended according to (Hasmukh et al, 2011).The resins were characterized and the results suggested that the drying time reduced on increasing the amount of maleated / tetrahydrophthalated cyclohexanone formaldehyde resin added. The good drying time was attributed to the presence of carbonyl groups in the polymer backbone, which activated the methylene groups in the maleated / tetrahydrophthalated cyclohexanone formaldehyde resins. In the presence of suitable driers, the oxygen activation of the methylene group was further accelerated, which resulted in faster drying time. Hasmukh et al, (2011) reported that the drying time was further improved as the concentration of epoxy resin increases. Films prepared from these blends showed outstanding excellent scratch hardness. As the concentration of cyclohexanone formaldehyde resin increases, gradual increase in hardness was observed.

Organic salts of cobalt were synthesized in the presence of amine, ethanol, and ethyl methyl ketoxime by Nader et al (2013) and were used as drier for alkyd resin. Considering the drying time of alkyd resin containing synthesized compound showed that amines, as electron releasing groups, increased the oxidizing activity of the drier and shortened drying time about an hour, whereas the drying time of the resin with ethyl methyl ketoxime lasted for more 2 hours.

Ibanga et al (2014) used African pear oil (APO) and palm kernel oil (PKO) to produce driers used in alkyd paint formulation. The synthesis of the driers was carried out by precipitation method using APO, palm kernel oil (PKO), sodium hydroxide, lead (II) trioxonitrate (V), cobalt (II) chloride hexahydrate and anhydrous calcium chloride. The colour of lead, cobalt and calcium driers of APO and PKO were found to be yellow, purple and white respectively. The specific gravity of PKO driers was greater than those of APO driers. The prepared driers and the commercial driers were used separately in the formulation of white gloss alkyd paints and the properties of APO driers were found to be better than those of PKO driers and were also found to be comparable with commercial samples.

The work of Griemel et al (2013) developed an alternative to replace the cobalt-based catalyst by environmentally friendlier and less toxic alternatives. It was demonstrated for the first time that a laccase–mediator system can effectively replace the heavy-metal catalyst and cross-link alkyd resins.

In the work of Barbarab et al (2015), the influence of Fe bispidon (Fe drier) and Co ethylhexanoate (Co drier) surface driers with Sr carboxylate (Sr drier) through drier on the film formation of high solid alkyd coatings were studied. FT-IR spectroscopy was applied in analyzing the drying kinetics. Further applicative properties like drying time and film hardness were also examined. Electrochemical impedance spectroscopy was used to evaluate the quality of cured high solid alkyd coating films after exposure in the humidity chamber. It was established that the addition of the Sr drier to surface driers accelerates the autoxidation process. Increasing the amounts of Sr drier reduced the final drying times but increased the film hardnes. The lowest diffusivity of ions through cured high solid alkyd coating films was observed for Co/Sr and Fe/Sr drier combination at 1:1 concentration ratio.

Dyed polymers are prepared by mixing a polymeric material and a dye. Some dyes have such properties as hydrophilicity and tendency of dyes to form agglomerates, which negatively affect the dyeing process, require additional equipment. These difficulties can be eliminated dying the structure of polymer. Structurally-dyed alkyd resin has high pigment properties and can be used as an oligomeric dye (Tapahehko, 2014). Structurally-dyed resin, modified by oil was prepared by the reesterification of pentaerythritol by oil. At the second stage, azopigment was added to interesterificator then, phthalic anhydride and glycerol were added and the polycondensation was conducted up to the specified acid number.

Spyros, (2002) used one dimensional (1D) and two-dimensional (2D) H-NMR and C-NMR spectroscopy to characterize polyester and alkyd resins used in the coatings industry. It was concluded that the quantitative composition of the resins and especially the abundance of unsaturated fatty acid double bonds, which influences resin dry ability and hardness, can be easily extracted from the 1H-NMR spectra while the wealth of chemical composition information of the resins was revealed through 2D NMR experiment. The types of polyols, acids, and vegetable oils used to modify the resins were efficiently traced by NMR spectroscopic techniques.

2.1.2 Palm kernel and palm oil based alkyd resin.

Onukwuli and Obodo (2015) studied the optimization of copolymerization process of high performance styrenated resin from non-drying palm kernel oil (PKO). During the process of copolymerization, response surface methodology (RSM) based on three-level, three-factorial central composite rotatable design with categorical factor of zero was employed to optimize the process.The optimum conditions (reaction temperature of 150^{o}C, reaction time of 180min and styrene weight of 4.95g) were determined by the results of statistical analysis, under which experiment was carried out and the fractional conversion of 82.52% for PKO styrenated alkyd resin was obtained. The effect of reaction time, reaction temperature and amount of styrene were investigated. The predicted value of model (83.57%) was in excellent agreement with the experimental value (82.52%).

Uzoh et al (2015) used palm kernel oil to synthesis unstyrenated and styrenated alkyd resin. The kinetics of the resin preparation were studied using polycondensation and copolymerization processes. Three alkyd resin samples A,B and C of medium oil length were prepared using phthalic anhydride, maleic anhydride, and glycerol at stipulated ratios. The prepared alkyd resins were copolymerized with styrene using benzyol peroxide as an initiator at 150°C for 3 hr.

Viscosity and the reaction time were studied using integral method. The results showed that the resins A and B followed the first order reaction while resin C followed the second order reaction with rate constants of 13 × 10-3 min-1, 30 × 10-3 min-1, and 3 × 10-3 (Pa.S)(min)-1 respectively. For styrenated alkyds, kinetic study confirmed that styrenated alkyd A followed the first order kinetics and styrenated alkyds B and C followed the second order kinetics with rate constants of 8 × 10-3 min-1, 6 × 10-4 (Pa.S)(min)-1, and 6 × 10-4 (Pa.S)(min)-1 respectively.

Jem et al, (2014) utilized edible oils which include; palm oil, soya bean oil and sunflower oil in the production of alkyd resins. The alkyd samples were modified with urethane. The samples were analyzed for viscosity, solubility, iodine number testing, gel content, drying time test, thermogravimetric analysis (TGA), crosshatch adhesion tests, impact strength, pencil hardness, chemical and water resistance. It was concluded that palm oil modified with urethane showed good thermal stability.

Alireza et al, (2013) used palm stearin for alkyd resin production. The performance of the synthesized resins for coating applications were studied in this work. It was concluded that palm stearin which is a by-product is a successful alternative for alkyd resin production.

Palm oil-based alkyd resins were synthesized by Muhammad et al, (2014) using calcium oxide as a catalyst for the alcoholysis reaction between palm oil and glycerin. Esterification process was carried out by using phthalic anhydride and maleic anhydride.

Physico-chemical properties of the resins such as density, viscosity, acid value, iodine value, saponification value, specific gravity, and moisture content were measured following ASTM and standard methods. The structural confirmation and hydrogen density of the prepared resins were determined by Fourier transform infrared and proton nuclear magnetic resonance spectroscopy, respectively. Molecular weight of the resins was determined by using gel permeation chromatography.

Methyl ethyl ketone peroxide and cobalt-napthenate were used in the curing process at a temperature of $140^{o}C$. ASTM methods were followed to measure the gloss, hardness and chemical resistivity of the resins.Temperature behaviors were observed by differential scanning calorimetry and thermogravimetric analysis. Produced resins were found thermally stable (up to $300^{o}C$). The variations of the properties were noticed due to the types of anhydrides in terms of molecular weight, thermal and chemical resistivity of the resins, although the other properties were found close to each other. It was concluded that the overall, the reported properties were found suitable for the materials to be used for surface coating applications.

Alkyd resin was also synthesized by Issam and Cheun (2009) using palm oil and calcium oxide as the catalyst . Properties such as viscosity, drying time, solubility, hardness, adhesion and impact strength were analysed. The analysis showed that the alkyd resin based on palm oil had difficulty in drying with the absence of a drying agent though the adhesion property was excellent. According to Eromosele and Eromosele, (2002; Mevy et al, (2009), high level of saturation causes oil to have high induction period in connection to the presence of phytochemicals present in the oil. These phytochemicals act as free radical scavengers (Loius et al, 2015).

Conversion models for alkyd resin polycondensation reaction were based on the following ideal assumptions.

1) All functional groups of the same type (either acid or basic, but of different raw material) are equally reactive.
2) All functional groups react independently of the chain length,
3) No side reactions occur, and
4) The reaction rates of the elemental reactions are lumped in a global reaction rate.

Due to the complexity of the polymerization procedures, mechanism and raw materials, there are scarcely a detailed polycondensation kinetic model. The semi-empirical second, and apparent third order reaction rate models have been proposed in alkyd kinetics studies (Lin, and Hsieh, 1977; Aigbodion and Okieimen, 1996), however these researches succeeded in describing the course of reaction before the critical gel point and it do not apply to the entire course of the reaction.

2.1.3 Jatropha oil based alkyd resin

Satheesh, et al (2010) studied the kinetics of alkyd resin synthesised from non-edible jatropha seed oil. Glycerol and phthalic anhydride were the polyol and dibasic acid used for the synthesis. A series of alkyd resins having different amount of jatropha oil viz., 40–80% were prepared by employing two stage alcoholysis-polyesterification processes.

The extent of reaction and average degree of polymerisation were calculated from the end group analysis of the reaction mixture withdrawn at regular intervals of time.

The kinetics result revealed that the initial reaction rates followed the second order kinetics and thereafter deviations were observed. An appreciable degree of conversion was also noticed from the extent of the reaction which lies in the range of 49.5–62.5%. The average degree of polymerisation calculated in the region of deviation from second order suggested the occurrence of chain branching at relatively shorter intervals along the polymer chain. The reaction was found to be second order and rate constants were found to be of the order of 10^{-5} g (mg KOH)$^{-1}$ min^{-1}.

Plate 2.1: Jatropha Curcas seed

Jatropha curcas Linnaeus (JCL) seed oil was utilized in the preparation of four sets of alkyd resin (35%, 50%, 60% and 75% oil formulations) using a two-stage alcoholysis–polyesterification method by Odetoye et al (2010). Properties which include; solidification time, solubility, film thickness and drying time were investigated. The film thickness and solidification time were within the range of 0.014mm -0.08 mm and 278 s - 442 s The alkyd produced were also soluble in butanol, turpentine and xylene solvents. Cobalt naphthenate drier was used to improve the drying properties of all the alkyds at an outdoor temperature of 37 °C ± 2. The alkyd produced was utilized in the production of white gloss paints at a pigment-volume concentration of 20.67%. The produced paint was compareable with that formulated using a commercial alkyd resin. The structure of the alkyds was confirmed by H NMR.. It was concluded that *Jatropha Caracas* is one of the most potential raw oil in coating industry and suitable for alkyd resins.

2.1.4 Rheological studies of polymers

Chemical nano structures, rheological and mechanical properties of long oil alkyd resin which was synthesized using different polybasic acid catalysts were studied by IIkhani (2012). The catalyst used were phosphoric acid, 1,2,4-benzene tricarboxylic acid and succinic acid. A reference long oil alkyd resin was prepared. The nano compounds were compared with a reference long oil alkyd resin. Air drying varnishes were prepared using different long oil resins synthesized using the same formula. The nano chemical structures of the resins and varnishes were investigated with FTIR spectroscopy. The rheological properties of varnishes; viscosity, drying time, glossary and film thickness and the mechanical properties; hardness, adhesives test, bending test and impact tests of films which were investigated, revealed that nano chemical structure of the resins and those of the derived varnishes has the same structure . The result also revealed that the rheological and mechanical properties of varnish which was prepared with succinic acid catalyst was better than that which was prepared with 1,2,4-benzene tricarboxylic acid. The prepared vanishes were better than accustomed varnishes.

Lewandowska (2006) studied the rheological characteristics of polyacrylamide(PAM) and of partially hydrolyzed polyacrylamide (HPAM)(degree of hydrolysis up to 80%) in aqueous and sodium chloride solutions with changing experimental conditions such as polymer concentration, temperature, solvent quality, and shear rate applied.Whereas Lewandowska (2006) study was based on experimental conditions, that of Shirley et al (2017) was on the effect of the initial monomer,comonomer and surfactant concentrations on shear viscosity. Shear viscosity measurements results showed that the length of the hydrophobic comonomer augments the hydrophobic interactions causing an increase in viscosity and that the polymer thickening ability is higher for combined polymer.

The influence of PAM hydrolysis degree (DH in the range of 0–80%) on the rheological properties of PAM solutions was investigated. The obtained results confirmed that PAM and HPAM solutions; aqueous and NaCl solution respectively behave as non-Newtonian fluids, which before the critical value of shear rate show shear-thinning behavior. The shear-thickening behavior is observed when the shear rate is above the value. The onset of shear thickening depends mainly on the degree of HPAM hydrolysis, as well as on solution concentration, temperature, solvent quality, and polymer molecular weight.

The flow properties of PAM solutions depend on the polymer concentration. In the case of HPAM solutions, the increase of the PAM hydrolysis degree causes the decrease in the area of shear-thinning behavior and the increase in the area of shear-thickening behavior. The shear-thickening behavior is observed at lower value of shear rate with the increase of the degree of hydrolysis, and with the decrease of polymer concentration.

It was concluded that the decrease of HPAM molecular weight also increases the shear-thickening area of HPAM solutions. The rheological properties of the polymer solutions were evaluated by fitting the data to a power law model. The rheological parameter depends on the degree of hydrolysis ($n<1$for shear-thinning and $n>1$ for shear-thickening), on polymer concentration, and to a lesser extent on temperature. The effect of aging on the apparent viscosity was observed only for the PAM solutions. The fluctuation of apparent viscosity at imposed shear rate occurs also in the PAM solutions. Such behavior was believed to be due to structure breakdown under constant imposed shear rate.

According to Shirley et al (2017), inverse emulsion polymerization technique was employed to synthesize hydrophobically modified polyacrylamide polymers with hydrophobe contents near to feed composition. Three different structures were obtained: multisticker, telechelic, and combined. N-Dimethyl-acrylamide (DMAM), n-dodecylacrylamide (DAM), and n-hexadecylacrylamide (HDAM) were used as hydrophobic comonomers. In order to carry out rheological study on hydrophobically modified polyacrylamide polymer, a specific amount of polymer was dissolved in deionized water. These solutions were put into agitation for 48 hours. More concentrated solutions containing polymers with a larger hydrophobic chain were stirred until they were homogeneous. Interval concentration studied was 0.1% to 10% by wt.

In the work of Shirley et al (2017), solutions were measured in two rheometers, depending on the concentration of the sample. The more diluted samples were analyzed in a rotational rheometer Rheolab QC, using geometry double-walled cylinder (DG42) and more concentrated samples at the Physica UDS200 controlled stress rheometer equipped with a cone and plate (angle 2 and diameter 50 mm) at25±0.05∘C. The zero-shear viscosity (ηo) was obtained by extrapolation of the apparent viscosity.

The work of Shirley et al (2017), also demonstrated that viscosity which is the major parameter in rheological study is advantageous in obtaining higher molecular weight with emulsion. The results showed that molecular weight of the final polymer increased by increasing emulsifier concentration and then remained almost constant without further increase. This showed that the molecular weight of final polymer increased as monomer concentration increases. This aspect according to Shirley et al (2017) influences the behavior of viscosity of aqueous solution, because shear viscosity increases as the length of acrylamide blocks is increased. Lewandowska (2006) results showed that the molecular weight of copolymer increased with initial monomer concentration and by increasing emulsifier concentration it remained almost constant. Shirley et al (2017) concluded that the viscosity of aqueous solutions is function of the polymeric structure.

In the work of Jamal (2012), the effects of nano particle content, polymer concentration and molecular weight, and water temperature, pH, and salinity on their rheological behavior were investigated using a concentric cylinder dynamic rheometer. Series of polyacrylamide and laponite nanoparticle suspensions were prepared through solution mixing.

Rheological investigation showed that the polyacrylamide and a combination of polyacrylamide and laponite suspensions e non-Newtonian behavior in approximately the whole range of shear rate. Addition of laponite showed increase of shear viscosity and share stess at low shear rates. When the concentration of polymer was high, the suspension shear viscosity and stress exhibited less sensitivity to laponite concentrations. The viscosities of the polyacrylamide-laponite suspensions were comparable to those of the neat polyacrylamide solution at higher shear rates. The result indicated the shear viscosity and stress of the samples were increased with increasing polyacrylamide concentration and molecular weight, but were decreased with increasing salinity, temperature, and pH of water

Lewandowska (2012) studied the rheological properties of partially hydrolyzed polyacrylamide (HPAM) in solutions of chitosan (Ch). Combination of aqueous acetic acid and NaCl, aqueous acetic acid and lactic acid were used as solvents for HPAM, Ch-HPAM solution blends and chitosan. The rheological parameters from power law (Ostwald de Waele model) were calculated from the flow curve. It was found that studied polymer solutions exhibited the non-Newtonian behaviour with shear-thinning and/or shear-thickening areas. The final result depends on the thermodynamic goodness of the solvent and on the blend composition.

These solutions; chitosan, HPAM samples and their solution blends displayed non-Newtonian behavoiur. Apparent shear viscosity of chitosan chains depends on their conformation. The n values were below 1, showing the pseudoplastic behavior of HPAM, Ch and their blends. In the case of Ch solution in aqueous acetic acid, the n value was above1, which means shear-thickening behaviour.

2.1.5 Paints

Paint is a term used to describe a number of substances that consist of a pigment suspended in a liquid or paste vehicle, for example, oil or water. With a brush, a roller, or a spray gun, paint is applied in a thin coat to various surfaces, for instance, a wood, metal, or stone. Although it's primary purpose is to protect the surface to which it is applied, paint also provides decoration.

Early artists relied on easily available natural substances to make paint, for emple a natural earth pigments, charcoal, berry juice, lard, blood, and milkweed sap. Later, the ancient Chinese, Egyptians, Hebrews, Greeks, and Romans used more sophisticated materials to produce paints for limited decoration, for instance, painting walls. Oils were used as varnishes, and pigments like yellow and red ochres, chalk, arsenic sulfide yellow, and malachite green were mixed with binders such as gum arabic, lime, egg albumen and beeswax.

Paint was first used by Egyptians and Hebrews as a protective coating. Pitches and balsams were applied to the exposed wood of their ships. The artists started adding drying oil to paint around fifteenth century. This practice helped in hastening evaporation. They also adopted linseed oil as a solvent.

In Boston around 1700, Thomas Child built the earliest American paint mill, a granite trough within which a 1.6 foot (.5 meter) granite ball rolled, grinding the pigment. The first paint patent was issued for a product that improved whitewash, a water-slaked lime often used during the early days of the United States. In 1865 D. P. Flinn obtained a patent for a water-based paint that also contained zinc oxide, potassium hydroxide, resin, milk, and lin-seed oil. The first commercial paint mills replaced Child's granite ball with a buhrstone wheel, but these mills continued the practice of grinding only pigment (individual customers would then blend it with a vehicle at home). It wasn't until 1867 that manufacturers began mixing the vehicle and the pigment for consumers.

Today, synthetic pigments and stabilizers are commonly used to mass produce uniform batches of paint. New synthetic vehicles developed from polymers such as polyurethane and styrene-butadene emerged during the 1940s. Alkyd resins were synthesized, and they have dominated production since. Before 1930, pigment was ground with stone mills, and these were later replaced by steel balls. Today, sand mills and high-speed dispersion mixers are used to grind easily dispersible pigments.

The first step in making paint involves mixing the pigment with resin, solvents, and additives to form a paste. If the paint is to be for industrial use, it usually is then routed into a sand mill, a large cylinder that agitates the tiny particles of sand or silica to grind the pigment particles, making them smaller and dispersing them throughout the mixture. In contrast, most commercial-use point is processed in a high-speed dispersion tank, in which a circular, toothed blade attached to a rotating shaft agitates the mixture and blends the pigment into the solvent.

2.1.5.1 *Raw materials for making paints*

Paint is composed of pigments, solvents, extenders, resins, and various additives. The pigments impart colour and opacity to paint. The basic white pigment is titanium dioxide, selected for its excellent concealing properties, and black pigment is commonly made from carbon black. Other pigments used to make paint include iron oxide and cadmium sulfide for reds, metallic salts for yellows and oranges, and iron blue and chrome yellows for blues and greens.

Binders are polymers, often referred to as resin, forming a matrix to hold the pigment in place. The binders and solvents together are sometimes known as the vehicle.

The binders may be dissolved as a solution or carried as a dispersion of microscopically small particles in a liquid.

Extenders are larger pigment particles added to improve adhesion, strengthen the film and save the binders.

Solvents are various low viscosity, volatile liquids. They include petroleum mineral spirits and aromatic solvents such as benzol, alcohols, esters, ketones, and acetone. The natural resins most commonly used are linseed, coconut, and soybean oil, while alkyds, acrylics, epoxies, and polyurethanes number among the most popular synthetic resins. Solvents either an organic solvent or water is used to reduce the viscosity of the paint for better application.Water-borne paints are replacing some paints that use volatile organic compounds such as the hydrocarbons which are harmful to the atmosphere

Additives are used to modify the properties of the liquid paint or dry film. Additives serve many purposes. Some, like calcium carbonate and aluminum silicate, are simply fillers that give the paint body and substance without changing its properties. Other additives produce certain desired characteristics. Depending on the type of paint and intended use, additives may include:

- dispersants which separate and stabilise pigment particles
- silicones which improve weather resistance
- thixotropic agents these give paints a jelly-like consistency that breaks down to a liquid when stirred or when a brush is dipped into it
- driers accelerate the drying time
- anti-settling agents prevent pigment settling
- bactericides preserve water based paints in the can
- fungicides and algaecides protect exterior paint films against disfigurement from moulds, algae and lichen

Paints are formulated according to their proposed use; primer, undercoat, special finishes (matt, gloss, heat resistance, anti-corrosion, abrasion resistance). .

2.1.5.2 *The manufacturing process of paints*

Paint manufacturing processes include; pigment dispersion, paste thinning and paint Canning.

Pigment Dispersion

Pigments, solvent and binders are mixed to form a paste either in a sand mill or a ball mill. A sand mill is a large cylinder that agitates tiny particles of sand or silica to grind the pigment particles, making them smaller and dispersing them throughout the mixture. The mixture is then filtered to remove the sand particles. A ball mill is a high-speed dispersion tank. There, the premixed paste is subjected to high-speed agitation by a circular, toothed blade attached to a rotating shaft. This process blends the pigment into the solvent.

Paste Thinning

Whether created by a sand mill or a dispersion tank, the paste must now be thinned to produce the final product. The paste is transferred to large tanks where it is agitated with the proper number of solvent for the type of paint desired. Inside these tanks, other additives are also blended into the paint mix.

Paint Canning

After paste thinning, the finished paint product is then pumped into the canning. Empty cans are first rolled horizontally onto labels, then, set upright so that the paint can be pumped into them. A machine places lids onto the filled cans, and a second machine presses on the lids to seal them. From wire that is fed into it from coils, a bailometer cuts and shapes the handles before hooking them into holes precut in the cans. A certain number of cans (usually four) are then boxed and stacked before being sent to the warehouse. This operation can also be manually done.

2.1.5.3 *Quality control*

Paint manufacturers utilize an extensive array of quality control measures. The ingredients and the manufacturing process undergo stringent tests, and the finished product is checked to ensure that it is of high quality. A finished paint is inspected for its density, fineness of grind, dispersion, and viscosity. Paint is then applied to a surface and studied for bleed resistance, rate of drying, and texture.

In terms of the paint's aesthetic components, color is checked by an experienced observer and by spectral analysis to see if it matches a standard desired color. Resistance of the color to fading caused by the elements is determined by exposing a portion of a painted surface to an arc light and comparing the amount of fading to a painted surface that was not so exposed. The paint's hiding power is measured by painting it over a black surface and a white surface. The ratio of coverage on the black surface to coverage on the white surface is then determined, with .98 being high-quality paint. Gloss is measured by determining the amount of reflected light given off a painted surface.

Tests to measure the paint's more functional qualities include one for resistance, which entails scratching or abrading a dried coat of paint. Adhesion is tested by making a crosshatch, calibrated to .07 inch (2 millimeters), on a dried paint surface. A piece of tape is applied to the crosshatch, then pulled off; good paint will remain on the surface. Scrubbability is tested by a machine that rubs a soapy brush over the paint's surface. A system also exists to rate settling. An excellent paint can sit for six months with no settling and rate a ten. Poor paint, however, will settle into an immiscible lump of pigment on the bottom of the can and rate a zero. Weathering is tested by exposing the paint to outdoor conditions. Artificial weathering exposes a painted surface to the sun, water, extreme temperature, humidity, or sulfuric gases. Fire retardance is checked by burning the paint and determining its weight loss. If the amount lost is more than 10 percent, the paint is not considered fire-resistant.

2.1.5.4 *Paint uses*

Paint is used to decorate, protect and prolong the life of natural and synthetic materials, and acts as a barrier against environmental conditions.

Paints may be broadly classified into decorative paints, applied on site to decorate and protect buildings and other objects, and industrial coatings which are applied in factories to finish manufactured goods such as cars.

2.1.5.5 *Binders in paints*

The three most important binders used in modern paints are:

- Acrylic polymers (resins) used mainly in emulsion paints
- Alkyd polymers (resins), decorative gloss paints typically contain alkyd polymers (resins), a typical resin is that produced from a polyol such as propane-1,2,3-triol (glycerol) with a dibasic acid such as benzene-1,2-dicarboxylic (phthalic) anhydride and a drying oil (linseed or soybean oil). Alkyd resin in form of emulsion is also used in water based paint. There is also a resent technology which can shear alkyd resin into water based paint.
- Epoxy polymers (resins). Epoxy resins are often used as the binder in industrial coatings (primers). They give the paint excellent adhesion together with high resistance to chemicals (corrosion), and physical resistance necessary, for example, on ships and chemical storage tanks.

2.1.5.6 *Pigments used in paints*

Pigments give colour and opacity to paints. Amongst the organic pigments, particularly important are azo-, phthalocyanine and anthraquinone derivatives.

The most common inorganic pigment is white titanium dioxide (titanium (IV) oxide) which provides over 70% of total pigments used. It has a high refractive index and gives a 'gloss' to the paint. Another widely used inorganic pigment is finely divided calcium carbonate. This has a low refractive index and is used, together with titanium dioxide, to produce 'matt' paints. Other pigments include iron oxides (black, yellow and red), zinc oxide and carbon black.

Powdered metals such as zinc and some metal compounds, for example zinc phosphate, have corrosion inhibiting properties.

2.1.5.7 *Properties of an ideal paint*

These vary greatly according to the particular end use. The requirements for an automotive topcoat, for example, will be very different to those for a decorative ceiling paint.

Some of the typical attributes required can include: ease of application, good flow out of application marks (e.g. brush-marking), forming a continuous protective film, high opacity, quick drying, corrosion resistance, water resistance, heat resistance, colour stability (i.e. against visible and ultraviolet radiation), abrasion and scratch resistance, durability, flexibility and easily cleaned. The time it takes for a coating to dry after application is an important factor for the paint formulator (Osemeahon et al, 2007). This is because if the coating dries too fast, it will be prone to brittleness and if it dries too slowly, the coating may be subjected to pick up dirt (Trumbo et al, 2001 as cited in Loius et al, 2015).

2.1.5.8 *Paint application methods*

Numerous methods used for paint application including: brush, roller, dipping, flowcoating, spraying, hot spraying, electrostatic spraying, airless spraying, electrodeposition, powder coating, vacuum impregnation and immersion. According to BASF (2015), pseudoplastic paints are applied by brushing, thixotropic paints are applied by rolling and highly pseudoplastic paints are applied by spraying.

2.1.5.9 *Environmental friendly technology on paint manufacturing*

The use of lead compounds in automobile paints has been stopped. The quantity of lead drier used in some special industrial paints has been reduced drastically. Alternatives are being sourced for.This is also applicable to chromates which are also very toxic. Because volatile hydrocarbons can lead to pollution in the troposphere, coatings with lower organic solvent content are required.The routes to achieve this include the use of water-based polymers (emulsion paints), higher solids content polymers (using less solvent), water reducible alkyd, powder coatings and the use of the novel technology which disperses highly hydrophobic alkyd resin into water (Erin et al, 2016).

Water-based gloss paints are now available but the initial gloss of the finish is usually not as high as organic solvent based paints.The customer's choice is between a high performance product and a more environmentally friendly one. Intense research effort continues to improve these paints.

High solids paints (which are solvent-based) are also available but not without compromises in cost and performance.The relative molecular masses of the polymer resins are reduced to a maximum of ca 1000 compared to 5000 in conventional paints.This allows the proportion of the polymer to be increased from 20-30% to 40%, hence the term high solids. The main problem is the need to maintain a low viscosity. As the amount of solids increases so does the viscosity, reaching a point at which the paint cannot be applied properly.The lower proportion of solvent tends to slow down the drying and film hardening process, so changes are made to the structure of the polymer - increased branching tends to reduce viscosity for the same molecular mass. The application of the paint is more difficult. If applied by aerosol, the paint has to be under pressure. Sometimes the paint is applied hot. It is difficult to get as good a finish in appearance using high solids paint.

Powder coatings are used in particular for goods such as bicycles and white goods (refrigerators, washing machines). The powder is made up of a resin (often an epoxy resin), pigments, a catalyst to promote cross-linking when the powder is heated, and additives. The powder is sprayed on to the article using an electrostatic spray gun and is then heat cured to produce a hard coating. Recently acrylic powder coatings have been introduced as clear-coats on car bodies. Although an ideal solution for many applications, curing is achieved at high temperature in an oven and is therefore not universally applicable (e.g. painting of wood and plastics).

A new technology involves the dispersion of highly hydrophobic, high viscosity alkyd resins into water at near-zero VOC levels.These alkyd dispersions close the performance gaps of current WB alkyd options and offer formulators the opportunity to prepare high-performance WB alkyd paint at near-zero VOC.Water-borne paints and coatings are dispersions of sub-micrometer polymer particles. Paints and inks are multi component mixtures that include polymer particles, also called film formers or binders, and a variety of surfactants, processing aids, pigments and sometimes a small amount of solvent.

Paints form films by a process called coalescence where first the water evaporates drawing the binder particles together and then fusing them into irreversibly bound networked structures. All paints that use synthetic polymers such as acrylic, vinyl acrylic (PVA), styrene acrylic, etc. as binders are emulsion or latex coatings. Adhesive properties, long term aging, film-formation or lack of defects in the final film-formation are important product performance issues (Malvern, 2017).

2.1.6 Paint Rheology

Paints are colloidal dispersions of solid particles (dispersed phase) in liquid (dispersion medium) (Malvern, 2005). In such concentrated dispersions, small changes will have a significant effect on the rheological behaviour of the paint. Modern rheometers can be used to give information on processing and storage/stability, as well as performance characteristics of paint. Rheology can be defined as the study of deformation and flow of matters under the influence of applied stress (Rao, 2007). Rheological properties are affected by interaction between droplets. Three basic parameters (shear stress, shear rate and viscosity) are necessary for determination of rheological properties.

A frequent reason for the measurement of rheological properties can be found in the area of quality control, where raw materials must be consistent from batch to batch. For this purpose, flow behavior is an indirect measure of product consistency and quality.

Another reason for making flow behavior studies is that a direct assessment of processability can be obtained. For example, a high viscosity liquid requires more power to pump than a low viscosity one. Knowing its rheological behavior, therefore, is useful when designing pumping and piping systems (Ametek, 2005).

It has been suggested that rheology is the most sensitive method for material characterization because flow behavior is responsive to properties such as molecular weight and molecular weight distribution. This relationship is useful in polymer synthesis, for example, because it allows relative differences to be seen without making molecular weight measurements. Rheological measurements are also useful in following the course of a chemical reaction. Such measurements can be employed as a quality check during production or to monitor and/or control a process. Rheological measurements allow the study of chemical, mechanical, and thermal treatments, the effects of additives or the course of a curing reaction. They are also a way to predict and control a host of product properties, end use performance and material behavior (Ametek, 2005).

According to Anton paar rheometry, rheology helps to calculate the amount of shear rate which will affect a paint or coating sample during application, evaluate whether the viscosity values of a paint or coating will fit the requirements after application and measure the long-term storage stability of paints and coatings.

Often, two products that give similar single-point viscosity readings with same spindle at same rpm will exhibit differing flow properties in the "real world”. Results of viscosity test are very important in rheology world, because the appearance of the sample may contradict the viscometer reading. Once the viscometer reading is taken, then those differences will be quantified with a simple rheological model. Power Law (or Ostwald) Model can be used to fit a typical viscosity versus shear rate or stress versus shear rate curve within the range (Tim, 2016). Rheological properties of paints affect their applications such as sagging, storage stability and shelf life, leveling and brush mark.

To produce paint with good storage stability, rheological properties has to be known.Paints can be a pseudoplastic fluid or a thixotropic fluid or can exhibit both thixotropy and pseudoplasticity.

2.1.6.1 *Paint sagging behaviour*

Sagging is due to the action of gravitational forces on a coating applied to an inclined surface. Gravitational stresses will increase with film thickness, density and incline with the highest shear stress occurring on a vertical plane. The maximum shear rate will occur at the substrate interface and will be dependent on the viscosity at the corresponding shear stress(Malvern,2015). To reduce, sagging it is therefore necessary to increase the viscosity at the corresponding shear stress, which will slow the process, ideally until the film has dried sufficiently.

2.1.6.2 *Paint storage stability*

Achieving product stability is a critical aspect of a paint or coatings formulation. Since many coatings are suspensions of multiple components in an organic or aqueous continuous phase, the functionality of the finished product relies on maintaining these suspended components in a dispersed state for the life time of the product, under all the conditions that will be encountered (Malvern, 2015). Controlling the size of pigment particles can also help for improving the stability of emulsion.

Measuring the storage modulus G' of an emulsion at elevated temperature as a function of time provides an easy method for judging emulsion stability (TA Instrument, 2016). Rheological characterization of paint will also help in determining it stability.

2.1.6.3 *Paint levelling and brush mark*

Once a coating is applied to a substrate, especially if it has striations resulting from brush marks or the pile profile of the roller, it tends to form an undulated or rippled surface. After application, the striations need to flow out in order to form a smooth surface - this process is known as leveling (Malvern, 2015). Subsequent leveling is then driven largely by surface tension forces which try to minimize the area of the free surface and hence produce a uniform film of constant thickness. The rate at which the amplitude of these sinusoidal undulations level out for a Newtonian fluid can be described by Orchard equation (2.9, 2.10 and 2.8)(Orchard, 1962).

$$a = a_0 \left[- \frac{16\pi^4 h^3 \gamma t}{3\lambda^4 \eta} \right] \tag{2.9}$$

$$\frac{da}{dt} = \left[- \frac{16\pi^4 h^3 \gamma t}{3\lambda^4 \eta} \right] \tag{2.10}$$

with a the amplitude, λ the wavelength of the sinusoid, h the coating thickness and γ the surface tension. For non Newtonian fluid it is written as

$$\sigma_{\max} = \frac{8\Pi^3 \gamma a h}{\lambda^3} \tag{2.11}$$

2.1.6.4 *Yield stress in paints*

There are various methods for estimating yield stress (Larsson et al, 2013). The best way to determine a value for the dynamic yield stress is fitting a flow curve with an appropriate yield stress model such as the Power law, Bingham, Casson or Herschel-Bulkley models. Using this approach, you are effectively predicting the onset of solid state behavior from an initial flow state by means of extrapolation. The methods for estimating the static yield stress include; stress ramp, stress growth, creep testing and oscillatory methods. Again the most relevant method is likely to depend on the process you are trying to mimic (Malvern, 2015).

Another method which has generated yield values that correlate well with sagging is an oscillatory amplitude sweep test (Strivain,1999). A quicker method which accounts for some time dependency is a stress growth test, which involves applying a constant shear rate and measuring the resultant stress. The yield point corresponds with the peak stress and its value the yield stress. For the coatings industry in particular, the presence of yield-like behavior can have effects in a wide range of situations—for example, the process control of suspensions (pumpability, cavitation, freezing of valves, loss of metering, and time dependent effects leading to loss of control) (Malvern, 2015).

Yield stresses can improve the kinetic stability of suspensions, particularly resistance to flocculation and sedimentation. A yield point is a sign of a flocculated system that will not form a hard sediment on settling, but will be re-dispersible. Provided the driving stress is inferior in magnitude, a yield stress can obviously inhibit undesired flows at low stresses during film formation, such as sagging, crater formation, and withdrawal from sharp edges, but also can hinder leveling and the release of gases trapped within a coating layer(Malvern,2015). The appearance of sagging goes away if the coating is reformulated to reduce yield behavior(Eley, 2005).

2.1.6.5 *Thixotropic behaviour of paints*

When measuring the ‘flow’ attributes of a paint or coating and also its leveling behavior an important property to consider is thixotropy, which is the time dependent viscosity change under application of shear (Barnes,1997).Whether or not thixotropy is beneficial depends on the system and application in question.Thixotropy plays an important role in paint leveling and coating finish as lower viscosity will ensure flow out before high viscosity is regained. This becomes even more critical if the coating has a yield stress, in which case the elastic structure should only reform after leveling is complete (Malvern, 2015).Too much thixotropy, however, may be detrimental as an extended period of low viscosity will enhance sag and possible drip formation, so finding the right balance is important.

The most suitable test for assessing thixotropy is a step shear test. Here a low shear rate is applied until a steady viscosity value is attained and then the shear rate is increased stepwise to a value ideally corresponding with the shear rate of interest, such as brushing or rolling. After a period of time under these high shear conditions, the shear rate is dropped back to the initial low value and subsequent recovery followed with time. Thixotropy can then be quantified in terms of the amount of time it takes to recover a percentage of the original viscosity or the amount of recovery attained after a given time. Thixotropic recovery can also be modeled using the stretched exponential model.

2.1.6.6 *Power-law model for fluids*

A power-law fluid or the Ostwald–de Waele relationship, is a type of generalized Newtonian fluid for which the shear stress, τ, is given by the equations below;

$$\tau = \mathrm{k}\gamma^{n} \tag{2.12}$$

$$\eta = k\gamma^{n-1} \tag{2.13}$$

Where:

- K is the *flow consistency index* (SI units Pa s^{n}),
- γ is the shear rate or the velocity gradient perpendicular to the plane of shear (SI unit s^{-1}), and
- n is the *flow behavior index* (dimensionless).
- η represents an *apparent* or *effective viscosity* as a function of the shear rate (SI unit Pa s).

This mathematical model, though simple but useful, but can only describe the behaviour of a real non-Newtonian fluid. For example, if n were less than one, the power law would predict that the effective viscosity would decrease with increasing shear rate indefinitely, requiring a fluid with infinite viscosity at stationary condition and viscosity of zero as the shear rate approaches infinity. A real fluid has both a maximum and a minimum effective viscosity which depend on the physical chemistry at the molecular level. Hence, the power law is only a good description of the behavior of fluid over the range of shear rates to which the coefficients were fitted. There are several other models that better describe the flow behaviour of shear-dependent fluids, but they are rather complex.

Therefore, the power law model is predominately used in describing fluid behaviour, permitting mathematical predictions, and correlating experimental data. Power-law fluids can be subdivided into three different types of fluids based on the value of their flow behaviour index: n < 1 is Pseudoplastic, n > 1 is Dilatant and for n = 1 shows a Newtonian fluid.

2.1.6.7 *Pseudoplastic behaviour of fluids*

Pseudoplastic or shear-thinning fluids are fluids with a lower apparent viscosity at higher shear rates, and are mostly solutions of polymeric molecules in a solvent. Large volumes of fluid under low shear are affected by large molecule chain, but they gradually self-aligned in the direction of increasing shear and produce less resistance. A common example of a strongly shear-thinning fluid is styling gel.

2.1.6.8 *Newtonian behaviour of fluids*

Newtonian fluids are those power-law fluids which has a behaviour index of 1, and, the shear stress is directly proportional to the shear rate.

$$\tau = \eta\gamma \tag{2.14}$$

These fluids have a constant viscosity. Most common fluids like air, oils, water, most aqueous solutions, corn syrup, glycerine and other gases are Newtonian fluids. While this holds true for relatively low shear rates, at high rates most oils reality also behave in a non-Newtonian fashion. Common examples are oil films in automotive engine shell bearings and gear tooth contacts.

2.1.6.9 *Dilatant behaviour of fluids*

At higher shear rates, dilatants fluids which are also known as shear-thickening fluids increase in apparent viscosity.They are rarely encountered, but one common example is an uncooked paste of cornstarch and water, sometimes known as oobleck. Another example of dilatants fluid is Silly Putty.

2.1.6.10 *Viscosity of fluids*

Sir Issac Newton first described viscosity as the ratio of the shear stress to the shear rate. The measured viscosity of waterborne formulation is dependent on the shear rate and the shear time. The application, workability and final appearance of waterborne formulation are provided in these formulations through various rheology control systems. These, in turn, influence the viscosity behavior. Formulated waterborne coatings display a high amount of non-Newtonian behavior which is pseudoplasticity and thixotropy.

2.1.7 Emulsion technology

An emulsion is colloidal dispersion of two immiscible liquids such as oils and water in which one liquid is dispersed in another (McClement, 2005).There are two types of emulsion oil-in-water (O/W) and water-in-oil (W/O) emulsions. In O/W oil is dispersed in a continuous water phase while in W/O emulsion water is the dispersed in a continuous water phase. Surfactants (emulsifiers) are essential in formation and stabilization of emulsions. These surfactants, form protective layer around emulsion droplet by reducing the surface tension of an oil and water interface. Energy is needed to deform break up the droplet and is usually provided by intense agitation (Walstra, 1996).

2.1.8 Emulsion stability

Emulsions are thermodynamically unstable (Kontogiorgos, 2004). There are both physical and chemical instability affecting emulsion. Emulsion can be physically affected by Ostwald ripening, flocculation, coalescence, creaming and phase inversion (Rousseau, 2000). Chemical instabilities are oxidation and hydrolysis (McClements, 2005).

Ostwald ripening refers to the growth of large droplet by diffusion of the emulsified monomer from small to large droplets through continuous phase. This results in decrease in number of small droplets and increase in the number of large droplets leading to emulsion instability by creaming (McClements, 2005).Creaming is the separation of emulsion droplets, it can be described as the upward movement of the dispersed droplet as a result of a difference in density between the dispersed phase and the continuous phase (Walstra, 1996).

Flocculation is a type of droplets aggregation in emulsions caused by frequent encounter of droplet particles by Brownian motion (Walstra, 1996). Coalescence occurs when two droplets merge together and become one large droplet due to the rupture of thin films between them (Walstra, 1996). Phase inversion occurs when an oil in water emulsion changes to a water in oil emulsion or water to oil emulsion changes to oil in water emulsion. Phase inversion is a complex process which involves flocculation, coalescence and partial coalescence (Brook et al, 1998; McClements, 2005).

2.2 Summary of Literature Review

There are evidences from literature that many researches are in progress in the study of alkyd resin and its emulsion. The regulations for non-toxic coatings have made attractive the search for a new process to replace the solvent based alkyd resin, which are diluted using low vapour pressure solvents with environmental friendly resins. Hence alkyd emulsion is one of the products that can replace the solvent based alkyd (Sorensen, 2008) and in turn promote the waterborne coating. The quality of these emulsions can be determined through their rheological behavior. With rheological characterization, it will be easy to directly assess and obtain the process ability. For instance, liquid high in viscosity requires more power to pump than one with low viscosity.

The use of linear alkyl benzene sulphonate as an emulsifier and polyvinyl acetate have been reported to be effective in producing an environmentally friendly resin with good chemical and water resistance (Aigbodion et al, 2003). Alireza et al, (2013) reported that fusion process is an environmental friendly method for alkyd resin production and also consumes lower energy. According to Njuku et al, (2014) using reactive diluents produced from cashew nut shells in diluting long oil alkyd resin reduced the VOC content. Gamze (2012) reported that alkyd resin for water reducible coatings can also be produced from waste PET with excellent mechanical properties.

While alkyd resin can be produced from oil with low number of doubl bond and antioxidants such as rice bran oil, the film showed long drying time. It was also reported that an increase in reaction temperature can positively affect the drying time but, will darken the resin (Vikkasit et al, 2006).

Kinetics of polycondensation reaction for the production of alkyd resin was also reported by some researchers. Kinetics of jatropha seed oil based alkyd resins production revealed that initial reaction rates followed second order kinetics and thereafter deviations were observed. The second order rate constants were found to be of the order of 10^{-5} g (mg KOH) according to Satheesh et al, (2010) and the order 10^{-4} $g(mgKOH)^{-1}min^{-1}$ as reported by Ibanga and Nyeneime, (2014).

2.2.1 Research gap

Most of the works on alkyd resin production were based on different drying, semi drying and non-drying oils. Only few works were reported on the use of PKO (*Eleasis guinnensis dura)* and JSO (*jatropha curcas*) oil on alkyd resin production.

Works on alkyd emulsion are available in the literature, but there is none on the use of PKO (*Eleasis guinnensis dura)* and JSO (*jatropha curcas*) oil. The few works reported on the use of PKO (*Eleasis guinnensis dura)* are on solvent based alkyd resins, where styrene monomer was used in the copolymerization process. JSO (*jatropha curcas*) was reported to have been used in the production of solvent based alkyd resin.

Works on classical third order conversion rate model have not received adequate attention. So far in literature review, it appears that only few aspects have been discussed.

This research has gone a long way in covering the gaps in the literature highlighted above by producing reliable data on the utilisation of raw PKO and Jatropha seed oil in alkyd emulsion.

CHAPTER THREE

MATERIALS AND METHOD

3.1 Materials Used

Ammonia solution from Sure Chem Product Ltd England, benzoic acid 99.5% assay from Kermel Chemicals, chloroform from FSA laboratory supplies England, glacial acetic acid 99.5% assay from BDH Chemicals Ltd Poole England, glycerol 99% assay from BDH Chemicals Ltd Poole England, isopropyl alcohol 99.8% assay from Honeywell Germany, industrail grade calcium trioxocarbonate iv, titanium dioxide, cobalt naphthanate and polystyrene acrylic, lithium hydroxide from Loba Chemie reagent and pure Chemical, India, methyl orange indicator from Guaguangdong guanghua Chemical Factory Company ltd China, phenolphthalein indicator from Loba Chemie reagent and pure Chemical, India, Phthalic anhydride, analytical grade, 99.7% assay from Xilong Chemical Co Ltd,China, potassium hydroxide 98% purity from Loba Chemie reagent and pure Chemical, India, potassium iodide, 99.5% assay from Kermel Chemicals, Sodium thiosulphate from Loba Chemie reagent and pure Chemical, India, 98 % purity Sodium hydroxide from Loba Chemie reagent and pure Chemical, India, Starch indicator from Burgoyne Burbidges &Co. India, Wij's solution with 0.002M assay from LOBA Chemie reagent and pure Chemical, India, Xylene 99.5 % assay from BDH Chemicals Ltd Poole England. 99.8 % assay analytical grade ethanol, 99.8% assay laboratory grade methanol and 99.5% analytical grade toluene from BDH Chemicals Ltd Poole England. Also palm kernel oil (*Elaesis guineensis pisifera, dura, tenera* and jatropha seed oil *(Jatropha curcas)*.

Electronic weighing balance, rotational viscometer from Techmel and Techmel USA, laboratory oven, heating mantle, durometer, UV box from Luco Scientific Lab, Benin and Infra red spectrophotometer. 250 ml beakers, 250 ml conical flasks,50ml measuring cylinders, stoppers, 1 litre three necked round bottom flask, nitrogen inlet pipe 1 cubic ft nitrogen gas cylinder, condenser, 300°C thermometer and stirring rod.

3.2 Laboratory Procedure

3.2.1 Extraction and characterisation of palm kernel oil and jatropha seed oil

Raw palm fruits were sourced, processed and the kernels were used for palm kernel oil extraction**.**

3.2.1.1 *Extraction of palm kernel oil (PKO)*

Palm kernel were cracked the nuts were also manually separated from the shells. The shell was disposed. 2kg of palm nuts was first placed in a bowl and suspended on top of boiling water. This was done to losen the oil in the kernel and also to improve yield. The nuts were introduced into a screw expeller, and the palm kernel oil was extracted. The oil extracted was weighed, characterised and set aside for alkyd resin production.

3.2.1.2 *Sourcing of jatropha seed oil (JSO)*

3 liters of jatropha oil was purchased from Luco Scientific Laboratory, Benin, Edo State. The oil was characterised and was used for alkyd emulsion production.

3.2.1.3 *Characterisation of PKO and JSO.*

The properties of the oil samples and alkyd emulsion samples determined include; density and specific gravity, viscosity, free fatty acid, peroxide value, iodine value and acid value.

a. Density and specific gravity determination using ordinary laboratory method.

50ml of *Elaesis guineensis dura and* jatropha oils were placed in a 250ml beaker and placed in a hot water bath to a temperature of 30^{o}C and weighed using an electronic weighing balance.The temperature of the oil was monitored using a laboratory thermometer of 300^{O}C caliberation. The weights of the oils were also recorded.

The same beaker was used for all the samples. Each of the samples was removed, and the beaker washed very well with detergent and rinsed. The beaker was then refilled to the same level with water and then reweighed. The weight of the beaker was also recorded. The same procedure was repeated for each of *Elaesis guineensis pisifera, Elaesis guineensis tenera* and jatropha seed oil *(Jatropha curcas).*

Density was calculated using equation (3.1).

$$\rho = \frac{m}{v} \tag{3.1}$$

Where, ρ is the density of the oil samples, *m* is of the oil samples and *v* is the volume of the oil samples.

The specific gravity was calculated using equation (3.2).

$$Specific\ gravity = \frac{density\ of\ oil}{density\ of\ equal\ volume\ of\ water} \tag{3.2}$$

b. Determination of moisture content of *Elaesis guineensis dura* oil using ordinary laboratory method.

250ml beaker containing a stirring rod was weighed empty (W_1) using an electronic weighing balance. 5g of *Elaesis guineensis dura* oil was then weighed (W_2) into the 250ml beaker containing stirring rod using the same electronic weighing balance. 2g potassium hydroxide (W_3) was added to the content of the beaker to increase evaporation of moisture. Complete evaporation of water was indicated when no more bubbles were observed. The beaker with the content was weighed again (W_4) using the same electronic weighing balance and the result recorded. The same procedure was repeated for each of *Elaesis guineensis pisifera, Elaesis guineensis tenera and* jatropha seeds *(jatropha curcas)* oils.

Weight of moisture was calculated using equation (3.3).

$$\text{Weight of moisture} = W_3 - W_4 \tag{3.3}$$

W_1 is weight of the beaker and stirring rod, W_2 is weight of the beaker, stirring rod and oil, W_3 is weight of the beaker stirring rod, oil and potassium hydroxide, W_4 is weight of the beaker content after evaporation of moisture and W_5 is the total weight of all the content of the beaker.

$$Moisture\ content = \frac{weight\ of\ moisture}{weight\ of\ oil\ sample}\ x\ 100 \tag{3.4}$$

The same procedure was repeated for each of *Elaesis guineensis pisifera, Elaesis guineensis tenera* and jatropha oils.

c. Determination of peroxide value using AOAC 965:33 (1990) standard method

5g of *Elaesis guineensis dura* oil was dissolved in a 250 ml conical flask containing 30 ml of glacial acetic acid (3:2, v/v). 0.5 ml of saturated KI was added to the conical flask. 30 ml of water was also added.The solution was then titrated with 0.1M standard sodium thiosulphate using starch indicator.The end point was indicated when the mixture turned green. Another titration without the oil sample (blank titration) was done using the same reagents. The values were recorded and used for calculating the peroxide value.The same procedure was repeated for each of *Elaesis guineensis pisifera*, *Elaesis guineensis tenera*, jatropha seeds oil.

The value was calculated using equation (3.5).

$$Peroxide\ value = \frac{(S - B)M10}{W} \tag{3.5}$$

Where; *S* is titre value of sodium thiosulphates (ml), *B* is the titre value for blank titration.

M is molarity of sodium thiosulphate solutions. *W* is the weight of oil/samples,

d. Determination of iodine value according to ASTM 1959-69 (1979).

1.0 g of *Eleasis guinnensis dura* kernel oil was dissolved in a 250 ml beaker containing 7.5 ml of chloroform. 12.5 ml of Wij's solution was also added to the mixture. The mixture was covered and was kept in a dark place and allowed to stand for about 30 minutes. Thereafter, 10 ml of 10% potassium hydroxide was added to the same mixture followed by 25 ml of water and 5 ml of a starch indicator. The mixture was titrated against a standard 0.1M sodium thiosulphate solution. The reagent was added with constant shaking until the yellow color of the iodine disappears.

A solution containing no oil (blank solution) was also titrated and used for calculation. Iodine value was calculated using the equation (3.6). The same procedure was repeated for each of *Elaesis guineensis pisifera*, *Elaesis guineensis tenera* and jatropha seeds oils.

$$Iodine\ value = \frac{12.69M(X - V)}{W} \tag{3.6}$$

Where $X$is the volume of the standard sodium thiosulphate used in blank titration, V is the volume of the standard sodium thiosulphate used for the titration, M is the molarity of the standard sodium thiosulphate solution, W is weight of the oil/ samples used for the titration.

e. Determination of acid value according to ASTMD 1639-90 (1994)

1 g of *Elaesis guineensis dura* oil sample was weighed and placed in an oven for 5 mins.20 ml of 99% ethanol was measured into a beaker containing 1 g of *Elaesis guineensis dura* oil sample. The two samples were mixed and placed in an oven for 5 mins. 2 drops of methyl orange indicator were dropped into the mixture after removing from the oven. The mixture was then titrated with 0.1M sodium hydroxide. A pink solution showed the end point. The value was calculated using equation (3.7). The same procedure was repeated for each of *Elaesis guineensis pisifera, Elaesis guineensis tenera* and jatropha oils *(Jatropha curcas).*

$$Acid\ value = \frac{56.1\mathrm{MV}}{\mathrm{W}} \tag{3.7}$$

M is molarity of sodium hydroxide solution used for the titration. V is the volume of sodium hydroxide solution consumed during titration. W is the weight of oil/sample.

f. Determination of viscosity of oil samples.

Techmel rotational viscometer was used according to ASTM D2196-15 (2015) to determine the viscosity of PKO *(Elaesis guineensis dura)* and Jatropha seeds oils *(jatropha curcas).* The oil samples were respectively poured in a beaker and placed under a techmel viscometer. The viscometer was spined at 60 rpm. The viscosity readings were taken when the viscometer displayed a constant reading.

3.2.2. Determination of the effect of PKO species on the acid value and VOC of alkyd emulsion.

(a) Latin square analysis of variance was used to study the effect of different PKO species on the acid value of alkyd resin and volatile organic content of alkyd emulsion.

Table 3.1: Latin Square Plan of Experiment

Oil type/Temperature	230 °C	240 °C	250°C
A	W_1	W_2	W_3
B	W_2	W_3	W_1
C	W_3	W_1	W_2

(b) Latin square design was used to check the effect of the three different species of palm kernel oil on the drying property and non volatile content of alkyd resin.

3.2.3 Production and characterisation of alkyd emulsion

3.2.3.1 *Production of alkyd emulsion from palm kernel and jatropha seed oils*

Alkyd emulsion was produced according to the formulation in table 3.2. The production involved three steps; alcoholysis process, polycondensation and emulsification processes.

Table 3.2: Formulation for the Reaction

Reactants	Weight(g)
Oil	58.19
Pthalic anhydride	23.46
Benzoic acid	3.40
Glycerol	21
Catalyst	0.1
Total	**106.15**

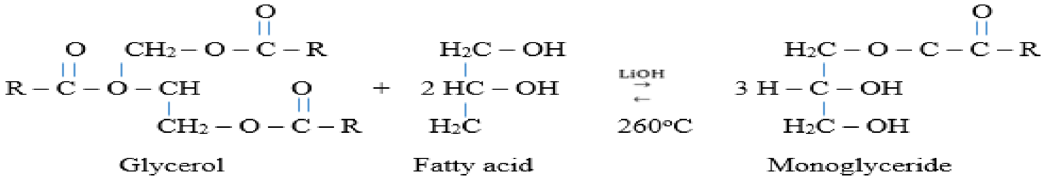
In this research work, alkyd samples were prepared by fusion process with raw palm kernel and jatropha seeds oils. In fusion process, after alcoholysis, the reactants, were charged in the reactor at a temperature of 120°C. Nitrogen gas was introduced to blanket the vapour space at the top of the reaction vessel (Aeitkamp and Don, 1995).

Alcoholysis process**:** This is the first stage involved in alkyd resin production.This process was carried out at a temperature of 260°C for 1 hour using a heating mantle.The heating mantle was set to a temperature of 260°C. In this stage, raw 58.19 g of *Elaesis guineensis* kernel oil and 21g of glycerol were heated together in the presence of 0.1g lithium hydroxide as a catalyst. Nitrogen was purged at a rate of 0.06ft^3/sec.This process converts the oil samples into reactive monoglyceride which can easily take part in polycondensation reaction.This process was completed when the mixtures became soluble in anhydrous methanol (1:3) (w/v).

Polycondensation reaction**:** This is the second stage involved in alkyd emulsion production**.** The reactions were carried out in a half litre three-necked flask fitted with a nitrogen in-let tube, stirrer, digital heating mantle and temperature loop. After alcoholysis, the heating mantle was setted to 120 ˚C. 23.46 g of phthalic anhydride and 3.40 g of benzoic acid was added to the reactor, and the reaction temperature was set to 230–250 ˚C for the polycondensation processes. Nitrogen was purge at a rate of $0.1ft^3$/sec. The progress of the reaction was monitored at every 10 mins interval. An aliquot of the reacting mixture was taking every 10mins using a micro pipette and was diluted in toluene. This was then titrated with 16 ml – 2.2 ml of 0.1M ethanolic potassium hydroxide solutions to phenolphthalein end-point (Agbodion et al, 2003; Ikhuora et al, 2004). The reaction was carried out according to the formulation in table 3.2.

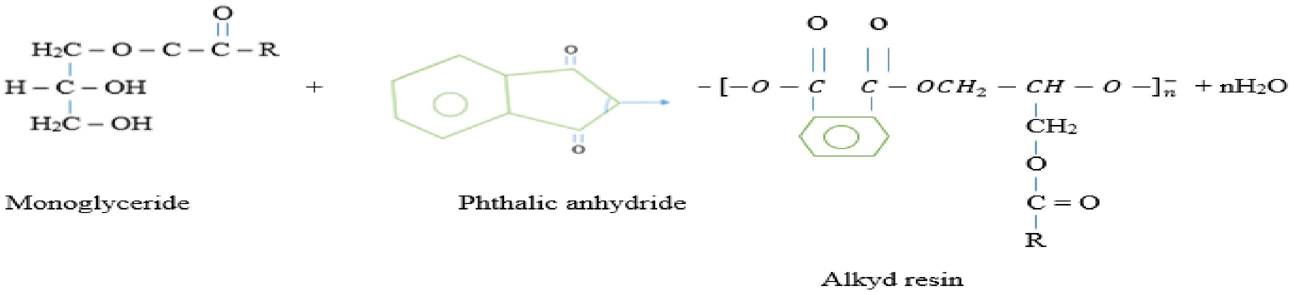
Emulsification process: After polycondensation reaction, the resultant alkyd resin was diluted with water (50-100% v/w) at a temperature of $120^{o}C$ in the presence of isopropyl alcohol (10% v/w) to give alkyd emulsion. The mixture was thoroughly agitated using a motorized stirrer. At the end of the emulsification process, the sample was filtered to obtain a more solid resin.

Equations (3.9) and (3.10) are alcoholysis and polycondensation reaction equations respectively.



(3.12)

Stage 1: Alcoholysis stage



(3.13)

Stage 2: Polycondensation reaction

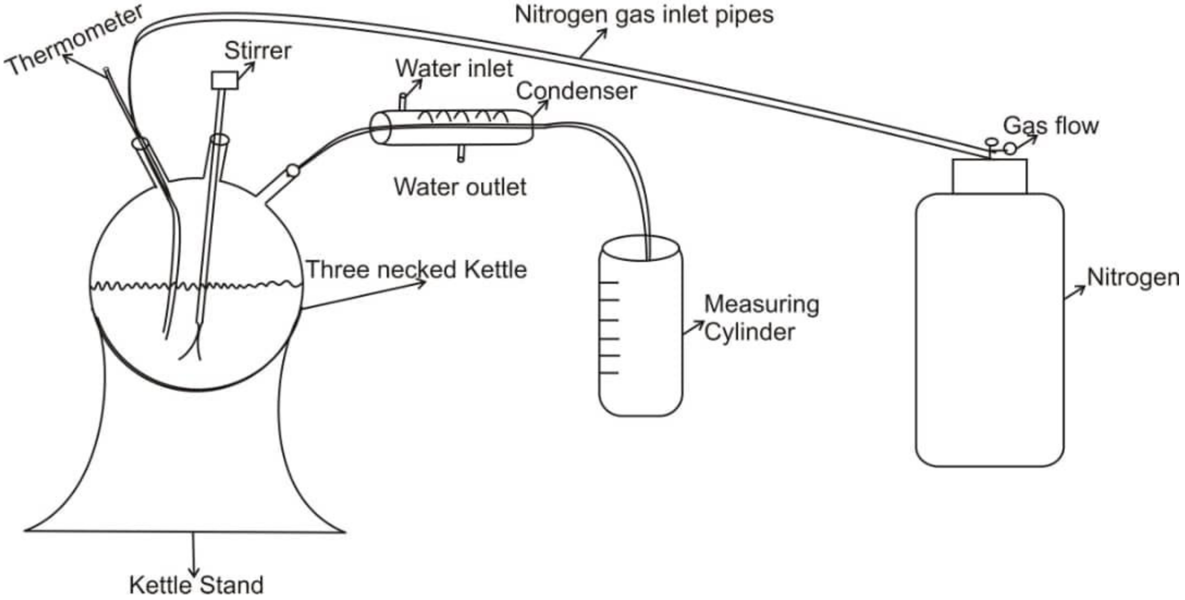


Figure 3.1: Experimental set-up for alkyd resin production

3.2.4 Characterisation of alkyd emulsions

a. Physiochemical properties of alkyd resin

The properties of the oil samples and alkyd emulsion samples determined include; density and specific gravity, viscosity, free fatty acid, peroxide value, iodine value, acid value, solubility, volatile organic content, structural and functional. The procedures for determining density and specific gravity, viscosity, free fatty acid, peroxide value, iodine value, acid value are outlined in section 3.1.

b. Volatile organic content in the resins samples were determined in accordance with ISO 11890-1:2007

According to ISO11890-1:2007, VOC is determined as total volatiles by monitoring weight loss during 1 hour heating at 110ºC. In this method, aluminum dishes were weighed empty and preconditioned by heating in an electric oven for 30 mins at 110ºC, after which they were transferred and stored in a desiccator prior to use. 1g each of the resins and paints were then dispensed into the preconditioned dishes using micro pipettes and were also weighed. The samples were dispersed using spatulas and heated in an electric oven at 110ºC for 60 mins. The samples were put back in a desiccator and allowed to cool. The cooled samples were then weighed and the results recorded. The volatile organic content was calculated from the weight loss displayed according to equation (3.10).

$$W_{voc} = (W_a - W_b) - W_e \qquad (3.10)$$

Where, W_{voc} is weight of volatile organic content. W_e is weight of the empty dish, W_b is weight of the dish with resin/paint before heating and W_a is weight of resin/paint after heating. All weights were measured in gram.

The non-volatile matter was then calculated through weight difference using equation (3.10a).

$$\%\, non - VOC = (100 - \%\, VOC) \qquad (3.10a)$$

c. Determination of chemical and water resistance of alkyd samples using ASTM (D1308-02, 2013) standard test method below.

Alkyd/paint samples were respectively spread on flat Al-dish surface and oven dried at 100ºC for 1hr.The film was used to test the resistance of the alkyd/paint samples. The resistance of the alkyds and paints film were determined in two media: distilled water and NaOH solutions. Alkyd film was immersed in water and NaOH solution respectively for 18hrs to examine the water and chemical resistance respectively.

d. Determination of the drying time of the alkyd emulsion/samples according to ASTM (D1640-83, 1991).

2 g each of the alkyd emulsion and paint samples were applied separately on clean glass plates and mixed with 0.2g of cobalt drier. The samples were spread all over the surface using a small painters brush. The samples were oven-baked for about 90 min at 100 °C. Two drying tests were carried out: set to touch test condition and tack free condition.

For the set to touch, the films were gently touched with the tip of the finger and immediately placed the finger tip against a piece of clean, clear glass. The pressure of the fingertip against the coating was not great. It was observed if any of the alkyd or paint samples was transferred to the glass. One can pass the test if the film is still tacky and none of it adheres to the finger.

For tack-free condition, the alkyd and the paints samples were monitored as they dry. The films passed the test at a period when surface was dried and free from tackiness then the film is said to be tack- free. At this stage, a paper pressed unto the film surface for 50 sec under a 100g weight felled to stick or rip away with a noticeable tack. This was monitored with a harder touch on the films at interval of 30mins.The films were said to be dry through if completely dried**.**

e. UV Curing and hardness tests

Samples were weighed into a Teflon dish and were placed inside a UV box which contains UV bulbs. The UV lights were switched on. The weights of the samples were monitored until a consistence weight was achieved. The cured samples were then tested for hardness according to (ASTM D2240). Shore-A Durometer was used in the determination of hardness of PKOBAE and JSOBAE. The displayed reading was zeroised before use. The sample was placed on a stable plane and the indentor of the machine was vertically pressed on the sample reposefully until the durometer end and the sample contact completely. The reading displayed was recorded. This was repeated about 4 to 5 times, and the average was taken as the hardness reading. The procedure was also used for hardness of PKOP, JSOP, JOS_2P, JOS_3P, PSNA and CP samples.

f. Alkyd emulsion solubility test

In order to test for solubility, 0.5 g each of the alkyd samples were weighed into different 150 ml beakers. 10 ml of each of ethanol, methanol and xylene were respectively used to dissolve the 0.5 g alkyd samples.

g. Emulsion stability test

Rheological characterisation was used to test the stability of the alkyd and paint samples. Two rheological properties which include zero-shear viscosity or viscosity at rest and thixotropic recovery after shearing of the emulsion were measured according to ASTM 2196-15(2015). Techmel and Techmel USA brand of viscometer was used to measure the shear viscosity at 6 rpm, 12 rpm, 30 rpm and 60rpm respectively.

Alkyd samples were filled in 250 ml beaker. Spindle #3 of Techmel and Techmel rotational viscometer was inserted into the beaker and the viscometer was powered on. The viscometer was set to the shear rate of 6rpm. It was allowed to shear the beaker content for few minutes until a steady viscosity reading was achieved.The viscosity reading was recorded. The same procedure was repeated at 12 rpm, 30 rpm and 60 rpm respectively. The viscosity readings were compared and used to determine the sedimentation and creaming behavior of the emulsions. After the 60 rpm shearing, the samples were allowed to rest for 20 minutes before another shearing from 60 rpm, 30 rpm, 12 rpm and 06 rpm respectively to determine the thixotropic behavior of the samples. The results were plotted in a thixotropic loop and used to determine if the samples will flocculate. These procedures were also repeated for the washable paint samples produced.

h. S**tructural and functional group analysis**.

A Fourier transform of infrared spectrophotometer was used to carry out the qualitative and quantitative investigation on nano structures of PKOBAE and JSOBAE. The samples were smeared on ZnSe prism, and the scanning method was adopted to determine the structural and functional groups in PKOBAE and JSOBAE.

3.2.4.1 Optimisation of the Polycondensation Reaction for Alkyd Emulsion Production

Box-behnken design was employed for the Response Surface Methodology in the design and optimization of the polycondensation reaction using PKO (*Elaesis guineensis dura)* and JSO *(jatropha curcas)*.The effects of reaction time, reaction temperature and water to alkyd ratio on the volatile content of alkyd emulsion were investigated. A total of seventeen experiments were conducted. The designs are shown in table 3.3 and table 3.4 respectively.

Table 3.3 RSM (Box-Behnken) Experimental Design for Palm Kernel Oil Based Alkyd Emulsion (PKOBAE).

	Factor A	Factor B	Factor C
Run	Reaction temp(°C)	Reaction time(mins)	water to alkyd ratio(%)
1	240	60	50
2	250	90	75
3	230	75	50
4	240	75	75
5	250	75	50
6	240	75	75
7	230	60	75
8	250	75	100
9	240	75	75
10	240	60	100
11	240	90	100
12	230	90	75
13	240	75	75
14	240	75	75
15	240	90	50
16	230	75	100
17	250	60	75

Table 3.4: RSM (Box-Behnken) Experimental Design for Jatropha Seed Oil Based Alkyd Emulsion (JSOBAE).

Run	Factor A Reaction temp (^{o}C).	Factor B Reaction time(mins)	Factor C Water to alkyd ratio (%)
1	250	90	75
2	240	75	75
3	230	90	75
4	250	75	50
5	240	75	75
6	240	90	50
7	240	90	100
8	240	60	100
9	230	60	75
10	240	60	50
11	240	75	75
12	230	75	50
13	250	75	100
14	250	60	75
15	240	75	75
16	230	75	100
17	240	75	75

Box-behnken design was chosen to produce the alkyd resins because of the ability of the design type to handle three factors at three levels.

The designated PKO stands for palm kernel oil.

The designated JSO stands for jatropha seed oil.

The designated PKOBAR stands for PKO based alkyd resin.

The designated PKOBAE stands for PKO based alkyd emulsion

The designated JSOBAR stands for JSO based alkyd.

The designated JSOBAE stands for JSO based alkyd emulsion.

3.2.5. Optimal working conditions for the production of PKOBAE and JSOBAE

After carrying out the different seventeen experiments, the responses (VOC) were determined. These were used to determine the optimal working conditions. The design expert software; Box bhenkin design was tunned to optimal reaction temperature, reaction time and water to alkyd ratio in order to carry out the optimization of the polycondensation reaction for PKOBAE and JSOBAE. These were tunned following the guide in the contour plot; figure 4.5.

For PKOBAE production, reaction temperature (A) was tunned to to 247. 978^{o}C, reaction time (B) was tunned to 239.21 mins while water to alkyd ratio was tunned to 96.36% of water content to weight of alkyd resin**.** These conditions were approximated for ease of taking the readings. Temperature was rounded off to 248 ^{o}C, reaction time to 240 mins while water to alkyd ratio was rounded to 96%. The response of 1.615 % of VOC was predicted by the RSM.

For JSOBAE production, reaction temperature (A) was tunned to to 246.85°C, reaction time (B) was tunned to 240 mins while water to alkyd ratio was tunned to 99.99 % of water content to weight of alkyd resin. These conditions were approximated for ease of taking the readings. Temperature was rounded off to 247 °C, while water to alkyd ratio was rounded to 100 %. The response of 2.933 % of VOC was predicted by the RSM.

The optimum PKOBAE and JSOBAE produced were analyzed for their physiochemical properties.

3.2.6 Kinetics study of the polycondensation reaction for PKOBAR and JSOBAR.

The kinetics of alkyd emulsion production was studied by monitoring the viscosity and acid value of the polycondensation reaction in line with other researches (Aigbodion and Okiemen, 2001; Eze et al., 2012) at every 20mins interval for a period of 4hrs. An aliquot of the reacting mixture was withdrawn using a micro pipette, dissolved in toluene and titrated with 0.1M sodium hydroxide to phenolphthalein end point. Titration was stopped when the mixture turned pink and the titre values were recorded. The values were used in calculating the acid values at every 20 minutes. Viscosity measurements were carried out using a rotational viscometer. The reacting mixture sample is cooled down and diluted because at high temperature (≈240°C) its viscosity barely decreases with conversion, and the cold sample is diluted because the viscosity of the solvent free sample is excessively large for a standard industrial viscometer. According to Zeno etal, (2007), the viscosity must be determined on a solution at some lower standard temperature. Hence, the solutions of the alkyd samples were prepared by dissolving weighed amount of alkyd sample in 25% acetone.

The polycondensation reaction kinetic was studied using integral method, graphical Santosh (2006) and third order conversion models (Uzo et al, 2015). Extent of reaction and degree of polymerization were calculated from the analysis of the aliquot withdrawn at every 20 mins interval using equations (3.11) and (3.12) respectively. The results were recorded in table 4.16 and 4.17 for PKOBA and JSOBA respectively.

3.2.6.1 *Integral method*

According to equation (2.4), polycondensation reaction follows a second order reaction with k as the second order rate constant.

3.2.6.2 *Evaluation of second order rate constants at various time intervals during the production of PKOBAE and JSOBAE.*

The reaction constants (k) at different time intervals were calculated and recorded in table 4.15. This is detailed in appendix C.

3.2.6.3 *Graphical method*

Second order rate equation as expressed by (Santosh, 2006; Ronald et al, 1998) is given in equation (2.7).

Second order reaction is given by equation (2.7) $k = \frac{1}{t}\left(\frac{1}{Ca} - \frac{1}{Co}\right)$

From (2.7), a plot of $\frac{1}{Ca}$ against t will give an intercept of (- $\frac{1}{Co}$) and slope k. If it is a straight line, the data fit the second order. If it is a curve the data do not fit a second order. Second order kinetic model was investigated by plotting 1/Ca against t.This is illustrated in figures 4.6 for PKOBA production and 4.7 for JSOBA production. 1/Ca was calculated from equation (3.13). The results are shown in table 4.16 and 4.17 for PKOBAE and JSOBAE respectively. These were used for second order kinetics tests.

Extent of reaction $Pav = \frac{Co-Ci}{Co}$ (3.11)

Average degree of polymerisation

$$Dp = (1 - Pav)^{-1} \quad (3.12)$$

$$Inverse\ of acid\ value = \left(\frac{1}{Ca}\right) \quad (3.13)$$

Where *Ca* is acid value, *Pav* is the extent of reaction, *Co* is the initial acid value, *Ci* is the final acid value and *Dp* is the degree of polymerisation.

3.2.6.4 *Alkyd conversion kinetics modeling*

The conversion of acid functional group can be modeled with third order reaction according to (Lin and Hsieh, 1977).

$$r = \rho(c,k,c_e); \quad \rho(c,k,c_e) := k(1-c)(C_e - C)^2 \quad (3.14)$$

Equation 3.14 could be made to adequately describe the entire course of the reaction by assuming a time varying reaction rate as follows

$$k(t) = k(c(t),T(t)) \quad (3.15)$$

$$\frac{dc}{dt} = r(c,k,c_e) = k(1-c)(C_e - C)^2 \quad (3.16)$$

An Equivalent first order model is written in order to simplify the integration of the third order conversion dynamics and enhance estimation of rate parameters, hence

$$\frac{dc}{dt} = r(c,k,C_e) = K^*(t)(1-c) \tag{3.17}$$

Equation 3.17 is integrated as follows

$$\int \frac{dc}{1-c} = \int K^* dt \tag{3.18}$$

$$-\ln(1-c) = K^* t + \gamma \tag{3.19}$$

$$\text{i.e} \qquad c = 1 - e^{-(K^*+\gamma)} \tag{3.20}$$

$$\text{Hence } Y = 1 - e^{-(K^*+\gamma)} \tag{3.21}$$

The generalized first order kinetics and integration constant k and y respectively can be estimated from the gradient and intercepts of the linear fit to the plot of a $-In(1-c)$ against time t respectively. The adequacy of the linear fit is monitored using statistically calculated coefficient of determination R^2

a. Parameter estimation

The kinetic parameters were estimated in order to model this system. In order to estimate the kinetic parameters, the output of the model was correlated with experimental data; acid value and viscosity. The acid number measurement from the two sets of experimental data were converted to conversion (c) and used to estimate the kinetic parameters. The overall reaction time was considered to be zero in the beginning of the reaction monitoring.

The study of reaction kinetics based on viscosity measurement was carried out using viscosity- conversion reaction suggested by classical free-volume theory (Nway and Mya ,2008).

$$V = \mu(c,\rho_\mu) = a_\mu e^{b_\mu / (c_\mu - c)} \tag{3.22}$$

$$\rho_{\mu} = [a_{\mu}, b_{\mu}, c_{\mu}] \tag{3.23}$$

The parameter estimation procedure was formulated in a non-linear least square fashion as shown by equation (3.23a). The approach requires initial guess of the model parameters k, ρ_{μ} and c_e kinetic parameter for predicting the reaction progress and product quality in a batch reactor involves fitting these calibration models to appropriate empirical data; selecting the mechanistic models that would provide adequate fit to the experimental data.This was selected using a computer software; ORIGIN.

The performance of the proposed third order conversion and the free volume type conversion-viscosity model (3.21) for time prediction of reaction progress and emerging product quality are tested based on the experimental data.

Non linear model for polycondensation reactions follows the form of equation 3.23a

$$Y = f(X, \theta) + \varepsilon \tag{3.23a}$$

Where

Y is an n by 1 vector observations

F is any function of X

X is an n-by-1 vector of unknown parameters

θ is a p-by-1 vector of unknown parameters

This model is of exactly the same form as the linear case except that the expected response Y is a non linear function of the parameter θ.

3.2.7 Thermodynamic study of alkyd emulsion

The behavoiur of the alkyd emulsion insuit viscosity was investigated at temperatures of 100°C, 120 °C, 140 °C, 160 °C, 180 °C, 200 °C, 220 °C and 240 °C respectively using a viscometer**.** The Arrhenius equation (3.27) describes the dependency of dynamic viscosity on temperature. According to this equation, viscosity decreases exponentially with temperature.

$$In\,\eta = InA_o + \frac{E}{R}\left(\frac{1}{T}\right) \qquad (3.24)$$

Where η is viscosity in Pa.S, A_o is the pre-exponential factor in Pa.S, E is the activation energy in KJ/mol, R is gas constant which is 8.314J/molK, T is temperature in 1/K, T* = E/R is Arrhenius temperature in 1/K.

The activation thermodynamics parameters (standard enthalpy, entropy and free energy) were calculated according to transition state theory (Wright, 2004 as cited in Olakunle et al, 2014).

$$A = \eta_0 = \frac{RT}{Nh} e^{\frac{\Delta S^{\#}}{R}} \qquad (3.25)$$

$$\Delta H^{\#} = \mathrm{Ea} - \mathrm{RT} \qquad (3.26)$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \qquad (3.27)$$

N is Avogadros constant 6.0221 X 10^{23}, h is Planck's constant 6.62607 X 10^{-34} m^2 kg/S, $\Delta G^{\#}$ is the activation Gibbs free energy, $\Delta S^{\#}$ is the activation entropy, $\Delta H^{\#}$ is the activation enthalpy.

3.2.8 Production and characterisation of washable Paint

3.2.8.1 *Production of washable paint*

Table 3.5: Compositions of Alkyd Emulsion and Polystyrene Acrylic Used for Washable Paint Production

S/N	Samples	Composition of Binders (g)	
		Alkyd Emulsion	Styrene
1	PKOP	50	0
2	PKS_1P	37.5	12.5
3	PKS_2P	25	25
4	PKS_3P	12.5	37.5
5	JSOP	50	0
6	JOS_1P	37.5	12.5
7	JOS_2P	25	25
8	JOS_3P	12.5	37.5
9	PSNA	0	50

Table 3.6: Formulation Detail for Washable Paint Production

Sample	Binders(g)	Preservative (g)	TiO_2 (g)	$CaCO_3$(g)	Water(g)	Antifoam (g)	Drier(g)
PKOP	50	0.89	30	8.14	10.69	0.28	1.8
PKS_1P	50	0.89	30	8.14	10.69	0.28	1.8
PKS_2P	50	0.89	30	8.14	10.69	0.28	1.8
PKS_3P	50	0.89	30	8.14	10.69	0.28	1.8
JSOP	50	0.89	30	8.14	10.69	0.28	1.8
JOS_1P	50	0.89	30	8.14	10.69	0.28	1.8
JOS_2P	50	0.89	30	8.14	10.69	0.28	1.8
JOS_3P	50	0.89	30	8.14	10.69	0.28	1.8
PSNA	50	0.89	30	8.14	10.69	0.28	1.8

Tables 3.5 shows the composition of alkyd emulsion and polystyrene acrylic binders used for the formulation of washable paints. Table 3.6 shows the formulation for the washable paints.

100 g of different samples of washable paints were prepared according to the formulation in table 3.5 & 3.6 and the procedure below using PKOBAE and JSOBAE respectively. The samples were named as follow; PKOP, PKS_1P, PKS_2P, PKS_3P, JSOP, JOS_1P, JOS_2P and JSO_3P and PSNA respectively. Commercial washable paint purshased from New market Owerri, Imo state and PSNA were used for control and comparison.

5 ml of water, 0.28 g antifoaming agent and 30 g titanium dioxide were first mixed in a 250 ml beaker to form paste. 50 g alkyd emulsion, 8.14 g calcium trioxocarbonate iv

and 5.6ml of water were mixed with the paste to form a paint sample which was modified with 1.8g of cobalt drier. The sample was preserved with 0.8g ammonia. Polystyrene acrylic was used to modify the paint samples at different proportions.

Titanium dioxide, calcium trioxocarbonate v, Polystyrene acrylic and dryers were all purchased at New market Owerri, Imo state.

The codes used for the paint samples studied in this work are explained in detail below;

PKOP represents paint sample produced from PKO based alkyd resin.

PKS_1P represents paint sample produced from PKO based alkyd resin modified with 25% of polystyrene acrylic to alkyd emulsion weight.

PKS_2P represents paint sample produced from PKO based alkyd resin modified with 50% polystyrene acrylic to alkyd emulsion weight.

PKS_3P represents paint sample produced from PKO based alkyd resin modified with 75% polystyrene acrylic to alkyd emulsion weight.

JSOP represents paint sample produced from jatropha seed oil based alkyd resin.

JOS_1P represents paint sample produced from jatropha seed oil based alkyd resin modified with 25% polystyrene acrylic to alkyd emulsion weight.

JOS_2P represents paint sample produced from jatropha seed oil based alkyd resin modified with 50% polystyrene acrylic to alkyd emulsion weight.

JOS_3P represents paint sample produced from jatropha seed oil based alkyd resin modified with 75% polystyrene acrylic to alkyd emulsion weight.

PSNA represents paint sample produced usig only polystyrene acrylic.

3.2.8.2 *Characterisation of washable paints*

The samples were characterized according to ASTM standard methods.

a. Physiochemical properties

This is reported in section 3.1.5

b. VOC

VOC test procedure is outlined in section 3.3.2

c. Chemical and water resistance

The procedure for chemical and water resistance can be found in section 3.3.2

d. Drying performance

Drying test procedure can also be found in section 3.3.2

e. UV Curing and hardness test

UV Curing and hardness test procedures can also be found in section 3.3.2

f . Adhesion resistance

Adhesion was tested using ASTM (D3359-90, 1991).To carry out adhesion test, a portion of the dried coat was marked out and a tape was placed on the portion and then pulled out. The film will pass the test if no sample adheres to the surface of the tape.

g. Bleed resistance

Bleed resistance was monitored by mere observation. Paint samples were applied on a surface and then monitored how they bleed. The film will pass the test if it does not show any sign of sweat on the surface.

h. Pigment volume concentration

Pigment volume concentration was also calculated from the paint formulation using equation (3.28) .A paint with solid portion above 50% will show better hiding power and durability.

$$PVC\% = \frac{volume\ of\ pigment}{solid\ portion\ of\ pigment + volume\ of\ binders.}\ x\ 100. \qquad (3.28)$$

3.2.8.3 *Rheological characterization of washable paints*

The rheological characterization of coatings was carried using Techmel and Techmel USA brand of Brookfield rotational viscometer (ASTM D 2196.2015) at low shear viscosity (LSV) of 6 rpm,12 rpm and 30 rpm respectively and a medium shear viscosity (MSV) of 60rpm. The consistency of a coating (i.e., in-can appearance, pouring and mixing behavior) are processing properties defined by medium shear viscosity (MSV). The LSV correlates to all low rate processes like leveling, sagging, settling and sedimentation (TA.Instruments, 2015). The high shear viscosity (HSV) which correlates to coating performance and application conditions like brushing, rolling and spraying was determined by plotting viscosity values against shear rate according to BASF (2015).

The result of the rheological characterization was fitted into power law model of equation (2.13) given below. $\eta = k\gamma^{n-1}$

The model was converted to a linear model by taking the log of both sides. The power law model also known as Ostwald de Waele equation measures the Newtonian behaviour of a fluid. The regression equation of (2.13) is written as equation (3.29).

$$\log\eta = n - 1\log\gamma + logk \qquad (3.29)$$

Plots of Logη against logγ will give a straight line of slope antilogk and intercept n-1. Antilog of k gives the value of consistency (k) and n gives power law or flow index. n is a measure of non-Newtonianness. For a Newtonian fluid, n = 1; for a shear-thinning fluid it is between 0 and 1 and for a shear thickening fluid it is greater than1.

3.3 Method of Data Analysis

The data provided in this research were analysed using quantitative method of data analysis. The data were collected from laboratory experiments, and were analysed using mathematical equations, Latin Square ANOVA and computer softwares. The following softwares were used in the data analysis: Design expert software and Microsoft excel. Mathematical equations were used to determine specific values of various parameters from the experimental readings and determine the reliability of the experimental process. Design expert software was used in determining the optimal experimental working conditions. Microsoft excel was used to present the experimental results in form of plots and charts.

CHAPTER FOUR

RESULTS AND DISCUSION

4.1 Oil Extraction and Characterisation

4.1.1 Oil extraction

Oils were extracted from three different species of palm kernel which include; Osukwu (*Elaesis guineensis pisifera*) coded as specie A, Ojukwu (*Elaesis guineensis tenera*) coded as specie B and Okporoko (*Elaesis guineensis dura*) coded as specie C. The results of the quantity of palm kernel used for extraction, quantity of oil produced, quantity of cake produced and oil yield are recorded in table 4.1.

Table 4.1: Oil Extraction

Products	Weight(kg) specie A	Weight(kg) specie B	Weight(kg) specie C
Palm kernel	2.00	2.00	2.00
Palm kernel oil	0.70	0.79	0.74
Palm kernel cake	1.29	1.20	1.25
Oil loss	0.01	0.01	0.01
Oil yield	0.698 (35%)	0.79 (39.5%)	0.74 (37%)

From table 4.1, osukwu specie *(Elaesis guineensis pisifera)* has a yield of 35%, ojukwu specie *(Elaesis guineensis tenera)* has a yield of 39.5% and okporoko specie *(Elaesis guineensisdura)* has a yield of 37%.

4.1.2 Characterisation

Oils extracted from the three species of palm kernel were characterized and the physico-chemical properties recorded in table 4.2.

Table 4.2: Physico-Chemical Properties of the Oils

Properties/Oil species	Specie A	Specie B	Specie C	JSO
Moisutre content (%)	0.3	0.34	0.32	0.40
Viscosity(mpa.s)	784.5	780	500	811
Density(kg/m3)	0.714	0.726	0.709	0.6834
Specific gravity	0.908	0.924	0.903	0.8695
Free fatty acid(mgNaOH/g)	4.21	3.98	3.92	7.0200
Acid value (mgNaOH/g)	8.42	7.95	7.84	14.025
Peroxide value(mEq/g)	10	12	11.6	4.0000
Iodine value(gI_2/100 g)	22.21	22.08	22.08	105.32

The densities of the PKO samples were found to be within the range of 0.709 g/cm^3 to 0.726 g/cm^3 where as that of JSO was found to be 0.6834 g/cm^3. At a shear rate of 6rpm and 24^{o}C the absolute viscosity of the samples measured around 500mPa.s to786.5 mPa.s. The specific gravity of the PKO samples were found to be between 0.903 to 0.924, that of JSO *(jatropha curcas)* oil is 0.8695. Acid values of the PKO samples were found to be between 8.42 (mgNaOH/g) and 7.84 (mgNaOH/g) where as that of JSO *(jatropha curcas)* oil is 14.025(mgNaOH/g). The lower the acid value of an oil the fewer the free fatty acids it contains which makes the phenomenon of rancidification less as reported by Aigbodion &

Pillai,(2001). A high acid value implies rancid oil. The acid value of JSO *(jatropha curcas)* oil is higher than that of PKO. This indicates that JSO contains more free-fatty acid than PKO.

The free fatty acid of PKO samples calculated from acid value was found to be 3.92 to 4.21 mg NaOH/g of oil. These are within the acceptable limit for edible oils which is less than 10 mg NaOH/g of (Belley, 1982). That of JSO (*jatropha curcas)* oil is 7.02 mg NaOH/g. Vegetable oil which contains high free fatty acids, interfer with the separation of fatty acid ester and glycerols this was reported by Hanna and Ma, (1999). This indicates that the oils would be good to under go polymerization reactions.

Peroxide values for the PKO oil samples were calculated to be within the range of 10mEq/g to 12mEq/g. The high peroxide value shows that the oils can easily go rancid and therefore has short shelf life.The peroxide value for JSO *(jatropha curcas)* is 4mEq/g. Oils having high percentages of peroxide are unstable and grow rancid easily as iindicated by Nzikuo et al, (2007). Peroxide value above 20meg/kg will have a rancid flavour (Connell, 1975 in Kong, 2011). JSO *(jatropha curcas)* is more stable than PKO. This indicates that if the oils are to be used for the purposes of alkyd emulsion production, then they have to be utilized as soon as they are produced or extracted.

The iodine value points at the level of unsaturation, an oil with iodine value less than 100(mgKOH/g) is classified as a non drying oil, that less than190(mgKOH/g) are classified as semi-drying oil while that above 190(mgKOH/g) are drying oils according to Mushtaq, (2016). The PKO oils are non-drying in nature. The iodine value of JSO *(jatropha curcas)* is higher than that of PKO.Hence JSO *(jatropha curcas)* is a semi drying oil. Consequently, the higher the iodine value, the higher the drying qualities of the oil as reported by Gardner,(1948). Alkyd emulsion and paint samples produced from these oils may likely show poor drying performance. This poor performance can be boosted by carrying out the polycondensation reaction in the presence of benzoic acid and polystyrene acrylic modification.

4.2 Effects of PKO Species on the Acid Value and VOC of the Alkyd Emulsion

Latin square design was used to screen 9 samples of alkyd emulsion produced from three different oil species. Acid values and volatile content of the nine samples were determined and the results recorded in table 4.3.

Table 4.3: Results of acid value and Volatile organic content for different PKO species

Run	Acid value	% Volatile organic content	% Non volatile content
1	7.2	33	67
2	7.0	42	58
3	5.7	26	74
4	5.0	15	85
5	4.6	46	54
6	5.7	16	84
7	7.5	53	47
8	8	49	51

Table 4.3 shows the acid value and percentage volatile organic matter used for latin square ANOVA. The samples were screened based on these properties. Volatile organic

content of the alkyd emulsion produced from the three different species of palm kernel oil was calculated from equation (3.10) (detailed in appendix B). The non volatile matter was then calculated through weight difference using equation (3.10b).This was used for latin square ANOVA (detailed in appendix C). The result is shown in table 4.4 below.

Table_4.4: Latin Square ANOVA Table On Volatile Organic Components Response

Source of variance	Sum of squares	No of degrees of freedom	Estimate of variance	Variance ratio
$X_{1=}$ Temp.	545.34	2	272.67	2.51
X_2 = Oil type	213.78	2	106.89	0.98
X_3 =Water to alkyd ratio	416.678	2	208.34	1.92
Residual	-216.94	2	-108.46	
Total	958.85	8		

Table 4.4 showed that reaction temperature, oil type and water to alkyd ratio, do not show significant effect on the resin volatile content at 5% and 1% significance respectively. This means that the percentage of volatile organic component does not substantially depend on these parameters. It can be inferred that this depends on raw materials and method of esterification process used. Using solvent in place of water will introduce high percentage of volatile organic component to the product and secondly fusion process eliminates the use of azeotropic solvent as reported by Aeitkamp and Don, (1995) which also stands a chance of affecting the volatile organic content.

From table 4.4 which is Latin Square analysis of variance, the variance ratios of factor X_1 (reaction temperature), X_2 (Oil type) and X_3 (Water to alkyd ratio) are 2.51, 0.98 and 1.92 respectively. F_{table} distribution, at 5% level of significance and 2 degrees of freedom gave a variance ratio of 19. At 1% level of significance and 2 degrees of freedom in F_{table} distribution, the variance ratio is 99. These values are greater than the values obtained in table 4.4. Since these values are greater, it implies that the factors $X_{1,}$ X_2, and X_3 are not significant factors. This means that the volatile content does not substantially depend on reaction temperature, oil type and water to alkyd ratio.Table 4.5 is the result of Latin Square analysis of variance which was also carried out using acid value as the response.

Table 4.5: Latin Square ANOVA Table on Acid Value Response

Source of variance	Sum of squares	No of degrees of freedom	Estimate of variance	Variance ratio
$X_{1=}$ Temp.	214.33	2	107.17	0.51
X_2 = Oli type	21.28	2	10.64	0.051
X_3 =Water to alkyd ratio	416.678	2	208.34	0.99
Residual	-420.75	2	210.38	
Total	231.53	8		

From table 4.5 which is latin square analysis of variance on acid value, the variance ratios of factor X_1 (reaction temperature), X_2 (Oil type) and X_3 (Water to alkyd ratio) are 0.51, 0.051 and 0.99 respectively. The variance ratio from F_{table} distribution, at 5% and 1%

levels of significance and 2 degrees of freedom are 19 and 99 respectively. These values are also greater than the values given in table 4.5. This implies that the factors X_1, X_2, and X_3 are not significant factors, meaning that the acid value does not substantially depend on these factors. Hence, there are no significant differences in properties of alkyd emulsion produced from oils of different species of palm kernel. Therefore, any of the species can fit in for the reaction.Okporoko *(Elaesis guineensis dura*) specie was selected since it is the most available. This has not been reported in the literature.

4.3 Production and Characterization of Alkyd Emulsions

4.3.1 Production of alkyd emulsions

Samples of water in oil PKOBAE and JSOBAE were successfully produced using isopropyl alcohol as an emulsifying agent.

4.3.2 Characterization of PKOBAR and JSOBAR.

Different properties of alkyd produced from PKO *(Eleasis guineensis dura)* and jatropha seed *(jatropha curcas)* oil which include, drying performance, water and chemical resistance, density, acid value, specific gravity, iodine value, viscosity and volatile component and VOC were determined. The results were recorded in tables 4.6 through 4.8. Physiochemical properties were recorded in table 4.6, drying performances were recorded in table 4.7 and table 4.8 shows the water and chemical resistance.

a. Physiochemical properties of PKOBAE and JSOBAE

Table 4.6: Physiochemical Properties of PKOBAE and JSOBAE

Test	PKOBAE	JSOBAE
Volatile organic content %	2.000	3.00
Acid value (mgKOH/g)	9.70	5.90
Density(g/m$^{3)}$	0.870	0.8412
Spg	1.207	1.0621
Viscosity(mPa.s) 6rpm	1722	1048
Iodine value(mgNaOH/g)	32.99	32.99

Table 4.6 showed that alkyd sample produced from PKO (*Eleasis guineensis dura*) specie, had acid value of 9.70mgKOH/g. This is comparable with the value obtained by (Aigbodion et al, 2003; Lane, 1994), which is in the range of 8 – 10 mgNaOH/g oil. The alkyd produced from JSO *(jatropha curcas)* has an acid value of 5.90 mgKOH/g. Low volatile organic content of 2% for PKOBAE and 3% for JSOBAE are indication that the alkyd emulsion has more solid portion and non polluting category. Though the VOCs are higher than the range of 1% to 1.5% reported by Aigbodion et al, (2003), they are still within the value of 0.30 - 7.99 % stipulated by EU for low VOC content. The iodine value points at the level of unsaturation, thus it affects the drying qualities.The higher the iodine value, the higher the drying qualities of the alkyd resin, hence exposure of this resin to oxygen may not cause appreciable drying. The viscosities indicate that the samples will be free from sedimentation during storage. High viscosity is also desired for pigment grinding during paint production.

b Drying performance of PKO (Eleasis guineensis dura) specie and jatropha seed oil based alkyd emulsion

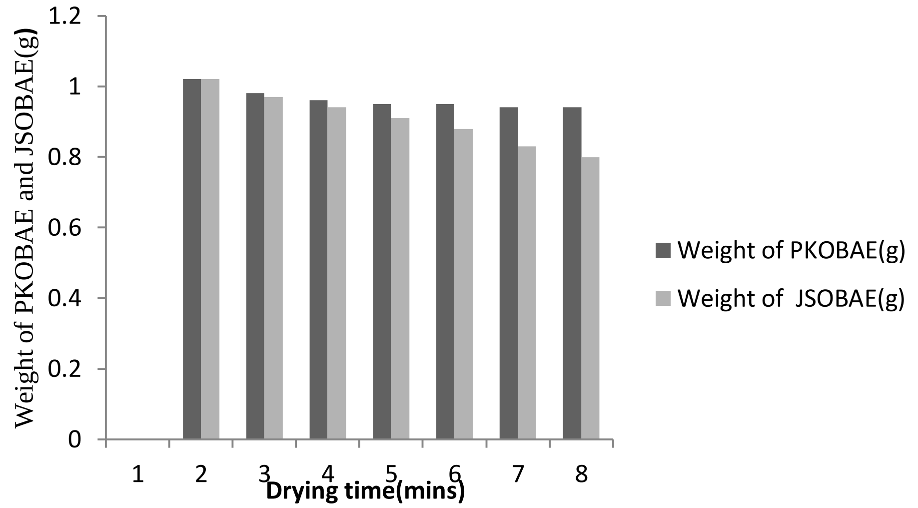


Figure 4.1: weight loss during the drying of the emulsions

The drying test result is recorded in table G1 (Appendix G). It shows the extent at which the alkyd samples loss weight when subjected to a temperature of 100^{o}C. The drying test was carried out for a period of 120 mins. The drying performance carried out at 20 minutes interval showed poor drying performance of the PKOBAE and JSOBAE in the presence of cobalt dryer. Figure 4.1 is the representation of the weight loss during the drying of the PKOBAE and JSOBAE respectively. From the result of the drying tests carried out for PKOBAE and JSOBAE using the same quantity of resins at the same length of time, JSOBAE dried to a lesser mass compared to PKOBAE. This suggests that JSOBAE showed better surface dry and tack-free dry relative to PKOBAE. However, these alkyd emulsions showed poor performance to tack-free test after 60 mins exposure to oven temperature at 100^{o}C as the paper fell off with little stain.

For set-to-touch test, there were also little stains left on the finger tip. These could be because the oils were used raw and are non-drying and semi-drying oils respectively which contain high degree of saturations compared to drying oil. This agrees with Muhammad et al (2014) that the limited unsaturation in the fatty acid chains of non drying oil is responsible for inferior curing properties of resins produced from the non drying oil compared to other drying oil based resins. The drying test result is also in agreement with (Eromosele and Eromosele, 2002; Mevy et al, 2009); that high saturation causes oil to have high induction period. Amina (2017) also reported that non drying oil yield non- drying or plasticing resins.

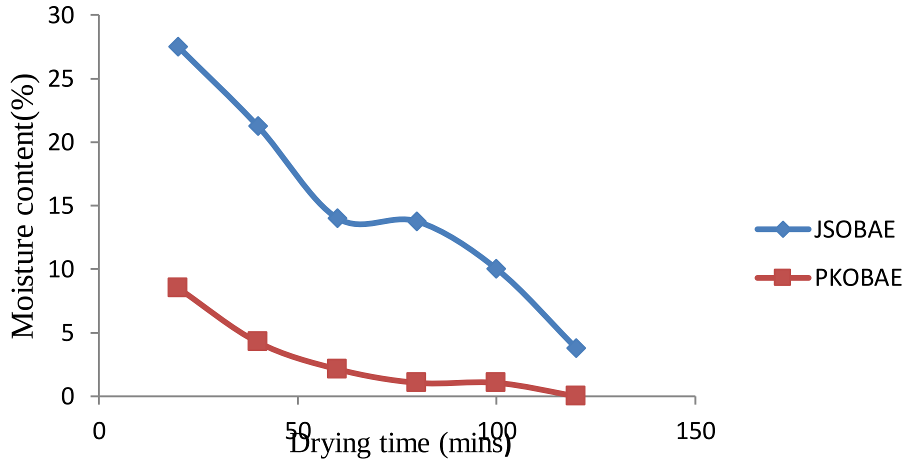


Figure 4.2: Drying curve

Figure 4.2 show the drying curves of PKOBAE and JSOBAE respectively. The curves show that as drying time of JSOBAE and PKOBAE samples progresses, the moisture content was reduced.

c. Chemical and water resistance of PKOBR and JSOBR emulsion.

Table 4.7: Chemical and Water Resistance of PKOBR and JSOBR Emulsions

	PKOBR		JSOBR	
Time(hrs)	Effect in NaOH(0.1N)	Effect in water	Effect in NaOH(0.1N)	Effect in water
1	No effect	No effect	No effect	No effect
6	No effect	No effect	No effect	No effect
12	Whitening	No effect	Whitening	No effect
18	Whitening	No effect	Whitening	No effect
24	Whitening	No effect	Whitening	No effect

Table 4.7 represents the performance of PKOBAE and JSOBAE films in alkali and water media. PKOBAE and JSOBAE showed different levels of resistance in the two media.The dried films of both samples on distilled water showed no visible effect after 24hrs. On exposure to 0.1N KOH after 12 hours of exposure, the dried films showed whitening effect.This is an indication that alkyds generally have low alkali resistance.The poor alkali resistance of the alkyds may be due to the fact that they contain ester groups, which are known to be susceptible to hydrolysis by alkali as reported by Uche, (2016).

d. Solubility of PKOBR and JSOBR emulsion

PKOBAE and JSOBAE were soluble in various solvents (xylene, methanol and ethanol) because their structures contain chemical groups such as (hydroxide, and ethers). This shows that the PKOBAE and JSOBAE can also be used in organic solvents.

e. Rheological properties of PKOBAE and JSOBAE

Table 4.8: Variation Of Viscosity Of PKOBAE and JSOBAE With Shear Rate

Share rate γ(rpm)	PKOBAE Viscosity η(mPa.s)	JSOBR Viscosity η(mPa.s)
6	1050	1048
12	577.3	522.3
30	210.6	208.4
60	105.4	106.6

Table 4.8 shows the average rotary viscometer reading at different shear rates. The readings show that the resins viscosities change with shear rates. This is an indication of non Newtonianness of the samples. The viscosity of a non Newtonian fluid changes as the shear rate changes.

Table 4.9: Average Viscosity Of PKOBAE and JSOBAE At Different Time And Shear Rate Of 60RPM

Time t(mins)	PKOBAE Viscosity η(mPa.S)	JSOBAE Viscosity η(mPa.S)
0	105.4	107.1
5	105.6	106.6
10	106	106.9
15	106.0	107.1

20	106.1	107.1
25	106.1	107.1
30	106.1	107.5

Table 4.9 shows the average samples viscosity readings at a shear rate of 06 rpm. The viscosity readings were taken at interval of 5 mins for a period of 30 mins. These were used to study the variation of PKOBAE and JSOBAE viscosity with time. The readings showed slightly change in viscosity with time. This is an indication of non-Newtonianness of the samples; a psuedoplastic behavior.

d. Structural and functional group of PKOBAE and JSOBAE.

Table 4.10: FTIR Results for PKOBAE and JSOBAE

Frequency range	Absorption (cm^{-1})		Group	Comments
	PKOBAE	JSOBAE		
4000 -3000(cm^{-1})	3391	3469	O-H stretching	Alcohol
3000 - 2500(cm^{-1})	2931	2932	C-H stretching	Alkane
1750 -1700(cm^{-1})	1707	1725	C=O stetching	Carboxylic acid, esters
1124 - 1087(cm^{-1})	1123	1119	C-O stretching	Secondary alcohol
1085 -1050(cm^{-1})	1072	1071	C-O stretching	Primary alcohol
1000 - 650(cm^{-1})	982	986	C=C bending	Alkene

Table 4.10 shows the result of the FTIR analysis for PKOBAE and JSOBAE. The spectra Figures G1 and G2 in appendix G identified the chemical nano structures of the PKOBAE and JSOBAE respectively. The broad spectra absorptions which occured in the range of 3570 cm^{-1} – 3200 cm^{-1} signifiy the presence of hydroxyl group (-OH).The intensity of peaks of FTIR spectra at –OH functional group for PKOBAE (3391cm^{-1}) and JSOBAE (3469 cm^{-1}) are different.The stretching vibrations of methylene and methyl groups are in the region of 2931 cm^{-1} and 2923 cm^{-1} for the two samples respectively**.** The presence of C=O (carbonyl compound) is indicated by 1707 cm^{-1} and 1725 cm^{-1} for PKOBAE and JSOBAE spectra respectively. The absorption which occurred within the range of 1750 cm^{-1} – 1700 cm^{-1} is an indication of a simple carbonyl compound such as ester or carboxylic acid. This implies that the resins contain some polar groups such as (–COOH) remnants of the polybasic acids and (O-H). As reported by Ilkhani, (2012), all long oil alkyd resin synthesized using different poly basic acid catalyst have same chemical nano structures in the region of 1123 cm^{-1} and 1072 cm^{-1}. 1040 cm^{-1},982 cm^{-1} for PKOBAE and 1119 cm^{-1},1071 cm^{-1} and 986 cm^{-1} for JSOBAE show the C-H bending vibration of aromatic compounds which can exist as complex band structure. The absorption bands 1260 cm^{-1} and 1207 cm^{-1} for PKOBAE and JSOBAE respectively originate from the stretching vibration of C-O group.

The presence of – C=O group shows that polycondensation reactions took place, and as a result polymers were formed. An important reason of different intensity of peaks in FTIR spectra for example the –OH peak can be attributed to difference in viscosity of the resins. This explains why PKOBAE has a lower viscosity than the JSOBAE. Polar groups (-COOH/-OH) are very active promoters of adhesion due to their attraction to substrate or by their influence in improving the wetting properties as reported by Issam and

Chuen, (2009). The presence of these groups explains the excellent adhesion property of PKOBAE and JSOBAE. Water resistance of PKOBAE and JSOBAE are also attributed to the presence of hydroxyl group as reported by Mohammed and Noor, (2017). The absorption in the regions of 1123 cm^{-1} and 1071 cm^{-1} which show the C-H bending vibration of aromatic compounds which can exist as a complex band structure proved that the PKOBAE and JSOBAE are long oil resins

4.4 Optimisation of the Polycondensation Reactions

4.4.1 Box-behnken response surface methodology (RSM) for PKOBAE production.

Responses for the seventeen experiments designed using Box-behnken RSM are recorded in table 4.11. The ANOVA result is given in table 4.12.

Table 4.11: Experimental Design and Response for Production Of PKOBR Emulsion

Run	Factor A Reaction temp (^{o}C)	Factor B Reaction time (sec)	Factor C water to alkyd ratio (%)	Response Volatile organic content (%)
1	240	120	50	25.23
2	250	240	75	6.00
3	230	180	50	10.00
4	240	180	75	8.00
5	250	180	50	7.00
6	240	180	75	6.00
7	230	120	75	20.00
8	250	180	100	5.00
9	240	180	75	7.00

10	240	120	100	16.00
11	240	240	100	4.00
12	230	240	75	8.00
13	240	180	75	5.00
14	240	180	75	10.00
15	240	240	50	4.00
16	230	180	100	8.00
17	250	120	75	6.00

Long oil length alkyd emulsion was successfully prepared with PKO from okporoko specie *(Elaesis guineensis dura)* according to the formulation in table 3.2. The polycondensation process was carried out according to the designed of experiment in tables 3.4 for PKOBAE using Box-behnken RSM. The designs suggested a polynomial model with an inverse square transform quadratic model. The model is a significant model which did not lack fit. Equation (4.1) is the model equation. After the elimination of insignificant terms, equation (4.1) was reduced to equation (4.2) which is the model final equation for VOC response.

$$VOC = +7.33 - 2.75A - 2.65\,B - 1.65\,C + 3.00\,AB + 8.31\,BC + 3.82\,B^2 \qquad (4.1)$$

Table 4.12: Analysis of Varience (ANOVA) for PKOBR Emulsion

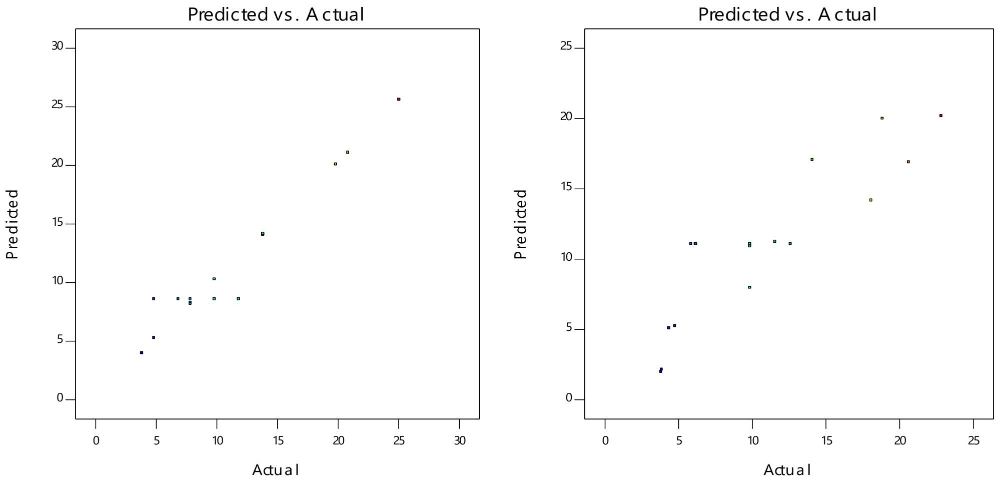
Analysis of variance table [Partial sum of Square- Type III

Source	Sum of square	df	Mean square	F Value	P-value Prob > F	
Model	512.59	6	85.43	20.09	< 0.0001	Significant
A-Reaction temp.	60.50	1	60.50	14.23	0.0037	
B- Reasction time	56.34	1	56.34	13.25	0.0045	
C-water to alkyd ratio	21.88	1	21.88	5.14	0.0467	
AB	36.00	1	36.00	8.47	0.0156	
BC	276.06	1	276.06	64.91	< 0.0001	
B^2	61.82	1	61.82	14.54	0.0034	
Residual	42.53	10	4.25			
Lack of fit	27.73	6	4.62	1.25	0.4335	Not significant
Pure Error	14.80	4	3.70			
Cor Total	555.12	16				
R-Square						0.9234
Adj R-Square						0.8774
Pred R- Square						0.6798

$$VOC = +7.33 - 2.75\text{A} - 2.65\text{ B} - 1.65\text{ C} + 3.00\text{ AB} + 8.31\text{ BC} + 3.82B^2 \qquad (4.2)$$

Table 4.12 shows the ANOVA result of significant quadratic model.P value greater than 0.1000 shows that the model terms are not significant. Hence, equation (4.1) reduces to equation (4.2). The model was used to test for any significant differences among the effects of the three process parameters which include; reaction temperature, reaction time and volatile organic content of the samples produced. The ANOVA employed to determine whether differences in means exist was carried out using Design Expert version 11. The results of the ANOVA represented by p-values less than 0.05 and coefficient of determination (R-square) approaching unity was used to validate the fitness of the model equation and the design of the experiment procedure employed.

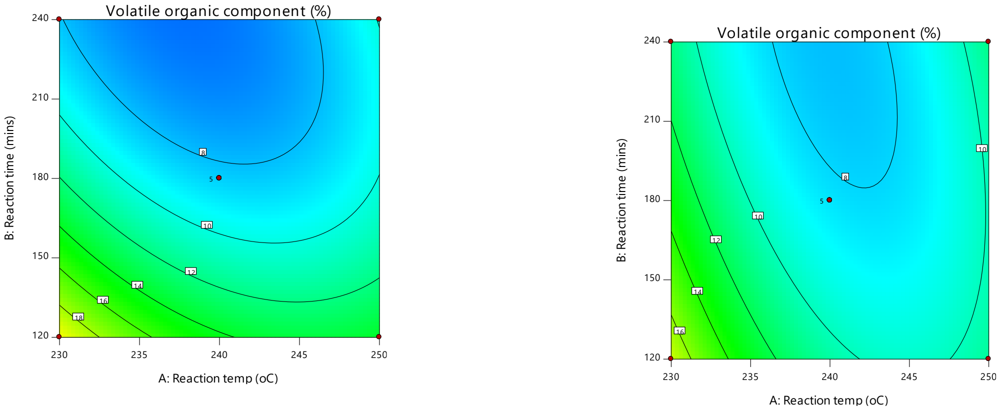
The high value of (0.9234) of R-square which approaches unity implies that the model is 92.34 % adequate for predicting the different VOC contents of PKOBAE at different reaction times and temperatures interaction. This is an indication that there is a high dependence and correlation between the predicted and observed/actual values of the response as reported by Sharma et al, (2009). The adjusted R-Square value is close to R-Square value which is necessary for a good design. The diagonistic plot is shown in figures 4.3(a).



(a) (b)

Figures 4.3: Diagonistic Plots for (a) PKOBAE Production (b) JSOBAE Production.

The diagnostic plots of the predicted versus actual values (figure 4.3) were used to check the models suitabilty and provide meaningful agreement between the experimental data and the values obtained from the models for the response. The straight line plot shows that the residual followed a normal distribution. The close distribution of points to the straight line of the plot confirms the good relationship between the experimental values and the predicted value of the response. The plots also confirm that the model was adequate in predicting the response in the experimental values.



(a) (b)

Figure 4.4: Model contuor plots for (a) PKOBAE (b) JSOBAE

The contour plots; figures 4.4(a) and (b) are the model plots which plot the response surface methodology model equations (4.2) and (4.4). These contour lines illustrate the response (VOC) of the experimental conditions (reaction time and reaction temperature). These can be used to spot out the major interaction between these parameters; reaction time and temperature, thereby allowing for a qualitative evaluation of the behavior of the system.

The contour lines show that the VOC obtained from the PKOBAE and JSOBAE depends on the interaction between reaction time and reaction temperature and not nessecarily on the volume of water used for diluting the resins. Below the centre point of the design of these polycondensation reactions; 180mins and 240^{o}C, the predicted VOC for any of the interaction is high and will continue to increase above 5%. Increasing the reaction time and temperature above these center points reduced the VOC. Therefore, the RSM predicted that if the reaction time and temperature are increased up to 240mins and above 240^{o}C, VOC values will decrease from 5% downwards. These contour lines serve as a guide for tuning the software to the desired goal which is minimal VOC.

Minimal VOC was set as criteria in determining the optimal conditions. Several solutions were provided by the design software. The solution with desirability of 90% and above was considered in choosing the best condition. These working conditions; 248^{o}C, 240 mins, 96% and VOC 1.615% for PKOBAE, 247^{o}C, 240 mins, 99% and VOC of 2.933% for JSOBAE which have desirability of 99% were chosen as the optimal conditions.

4.4.2 Box-behnken response surface methodology (RSM) for JSOBAE production

Responses for seventeen experiments designed and carried out for the selected specie using RSM were recorded in table 4.13. The ANOVA result is given in table 4.14.

Table 4.13: Experimental design and response for JSOBR emulsion production

Run	Factor A Reaction temp (oC)	Factor B Reaction time (mins)	Factor C Water to alkyd ratio (%)	Response Volatile organic component (%)
1	230	120	75	11.7
2	240	180	75	6
3	240	240	100	4
4	230	180	50	12.73
5	250	180	50	18.45
6	240	180	75	6.6
7	240	240	50	14.56
8	250	240	75	7.5
9	240	180	75	5.9
10	250	120	75	10.78
11	250	180	100	4.5
12	230	180	100	6.9
13	240	120	100	5
14	240	180	75	8
15	230	240	75	7.5
16	240	120	50	14.24
17	240	180	75	5.3

Long oil length alkyd emulsion was prepared with jatropha seed (jatropha curcas) oil according to the formulation in table 3.2. The polycondensation process was designed in table 3.5 using response surface methodology (RSM). The RSM is an inverse square transform quadratic model.

The model is a significant model which did not lack fit. Equation (4.3) is the model equation. After the elimination of insignificant terms, equation (4.3) was reduced to equation (4.4) which is the model final equation.

$$VOC = +6.64 + 0.1850A - 0.9475B - 4.91C - 1.95AC + 2.06A^2 + 2.39C^2 \quad (4.3)$$

Table 4.14: Analysis Of Varience (ANOVA) for Jatropha Based Alkyd Emulsion

Analysis of variance table [Partial sum of Square- Type III						
Source	Sum of square	df	Mean square	F Value	P-value Prob > F	
Model	259.89	6	43.32	26.80	< 0.0001	Significant
A-Reaction temp	0.2738	1	0.2738	0.1694	0.6893	
B- Reaction time	7.18	1	7.18	4.44	0.0613	
C- water to alkyd ratio	192.86	1	192.86	119.32	< 0.0001	
AC	15.13	1	15.13	9.36	0.0121	
A^2	17.94	1	17.94	11.10	0.0076	
C^2	24.05	1	24.05	14.88	0.0032	
Residual	16.16	10	1.62	-	-	
Lack of fit	12.02	6	2.00	1.94	0.2722	Not significant
Pure Error	4.14	4	1.04	-	-	
Cor Total	276.16	16	-	-	-	
R-Square						0.9414
Adj R-Square						0.9063
Pred R- Square						0.7849

$$VOC = +6.64 - 0.9475B - 4.91C- 1.95AC + 2.06A^2 + 2.39C^2 \quad (4.4)$$

Table 4.14 shows the ANOVA result of significant quadratic model. The model was used to test for any significant differences among the effects of the three process parameters which include; reaction temperature, reaction time and volatile organic content of the samples produced. The ANOVA employed to determine whether differences in means exist was carried out using Design Expert version 11. The results of the ANOVA represented by p-values less than 0.05 and coefficient of determination (R-square) approaching unity was used to validate the fitness of the model equation and the design of the experiment procedure employed.

The high value of (0.9414) of R-square which approaches unity, implies that the model is 94.14% adequate for predicting the different VOC contents at different reaction times and temperatures interaction. This also indicates that there is a high dependence and correlation between the predicted and observed/actual values of the response as reported by Sharma et al, (2009). The adjusted R-Square value (0.9063) is also close to R-Square value which is important for a good design. The diagonistic plots are shown in figures 4.3b and 4.4b.

4.4.3 Validation of the optimum voc obtained using Box-bhenkin RSM for PKOBAE and JSOBAE.

The optimal response (VOC 1.615%) for PKOBAE predicted by Box-bhenkin RSM using the optimal parameters; reaction temperature (248^{o}C), reaction time (240 mins) and volume of water to alkyd ratio (96%) was approximated to experimental response (VOC) of 2.00%. The experimental response (VOC) obtained from the optimal levels of the process parameters; reaction temperature (247^{o}C), reaction time (240 mins) and volume of water to alkyd ratio (100%) for JSOBAE preparation approximated the predicted response (2.933 %) to 3.00 %.

4.5 Kinetics Study of the Polycondensation Reaction for PKOBAE and JSOBAE Production.

The polycondensation reaction kinetics was studied using integral method, graphical, third order conversion and conversion models.

Extent of reaction and degree of polymerization were calculated from the analysis of the aliquot withdrawn at every 20 mins interval using equations (3.11) and (3.12) respectively. The results are shown in table 4.15.

a. Integral method

At equivalent concentrations of dicarboxylic acid and diol, equation (2.4) shows that polycondensation reaction follows a second order rate. Therefore production of alkyd resin which is a polycondensation reaction followed a second order reaction with k as the second order rate constant.

b. Evaluation of second order rate constant at various time interval during PKOBR and JSOBR Production.

Table 4.15: Rate Constant At Various Time Intervals During PKOBR and JSOBR Production.

Time(mins)	k in g(mg NaOH)min^{-1} for PKOBR	k in g(mg NaOH)min^{-1} for JSOBR
20	7.22×10^{-5}	8.59×10^{-5}
40	9.08×10^{-5}	1.21×10^{-4}
60	1.15×10^{-4}	1.14×10^{-4}
80	1.46×10^{-4}	1.55×10^{-4}
100	1.74×10^{-4}	1.93×10^{-4}
120	1.63×10^{-4}	2.21×10^{-4}
140	1.95×10^{-4}	2.55×10^{-4}
160	2.29×10^{-4}	2.84×10^{-4}
180	2.66×10^{-4}	3.05×10^{-4}
200	2.81×10^{-4}	3.37×10^{-4}
220	3.41×10^{-4}	3.95×10^{-4}
240	4.05×10^{-4}	6.83×10^{-4}

Table 4.15 shows the second order rate constant at various time intervals during PKOBR and JSOBR production. The reaction rate for PKOBR production followed a second order kinetics with rate constant order of 10^{-5}g (mg NaOH) min^{-1} during the first 40 mins of esterification process and incresead to order of 10^{-4} g (mg NaOH) min^{-1} up to the remaining after 180 mins of esterification process. This implies that the percentage of

monomers converted during the first 40 mins of the ester formation was high, and reduced as the reaction progressed.

The reaction rate for JSOBR production also followed a second order kinetic with rate constant of order of 10^{-5}g (mg NaOH) min^{-1} during the first 20 mins of the reaction. It then followed the order of 10^{-4}g (mg NaOH) min^{-1} through out the remaining 220 mins of esterification process. This is an indication that much of the reactants were converted at the first 20 mins of the polycondensation process. The change in the reaction order at various intervals implies that, as the reaction time increases, percentage of monomers converted also continued to increase.

c. Graphical method

The plots of 1/Ca against t are straight line graphs given in figures 4.5 and 4.6. This indicates that the polycondensation reaction for the production of the alkyd samples were of second order kinetics. k was calculated from the slopes to be of order of 10^{-4}g(mg NaOH)min^{-1}

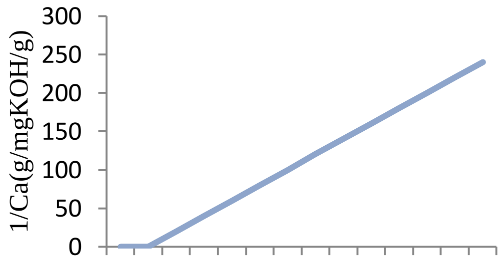


Figure 4.5: Second order plot for PKOBR

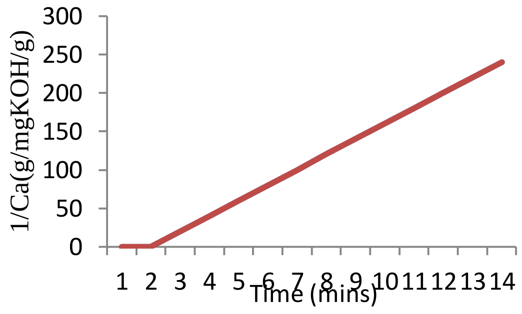


Figure 4.6: Second order plot for JSOBR

Table 4.16: Acid Value and Viscosity with Time from the Polycondensation Reaction of PKOBR

Reaction time(mins)	Acid value(mgKOH/g)	Viscosity(m.Pa.S)	1/Ca(g/mgKOH/g)
0	198.5	98.5	0.0102
20	154.5	108.4	0.0092
40	115.3	115.3	0.0087
60	83.6	129.0	0.0076
80	59.70	157.8	0.0063
100	45.45	185.8	0.0054
120	40.80	210.0	0.0048
140	30.90	221.3	0.0045
160	24.00	240.2	0.0042
180	18.89	269.4	0.0037
200	16.33	290.7	0.0034
220	12.50	301.5	0.0033
240	9.78	310.0	0.0032

Table 4.17: Acid Value and Viscosity with Time from the Polycondensation Reaction for JSOBR.

Reaction time interval(mins)	Acid value(mgKOH/g)	Viscosity(mPa.S)	1/Ca(g/mgKOH/g)
0	176.5	87.48	0.0057
20	135.4	99.50	0.0074
40	95.20	107.9	0.0105
60	79.80	118.7	0.0125
80	45.40	125.6	0.0220
100	40.07	152.3	0.0249
120	31.10	184.6	0.0322
140	24.30	212.3	0.0412
160	19.6	221.7	0.0510
180	16.5	242.8	0.0606
200	13.7	271.5	0.0729
220	10.8	298.4	0.0926
240	5.90	304.9	0.1695

Tables 4.16 and 4.17 show that the acid values and the in-suit viscosity readings. Acid value decrease as reaction time progresses whereas the in-suit viscosity increased. As more acid group is being converted, the reactor contents become more viscous.

Alkyds processed to a low acid value dry faster. This is because the F-COOH of the Phthalic anhydride known to delay drying would have been consumed. The decrease in acid implies a higher conversion of acid groups that were initially present in the alkyd mixture. It follows that as the the percentage conversion of the acid group increases, the reaction goes toward completion and the finished alkyd attains a low acid value. Consequently, the alkyd resin dries faster as the extent of conversion of the acid group in the alkyd mixture increases as also reported by Menkiti and Onukwuli, (2011).

d. Degree of polymerisation and extent of reaction

The degree of polymerization is defined as the rate with which the hydroxyl or carboxyl group reacts. Extent of reaction is defined as the fraction of hydroxyl group or carboxyl group that has reacted at a given time.

Table 4.18: Extent of Reaction during PKOBR and JSOBR Production

Reaction time(mins)	PKOBR, Pav (%)	JSOBR, Pav (%)
20	22.17	23.29
40	41.19	46.06
60	57.88	54.79
80	69.92	68.61
100	77.61	77.33
120	79.45	82.38
140	84.43	86.23
160	87.91	88.89
180	90.48	90.65
200	91.77	92.24
220	93.70	93.88
240	95.07	96.65

Table 4.19: Degree of Polymerization during PKOBR and JSOBR Production

Reaction time(mins)	PKOBR Dp	JSOBR Dp
20	1.2849	1.3036
40	1.7004	1.8539
60	2.3742	2.2119
80	3.3244	3.1857
100	4.4663	4.4111
120	4.8662	5.6754
140	6.4226	7.2621
160	8.2713	9.0009
180	10.5042	10.6952
200	12.1507	12.8866
220	15.8730	16.3399
240	20.2840	29.8507

Tables 4.18 and 4.19 show the degree of polymerization and extent of reaction. The degree of polymerization and extent of reaction increased with reaction time for both samples. As the percentage of conversion of the acid group increases, the reaction moves towards completion and low acid value. The reactions were completed at 95.07 % monomer conversion for PKOBR and 96.65% monomer conversion for JSOBR. This indicates that greater percentages of monomers were actually converted during the polycondensation reaction. Hence, the polymers produced were of high molecular weight.

e. Conversion Kinetics Model

A polycondensation reaction, expressed in terms of concentration of reacting functional group can be represented schematically as;

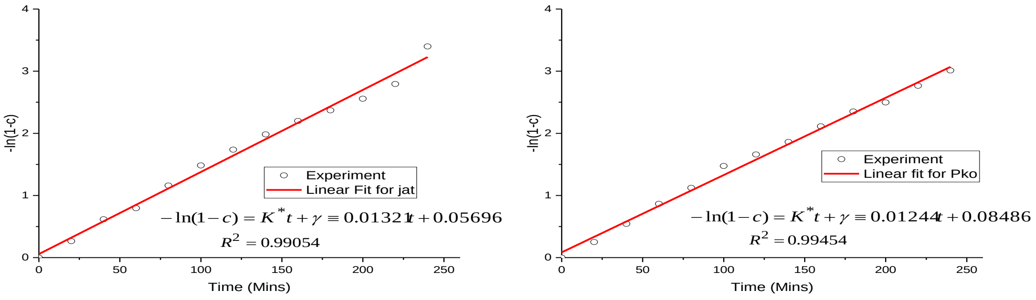
$$P_m + P_n = \overset{K_p}{\longleftrightarrow} P_{m+n} + W \tag{4.5}$$

Where P_{m+n} represents the growing polymer chain lenght

W represents the byproducts (water)

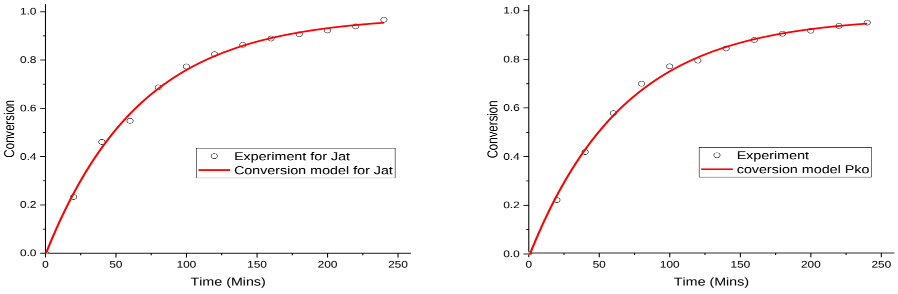
Kp represents the rate constant for the reaction.

The overall reaction time was plotted against -In(1-c) as shown in Fig 4.7



(a) (b)

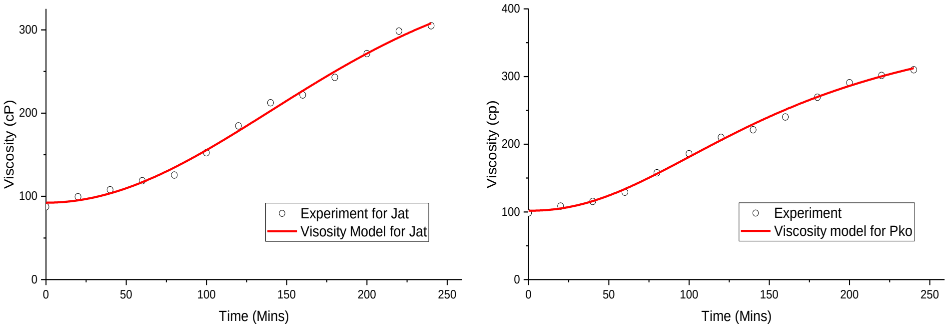
Figure 4.7: Linear Estimation of the Generalized Rate Constant Using the Rate of Change of the Unreacted Acid Group with Time.



(a) (b)

Figure 4.8: Experimental and Predicted Conversion Profile of the Alkyd Reaction System.

Figures 4.8 show the predicted and the experimental conversion profile of the alkyd polycondensation systems for (a) JSOBAE and (b) PKOBAE. The plots show both experimental conversion value and that predicted by conversion model followed the same trend. The trajectories show that monomer conversion increased with reaction. As monomer conversion increase, that rate of polyesterification decreased towards the end of the reaction as the concentration of the free acid decreased during the course of reaction.



(a) (b)

Figure 4.9: Experimental and Predicted Viscosity Profile of the Alkyd Reaction System

Figures 4.9 show the experimental and predicted viscosity for (a) JSOBAE and (b) PKOBAE. These plots show that viscosity of the resin increased with reaction time. There is also a reasonable agreement between the the experiment and the predicted data. It was also noted that there was a sustained increase in the viscosity of the alkyd as the reaction proceeds.

The model conversion viscosity model (3.28) was estimated to be for JSOBR

$$\rho_{\mu} = [a_{\mu}, b_{\mu}, c_{\mu}] = [53.13225, 0.58367, 1.29058] \tag{4.6}$$

The model conversion viscosity model (3.29) was estimated to be for PKOBR

$$\rho_{\mu} = [a_{\mu}, b_{\mu}, c_{\mu}] = [54.11941, 0.74862, 1.37354] \tag{4.7}$$

4.6 Thermodynamics of the Alkyd Emulsions

The results of the variation in the viscosities of the alkyd samples investigated are recorded in table 4.20. Equation (3.24) is a straight line equation with η_o as the intercept. The slope provides the information aabout the activation energy.

Table 4.20: Change in Viscosity with Temperature

T(^{o}C)	T(^{K})	1/T($^{K-1}$)	η(mPa.S) PKOBAR	η(Pa.S) PKOBAR	η(mPa.S) JSOBAR	η(Pa.S) JSOBAR	In η (PKOBAR)	Inη (JSOBAR)
100	373	0.0027	108.4	0.1084	99.50	0.0995	-2.2219	-2.3076
120	393	0.0025	115.3	0.1153	107.9	0.1079	-2.1602	-2.2266
140	413	0.0024	129	0.1290	118.7	0.1187	-2.0479	-2.1312
160	433	0.0023	157.8	0.1578	125.6	0.1256	-1.8464	-2.0747
180	453	0.0022	185.8	0.1858	152.6	0.1526	-1.6831	-1.8799
200	473	0.0021	210	0.2100	184.6	0.1846	-1.5606	-1.6896
220	493	0.0020	221.3	0.2213	212.3	0.2123	-1.5082	-1.5497
250	523	0.0188	240.2	0.2400	221.7	0.2217	-1.4271	-1.5064

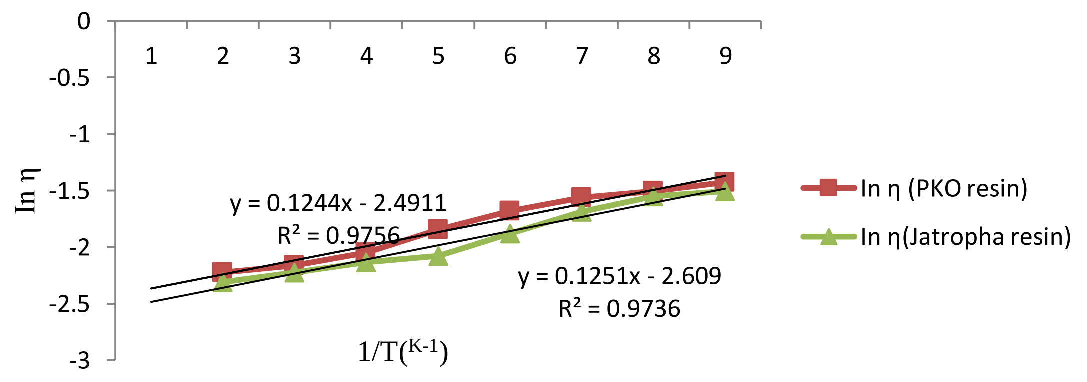


Figure 4.10: Plot Of lnη Vs 1/T for PKOBR/ JSOBR

The coefficients of regression for the graph of natural log of η vs 1/T for PKOBAE and JSOBAE are 0.975 and 0.973 respectively. This indicates a very good fit. Hence, the samples properties obeyed the Arrhenius viscosity model equation (3.24). Therefore, a logrithimic type model correlating the activation energy to Arrhenius temperature best fits the relationship between the Arrhenius parameters. The slope represents the activation energy of extraction and the intercept is the Arrhenius constant, InA_o. From figure 4.10, activation energy for the two reactions was determined using the regressional equations (4.8) and (4.9) respectively.

$$y = 0.124x - 2.491 \tag{4.8}$$

$$y = 0.125x - 2.609 \tag{4.9}$$

Table 4.21: Thermodynamics Parameters of PKOBAE and JSOBAE polycondensation Reaction

Parameters	Activation Energy Ea (kJ/mol)	Enthalpy $\Delta H^{\#}$(KJ/mol)	Entropy $\Delta S^{\#}$ (J/molK)	Gibbs free energy $\Delta G^{\#}$ (KJ/mol)
PKOBAR	-1.031	-4349.25	-5.866×10^{-7}	4349.25
JSOBAR	-1.039	-4349.26	-1.22×10^{-7}	4349.26

Table 4.21 shows the thermodynamics properties for the polycondensation reaction for the productions of PKOBAR and JSOBAR. The activation energy for PKOBAR is Ea = -1.031 kJ/mol and the activation thermodynamic parameters at 523K are $\Delta H^{\#}$=-$4349.25KJ/mol$, $\Delta S^{\#} = 5.866x\ 10^{-7}$J/molK and $\Delta G^{\#} = 4349.25KJ/mol$ The activation energy for JSOBAR are Ea = -1.039 kJ/mol and the activation thermodynamic parameters at 523K are $\Delta H^{\#}$= -4349.26 kJ/mol $\Delta S^{\#} = -1.22x\ 10^{-7}$J/molK and $\Delta G^{\#}$ = 4349.26 KJ/mol.

Negative enthalpy of activation prove that the reactions proceed by formation of stable intermediate. According to Lietuvus, (2017), reaction slows down with increasing temperature but, when the temperature is increased the molecules have more energy and can more easily break their bonds and the rate of the reaction increases. The negative activation energy obtained from the Arrhenuis equation implies that the polycondensation reactions favoured the production of PKOBAR and JSOBAR.

4.7 Alkyd Washable Paints Production, Characterisation and Rheological Study

4.7.1 Washable paint production

PKSP$_1$, PKSP$_2$, PKSP$_3$ and JOSP$_1$ out of the nine samples produced showed poor interaction with polystyrene and cobalt/lead driers. Samples, PKOP, JOSP, JOSP$_2$, and JOSP$_3$ showed good interaction with styrene and driers. PSNA and commercial paint (CP) were used for comparison and control respectively.

4.7.2 Properties of washable paint

a. Physiochemical properties of washable paints

Table 4.22: Washable Paint Properties

Sample	Density(g/m^3)	Viscosity(mPa.S) at 60RPM
PKOP	1.0016	106.4
JSOP	1.0416	107.1
JOS$_2$P	1.0698	107.5
JOS$_3$P	1.0782	106.8
PSNA	0.9966	106.3
CP	0.8968	219.5

Table 4.22 shows the density and the viscosity of washable paints at the shear rate of 60 rpm. The medium shear viscosity indicates that the samples will be easy to apply. The viscosities of the samples PKOP, JOS_2P and JOS_3P are comparable with that of PSNA but, vary from that of the CP sample. The sample may likely drip during application. Density is the property used to monitor how heavy the paint is. The high density indicates that the samples have high solid concentration. The samples densities were comparable to that of commercial.

b. VOC of washable paints

Table 4.23: Washable Paint VOC

Sample	VOC (%)
PKOP	7.00
JSOP	3.00
JOS_2P	4.00
JOS_3P	9.00
PSNA	2.00

Table 4.23 shows the values of percentage VOC of the paint samples. The VOC is within the range of 2.00 to 7.00 %. The VOC is within the range of low volatile component according to European Union as reported by Jennifer, (2018); Elios, (2012). Hence, the paint samples are said to be environmentally friendly; it will introduce less volatile organic compound to the ecosystem. The VOC are far less than that of the commercial samples.

c. Chemical resistance

Table 4.24: Acid Resistance

Time(hrs)	PKOP	JSOP	JOS_2P	JOS_3P	PSNA	CP
2	No effect	No effect	No effect	No effect	No effect	No effect
4	Blisters	No effect	No effect	No effect	No effect	No effect
6	Blisters	Blisters	No effect	No effect	No effect	Blisters
8	Blisters	Blisters	Blisters	Blisters	Blisters	Blisters
10	Blisters	Blisters	Blisters	Blisters	Blisters	Blisters
12	Blisters	Blisters	Blisters	Blisters	Blisters	Blisters

Table 4.25: Alkali Resistance

Time(hrs)	PKOP	JSOP	JOS_2P	JOS_3P	PSNA	CP
2	Blisters	No effect	No effect	No effect	No effect	No effect
4	Blisters	No effect	No effect	No effect	No effect	No effect
6	Blisters	Blisters	Blisters	Blisters	Blisters	Blisters
8	Blisters	Blisters	Blisters	Blisters	Blisters	Blisters
10	Blisters	Blisters	Blisters	Blisters	Blisters	Blisters
12	Blisters	Blisters	Blisters	Blisters	Blisters	Blisters

Tables 4.24 and 4.25 show respectively, the results for acid and alkali resistance after 12 hrs of exposure. The coatings from JOS_2P, JOS_3P and PSNA which are blends of acrylic show better resistance towards acid as the coatings exhibited blistering after six hours of exposure to the media compared to PKOP and JSOP which show blistering few hours during the soaking period. This is attributed to the poor cross-linking of the

alkyds film during film autoxidation reactions. Moreover, blending polystyrene acrylic in washable paints improved the chemical resistance. All the samples were resistant to water and brine.

Results from alkali test shows that alkyd coatings have poor resistance towards alkali solution where film defects start to appear within the first 2 hrs of immersion in the alkali solution. This is not totally unexpected as ester linkages in the alkyd are susceptible to alkali hydrolysis as reported by Loius et al, (2015).

d. Drying test

Table 4.26: Paint drying performance

Sample/Drying time (mins)	20	40	60	80	100	120	140	160
PKOP	Wet	Very sticky	Very sticky	Very sticky	Sticky	Sticky	Soft	Soft
JSOP	Wet	Sticky	Sticky	Sticky	Soft	Soft	Soft	Soft
JOS_2P	Wet	Sticky	Soft	Soft	Hard	Hard	Hard	Hard
$JOSP_3P$	Wet	Sticky	Soft	Soft	Soft	Hard	Hard	Hard
PSNA	Wet	Sticky	Soft	Hard	Hard	Hard	Hard	Hard
CP	Wet	Sticky	Soft	Soft	Hard	Hard	Hard	Hard

Table 4.26 shows the drying performance of the paint samples. Samples PKOP and JSOP showed poor drying performance by drying into soft films. Only the samples which

contain polystyrene acrylic were able to form hard films. All the paint samples including the commercial one when exposed to harsh weather were affected by algae growth, this indicates that these samples are better off in doors or better still may require biocides for exterior use.

e. UV Curing and hardness performances.

Table 4.27: UV Curing and Hardness Result

Samples	Initial mass (g)	Final mass (g)	Initial hardness HA	Final hardness HA	Curing time (min)	Curing time*(driers)* (min)
JSOP	25.63	25.20	0.5	1.0	658	350
JOS_3P	12.73	11.03	2.5	5.5	717	420
PKOP	14.35	14.11	0.5	1.5	478	300
JOS_2P	14.35	13.45	2.5	5.0	689	333
PSNA	14.35	13.01	3.5	6.0	300	-
CP	14.35	13.22	2.5	6.5	180	-

Table 4.27 shows the UV curing results of the paint samples. This showed that sample PKOP though cures faster than other samples containing alkyd resin, but the hardness is lower than that of other samples.Samples JOS_2P and JOS_3P which contain acrylic showed better curing performance in terms of hardness compared to the samples without acrylic. Adding driers to the samples affected the drying performance positively. CP and PSNA were not cured with driers since the later does not contain alkyd resin and the former was assumed to have been produced with driers. Paint samples with

durometer reading less than 20 are considered very soft as reported by Valerie, (2017). The paint films are therefore considered to be soft.

f. Adhesion and breed resistance

Table 4.28: Washable Paint Performance Results

Sample	Adhesion Test	Bleed Resistance
PKOP	Poor	Good
JSPO	Good	Excellent
JOS_2P	Good	Excellent
JOS_3P	Very good	Excellent
PSNA	Very good	Excellent
CP	Good	Excellent

Table 4.28 shows the film performance results of the paint samples in terms of adhesion and bleed resistance. Sample PKOP showed poor adhesion. This is attributed to the dried film texture. All the samples showed satisfactory performance in terms of bleed resistance. It was discovered that the performances of samples JOS_2P and JOS_3P were comparable to that of the commercial sample and PSNA. They showed outstanding performance compared to samples PKOP and JSOP. This can be attributed to the presence of polystyrene acrylic in the blends. It can be inferred that blending washable paints with acrylic helps to improve the performance of the paints.

g. PVC

The five paint samples were produced at a Pigment volume concentration (PVC) of 37.5%. The PVC of PKOP, JSOP, JOS_2P, JOS_3P and PSNA are within the range for washable paints PVC which vary from 30% to 50% as reported by Resene, (2005). Paints with PVC within this range show better the exterior durability, scrubbability, adhesion, hiding power, density and the gloss.

4.7.3 Rheological properties of washable paints

Rheological studies can predict paint behavior without large costly batch studies. It also predicts the behavior during storage, stirring, application and after application as reported by Malvern, (2015). Different rheological properties studied include; yield stress, viscosity and storage modulus, sagging, leveling, bleeding and stability are some of paint properties determined by rheological characterization.

a. Viscosity of the paint samples

Table 4.29: Average Viscosity of Washable Paint Samples at Different Time and Shear Rate of 60RPM

Time(mins)	Viscosity(mPa.s)					
	JSOP	JOS_2P	JOS_3P	PKOP	PSNA	CP
5	107.1	107.1	106.8	106.4	106.7	522.5
10	107.1	107.0	106.6	105.9	106.2	522.0
15	107.2	106.9	105.7	105.1	106.0	522.0
20	106.3	106.5	105.2	104.7	105.9	521.8
25	106.2	106.0	105.2	104.5	105.5	521.3
30	105.2	105.5	105.0	104.0	104.2	520.4

Table 4.29 shows the average viscosity of PKOP, JSOP, JOS_2P, JOS_3P, PSNA and CP samples.The samples viscosity readings at a shear rate of 60rpm taken at interval of 5mins for a period of 30 mins showed slight change in viscosity with time; this is a pseudoplastic behavior. The results of PKOP, JSOP, JOS_2P and JOS_3P are comparable with PSNA and CP. As reported by (Clifford, 2019),if the viscosity of paint is above 100cps (100 mPa.s), the brush drag will be so high that the painter will end up with a sore wrist, but viscosity much below 100 cps is likely to cause misting, and high viscosity probably will give ropiness and other unwanted surface pattern. Also, (TA Instrument, 2015) reported that typical paints are adjusted to 50–150 mPa.s for low drag during application.

b. Stability: flow and shear rate

The average viscosity readings for PKOP, JSOP, JOS_2P, JOS_3P, PSNA and CP at different shear rates were shown in table G2 (Appendix G). The values were used to plot the graphs of figure 4.11 through 4.14.

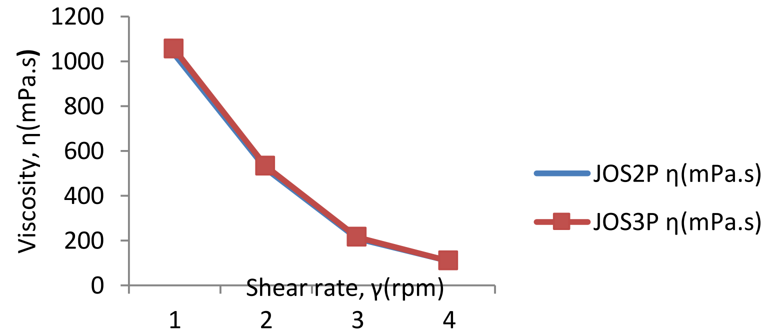


Figure 4.11: Variation of Viscosity with Shear Rate for JOS_2P & JOS_3P

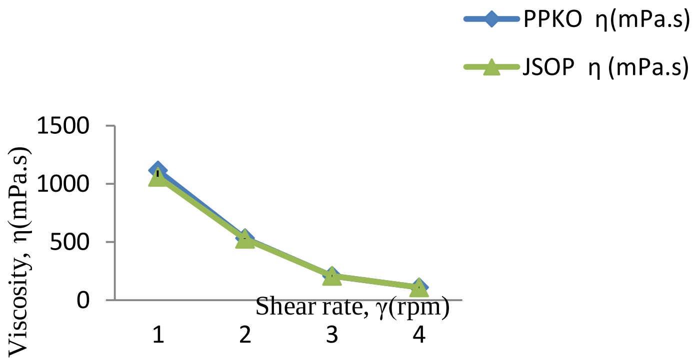


Figure 4.12: Variation of Viscosity with Shear Rate for JSOP & PKOP

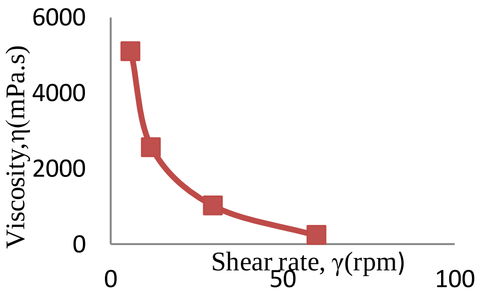


Figure 4.13: Variation of Viscosity with Shear Rate for CP

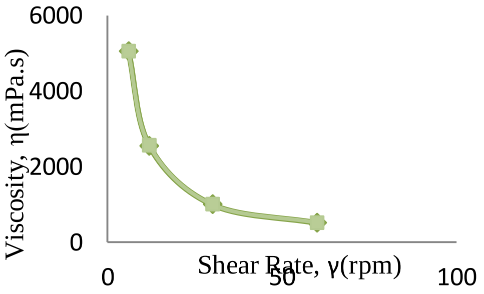


Figure 4.14: Variation of Viscosoty with Shear Rate for PSNA

From figures 4.11 through 4.14, the viscosity shear rate curves show drop or shear thinning behaviour of the paint samples; PKOP, JSOP, JOS$_2$P, JOS$_3$P, PSNA and CP with increasing shear rate. Hence, as the shear rate increases, the viscosity dropped. The samples are said to show high-low shear viscosity. The ease of structure breakdown of these paints at medium shear viscosity means that they are more likely to flow in to the bristles of a paint brush when dipped into the paint. The high low shear viscosity of the samples, will enable the samples withstand the force of gravity causing particles to sediment as reported by Malvern, (2005). Therefore, PKOP, JSOP, JOS$_2$P, JOS$_3$P, PSNA and CP are not susceptibile to sedimentation and therefore will maintain good consistency during storage. At high shear rate, a low viscosity is also beneficial for brushing: a too high viscosity will lead to undesired brush drag. According to de Viguerie et al, (2009), good brushing properties are obtained if the viscosity at high shear rates does not exceed 0.2–0.5 Pa s. This means that PKOP, JSOP, JOS_2P, JOS_3P, PSNA and CP will not show poor brush drag during application.

c. Yield stress: sagging and levelling

The results for variations of stress with rate for each of the samples were calculated from the viscometer readings and are recorded in table G3 (Appendix G). The details for the calculation can be found in appendix F. This was used to study the stress evolution of PKOP, JSOP, JOS_2P, JOS_3P, PSNA and CP respectively as shown in figures 4.15 through 4.20.

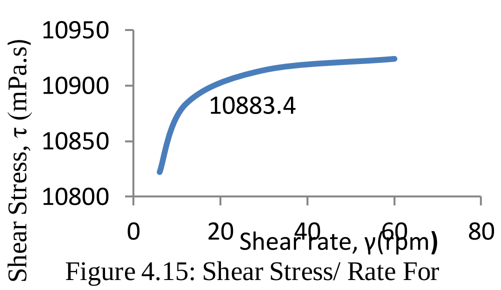


Figure 4.15: Shear Stress/ Rate For JSOP

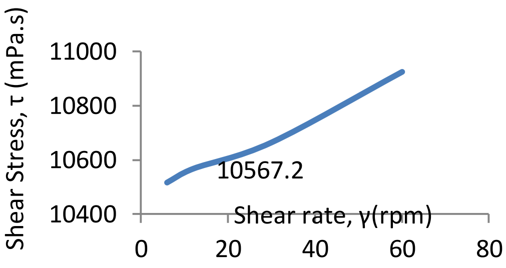


Figure 4.16: Shear Stress/ Rate for JOS_2P

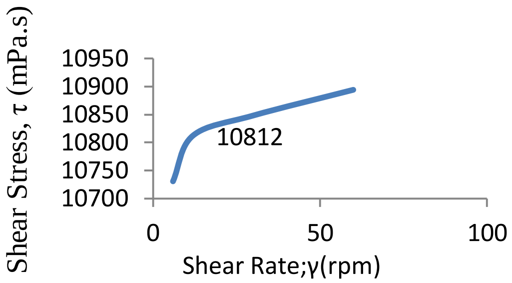


Figure 4.17: Shear Stress/ Rate for JOS_3P

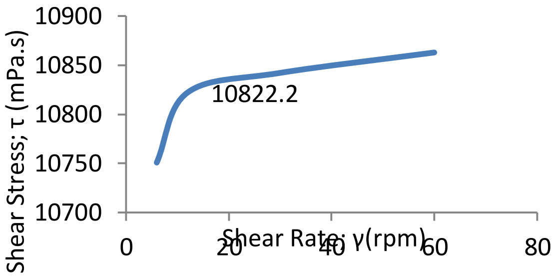


Figure 4.18:Shear Stress/ Rate for PKOP

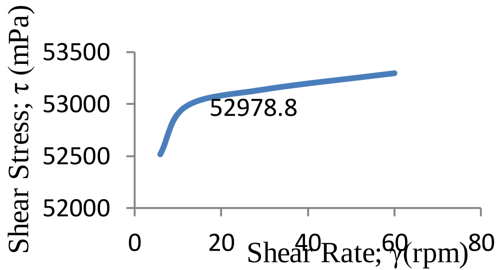


Figure 4.:19 Shear Stress/Rate for CP

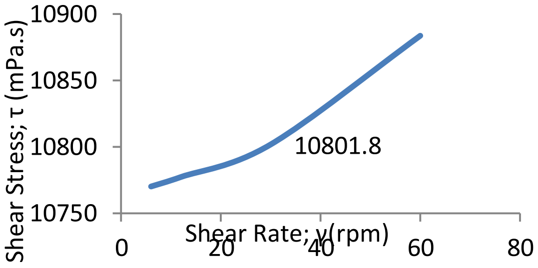


Figure 4.20: Shear Stress/Rate for PSNA

Figures 4.15 through 4.20 show the yield stresses for samples PKOP, JSOP, JOS_2P, JOS_3P, PSNA and CP as 10883.4 mpa, 10567.2 mpa, 10812 mpa, 10822.2 mpa, 10808.8 mpa and 52978.8 mpa respectively. The samples have large yield stresses greater than 1Pa. Coatings with high yield stress will regain their elastic structure after levelling is completed. This is an indication of good sagging and levelling properties as reported by TA Instruments, (2015). This means that these coatings; PKOP, JSOP, JOS_2P, JOS_3P, PSNA and CP will show good levelling behaviour.

d. Rheological behavoiur; samples consistency.

The consistency of PKOP, JSOP, JOS_2P, JOS_3P, PSNA and CP were determined using Oswald de Waele power law model. The Power law model; equation (2.13) was converted to a linear equation (3.29) by taking log of both sides. The log readings are recorded in table G4 (Appendix G) and fitted into linear graphs of figure 4.21 through 4.25.

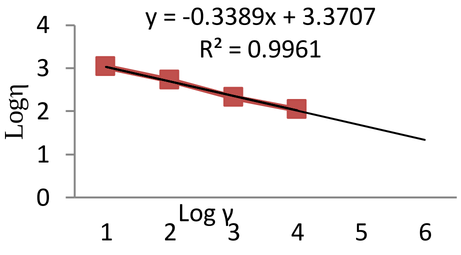


Figure 4.21: Power Law Plot for JSOP

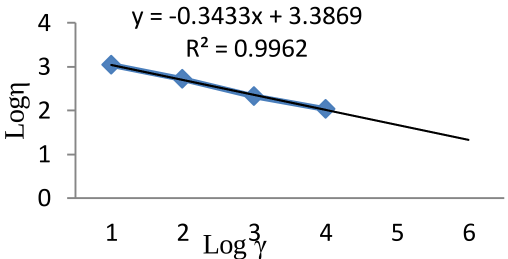


Figure 4.22: Power Law Plot for JOS_2P

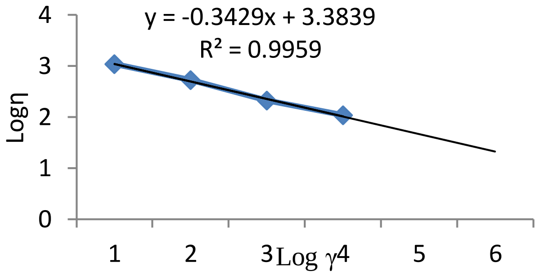


Figure 4.23: Power Law Plot for JOS_3P

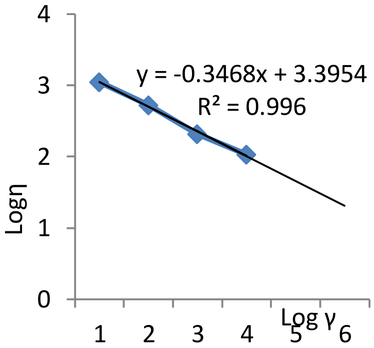


Figure 4.24: Power Law Plot for PKOP

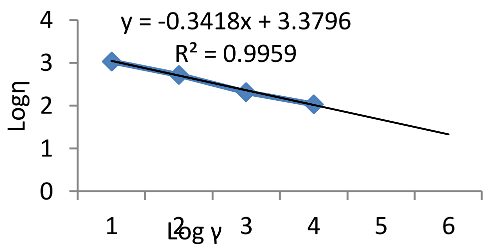


Figure 4.25: Power Law Plot for PSNA

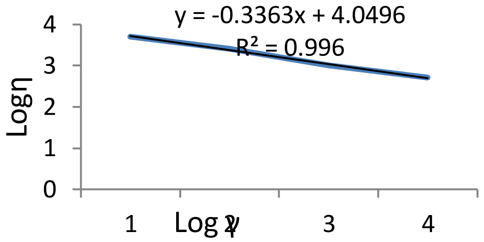


Figure 4.26: Power Law Plot For CP

Table 4.30: Power Law Parameters

Power law values Samples	n	k	R^2
JSOP	0.6620	2344.23	0.9960
JOS_2P	0.6570	2432.00	0.9960
JOS_3P	0.6580	2415.46	0.9950
PKOP	0.6540	2483.13	0.9960
PSNA	0.6590	2393.3	0.9950
CP	0.6640	11194.13	0.9960

The power law parameters; n and k are presented in Table 4.30. Power law model gave a non-Newtonian behaviour of the samples with power law index (n) of less than 1. These low shear viscosity values show that these samples are pseudoplastic. According BASF (2015), pseudoplastic samples are applied by brushing. Therefore, these samples can be applied using paint brush.

Consistency index (k) for PKOP, JSOP, JOS_2P, JOS_3P, PSNA and CP were respectively calculated using the linear equations of each of their plots. The value of k is the viscosity at 1sec^{-1}. This value can be used for viscosity measurement for comparative purposes.With the known 'n' and 'k' values, the viscosity can be predicted at any shear rate by applying the power law equation;$\eta = k\gamma^{n-1}$. Reformulation of these products to satisfy specific needs, such as method of application which is brushing can be changed to spraying or dipping with these known values.

The rheological study showed that the paint samples; PKOP, JSOP, JSO$_2$P, JSO$_3$P and PSNA are non Newtonian fluid which exhibit outstanding performances at a given shear rate. Canning, pumping, brushing, rolling and leveling can be carried out on the samples without experiencing any form of deformation.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Palm kernel oil and jatropha seed oil based resin were found suitable for the production of low volatile organic content (VOC) alkyd emulsion using isopropyl alcohol as an emulsifying agent. In the production of JSOBAE, the best reaction temperature, time and ratio of water to the weight of alkyd for emulsification were found to be 246.85^{o}C, 240 mins and 99.99% water to alkyd ratio respectively, whereas, that of PKOBAE was found to be 247.978^{O}C, 239.21mins and 96.36% water to alkyd ratio respectively. These parameters were used to produce alkyd emulsion with 2.00% and 3.00% VOC for PKOBAE and JSOBAE respectively.

The response surface modeling yielded the equations,

$$VOC = +6.64 - 0.9475B - 4.91C - 1.95AC + 2.06A^2 + 2.39C^2$$

which was proven to be adequate and accurate for predicting percentage VOC within the intervals of the specified variables for JSOBAE and

$$VOC = +7.33 - 2.75A - 2.65\,B - 1.65\,C + 3.00\,AB + 8.31\,BC + 3.82B^2$$

which was proven to be adequate and accurate for predicting percentage VOC within the intervals of the specified variables PKOBAE.

The emulsified resins were also suitable for the production of washable paints. Blending jatropha seed oil based alkyd emulsion with 25% acrylic to total weight of paint sample was found suitable in modifying the flow and film properties of washable paints, blending acrylic and palm kernel oil based alkyd emulsion with up to 25% acrylic to total weight of paint sample gave an undesirable result. This research has proven that;

Polystyrene acrylic improved the drying performance of washable paints produced from PKOBAE and JSOBAE.

Polystyrene acrylic improved the rheological properties of washable paints produced from PKOBAE and JSOBAE.

Washable paints are environmental friendly with low emission.

5.2 Recommendation

1. Polycondensation of alkyd resin has been established to ocurr between 230^0C to 250^oC, this most times affects the reactors during laboratory experiment. The use of appropriate CSTRs is advocated.
2. Further research in using lower proportion of acrylic as a rheology and film modifier in washable paint production is also recommended.
3. Since jatropha seed oil is non-edible oil which is good in alkyd emulsion production. It is recommended that Jatropha plants be extensively cultivated and utilized for this and other purposes, hence reducing the cost in importation of linseed oil and at the same time providing employment and foreign exchange.
4. Further research in alkyd emulsion synthesis using the fatty acid from PKO is recommended. This hopefully will reduce the stress on PKO as food and industrial raw material. Hence, the cost of alkyd production will also be reduced.

5.3 Contributions to knowledge

This research has contributed to the existing knowledge in the following areas:

1. In providing data on the best esterification and emulsification parameters for low VOC compliant palm kernel and jatropha seed oil based alkyd emulsion.
2. In providing data for the flow behavoiur of paint samples produced from PKOBAE and JSOBAE.
3. Providing the knowledge of paint applications and processes at different shear rates.
4. The following parameters; n and k were determined for optimum packaging, pumping and application of the samples.

REFERENCE

Aietkamp A., & Don, P. (1995). *Paint and coating testing manual.* Retrieved from http://www.google.com/books, on 11 Jan, 2015.

Aghaie, H., Ilkhani, A. R., & Sadat,S. M.(2011).*Utilization of soya bean fatty acid for synthesis of alkyd resin and comparation of properties with other vegetable oils.* Retrieved from http://www.researchgate.net>publication, on 22 Jan, 2015.

Aigbodion, A.I, Okieimen, F. E., Obazee, E.O., & Bakare, I.O. (2003). Utilisation of maleinized rubber seed oil and its alkyd resin as binders in water-borne coatings. *Progress In Organic Coatings*, **46**, 28–31.doi.org/10.1002/app.12446. 10 March, 2015.

Aigbodion, A. I. & Pillai, C. K., 2001, Synthesis and molecular weight characterization of rubber seed oil-modified alkyd resins. *Journal of Applied Polymer Science*, 79, 2431-2438. doi:10.1002/1097-4628(20010328)79:13<2431:AID-APP1050>3.0.CO;2-A. 10 March, 2015.

Aigbodion, A.I., & Okieimen, F.E. (2001). An investigation of the utilisation of African locustbean seed oil in the preparation of alkyd resins. *Industrial Crops and Products*, 13, 29–34. doi:10.1016/s0926-6690(00)00050-9. 11 Jan, 2015

Aigbodion, A.,.I .& Okieimen,F., E.(1996). Kinetics of the preparation of rubber seed oil Alkyds.*Eur.Polym. J.*, 32, 1105–1108. https://www.journals.elsevier.com/european-polymer-journal

Alireza, A. N., Rosiyah Y., & Seng-Neon G.(2013).Cleaner production through using by-product palm stearin to synthesis alkyd resin for coating applications**.** *Journal of Cleaner Production***,** **54**(1), 307–314. Retrieved from https://www.journals.elsevier.com/journal-of-cleaner-production on 22 Jan 2015.

Amateek Brookfield (2005). *Why measure viscosity*. Retrieved from http:www.brookfieldengineering.com/learning-center. 22 May,2017.

Amina, N. (2017, May 9). *Alkyd resin*. Retrieved from https://www.slideshare.net/AminNavabi/alkyd-resin. 2nd Dec, 2019.

Andrei I. S., Irina I., Cristina-Gabriela G., Lidia G. F., Lucian G. (2015). Development and optimization of water based paint formula in order to reduce vocs emissions. E*nvironmental Engineering and Management Journal*, **14**(2), 277-288.

AOAC (1990). *Official Method 965.33 of Analysis*, Association of Official Analytical Chemists. Retieved from http://rucore.libraries.rutgers.edu on 23, March, 2015

ASTM D 2196-15(2015).*Standard Test Method For Rheological Properties of Non Newtonian Materials by Rotational Viscometer*. Doi: 10.1520/D2196-15 on 22 March, 2015.

ASTM D 2240 (2015). *Standard Test Method for rubber Property – Durometer hardness*. Doi:10.1520/D2240-15 on 11/10/2018.

ASTM D 1308-2 (2013). *Standard Test Method for effect of Household Chemicals on clear and pigmented organic finishes*. Retrieved from www.astm.org on 05 March,2015.

ASTM D 1959 – 69(1997).Test for Iodine Value of drying Oils and their Derivatives. *Annual book of American society for testing and material standards.* Philadelphia, PA, 29: 265-7.

ASTM D 1639 – 90(1994). Standard Method for Acid Value of Organic Materials. *Annual book of American society for testing and material standards*. Philadelphia, PA: 06.01, 260-1.

ASTM D 3359-90(1991). *Standard Test Method for Measuring Adhesion*. Retrieved fron www.astm.org on 05 July,2015.

ASTM 1640-83(1991). Standard Test Methods for Drying, Curing, or Film Formation of Organic Coatings**.** *Annual Book of ASTM Standards*, 06 (01): 223-226.

Athawale, V.D. & Chamankar, A.V.(1998).Coating properties of alkyd–ketonic (cyclohexanone formaldehyde) resin blends. *Journal of American oil chemists society*, **75**(7), 887-889. Doi:10.1007/S11746-998-0242-1. 22 March,2015.

Athawale, V.D., & Chamanker, A.V., (1997). The effects of driers on film properties of alkyd resin. *Pigment & resin technology*, **26** (6),378 – 381. Doi:10.1108/03699429710191351 on 22 March, 2015.

Ayman, M. A., Rasha, A., El-Ghazawy, & Ashraf, M. E.(2013).Corrosion protective coating based on alkyd resins derived from recycled poly (ethylene terephthalate) waste for carbon steel. *International journal of electrochemical science*, **8**,5136 – 5152. Retrieved from www. electrochemsci.org on 05 july, 2015.

Balley,A. E.(1982). *Industrial oil and fat product*, New York, NY: John Wiley interscience, 3rd edition.

Barbara, P., Bogdan, Z., Skale, S., Jo`efa, Z., Jerneja, G., Peter, B., & Peter, V.(2015) The influence of co/sr and fe/sr driers on film formation of high solid alkyd coatings. *Acta chim. slov*., **62**,52–59. Doi: 10.17344/acsi2014.708. 22 Jan, 2015.

Barnes, H.A.(1997).Thixotropy – a review. *Journal of non-newtonian fluid mech*, **70**, 1-33. Doi:10.1016/S0377-0257(97)00004-9 on 10 March, 2015.

BASF Chemical Industry (2015). "*The rheology modifiers practical guide*" Retrieved from www.dispersions-pigments.basf.com. 11 Jan, 2015.

Blaise, V. I., Ogunniyi, D. S., Ongoka, P. R., Moussounga, J. E., &Ouamba, J. M.(2012). Physico-chemical properties of alkyd resin and palm oil blends. *Malaysian polymer journal*, **7** (2), 42-45.

Brooks B., W., Richmon H., N. & Zarfa, M. (1998). Phase inversion and drop formation in agitated liquid – liquid dispersions in the presence of non ionic surfactant. In Blinks B. P. editor. *Modern aspect of emulsion science*. Cambridge, UK. The royal society of chemistry.

Clifford, K., S.(2019).Optimum viscosity for paint application. American Coatings Association. Retrieved from https://www.paint.org/article/optimum-viscosity-paint-application. 9 Dec, 2019.

Changchun, W., Geng, L., Joon-Hwan, P., Frank, N., & Jones, H.(2000). Novel synthesis of carboxy-functional soybean acrylic alkyd resins for water reducible coating. *Journal of coating technology*,**72** (904), 55-61.

Duce, C., Bernazzani, L., Bramanti, E., Spepi, A., Colombini, M.P.,& Tiné, M.R.(2014). Alkyd artists' paints: do pigments affect the stability of the resin? A TG and DSC study on fast- drying oil colours. *Polymer degradation and stability*, **105**, 48–58.

Ekpunobi, U. E., Chukwuka, O. M., Ogboagu, A. S., Ofora, U. P., Ohaekenyem, C. E. (2014). Efficiency of heavy metallic soap produced from napthtalic acid recovered from used lubricating oil in paint formulation. *American journal of science and technology*, 298- 302.

Elios.(2012). Case –study-10-low VOC materials. *European liability insurance organisation scheme*. 1-18. Retrieved from www.elios-ec.eu. 10 March, 2015.

El-Said, H. El-Mosallamy, & Mohamed, Y.G.(2008). Preparation and evaluation of the antibacterial alkyd resin modified with 2, 2\ -di-thiosalicylic acid macromolecules. *An Indian journal*, **10**(2), 53-59.

Eley, R.R. (2005). Applied rheology in the protective and decorative coatings industry. *Rheology reviews*, 173 – 240. Retrieved from https://vdocuments.site. 29 March, 2018.

EPA 2017, Indoor air quality. *Technical overview of volatile organic compounds*. Retrieved from www.epa.gov/indoor-air-quality. 19 March, 2016.

Eromosele, C.O., Eromosele, I.C. (2002). Fatty acid compositions of seed oil of Haematostaphis barteri and Ximenia americana. *Biores. Tech.*, 82, 303-304. Doi: DOI:10.1016/s0960-8524(01)00179-1 on 11 Dec, 2014

Enrique A.,M. (2007). Monte Carlo simulation to propose improvements of an alkyd resin process. *Proceedings of the 7th WSEAS international conference on simulation, modelling and optimization, Beijing, China, September*, 16-17. Retrieved from. https://pdfs.semanticscholar.org/fe5d. 11 Jan, 2015.

Erin, V., Marty, B., Bob B., Christina, E., Machelski, S., Jamie, S., Jay, R., & Vennesa W. (2016). Near zero VOC waterborne dispersions with solventborne alkyd performance. *American coatings association*. Retrieved from https://www.paint.org/article/near-zero-voc-waterborne-alkyd-dispersions. 22 Jan, 2015.

Ezeh, I.,E., Umoren, S.,A., Essien, E., E. & Udoh, A., P. (2012). Studies on the utilization of Hura crepitans L. seed oil in the preparation of alkyd resins. *Industrial Crops and Products, (*36),94–99. Retrieved from www.elsevier.com/locate/indcrop. 10 March, 2015.

Gan, S.N., & Ang, D. T. C. (2012), Environment friendly UV-curable resins from palm stearin alkyds. *Journal of applied. polymer science*, **125**,306–313. Doi: 10.1002/app.36858. 12 March, 2015.

Gardner, H.A (1948); Driers for drying oil; *Journal of the American oil chemist' society*; **36**:570-571 :In Menkiti,M.C. and Onukwuli, O.D. (2011). Utilization potentials of rubber seed oil for the production of alkyd resin using variable base oil lengths. *New York science journal*, **4**(2), 53.

Gamze, G. (2012). Alkyd resins based on waste PET for water-reducible coating applications. *Polymer bulletin*, **64**(8), 739-748. Doi:10.1007/s00289-009-0166-4. 20 March 2010.

George, P. K., Dimitris, S.A., Irini, D. S., & Dimitris, N. B.(2005). Alkyd resins derived from glycolized waste poly(ethylene terephthalate). *European polymer journal*, **41**(2), 201- 210.

Greimel, K.J., Veronika, P., Klaus, K., Roland, F., Armin, T., Christian, S., Enrique, H. A., Ingo, K., & George, M.G. (2013). Banning toxic heavy-metal catalysts from paints: enzymatic cross-linking of alkyd resins. *Green chemistry*,**15**, 381-388

Hanna, M. A. & Ma, F.(1999). "Biodiesel production: a review.*Bioresource technology*, **70** (1), 1–15. Doi: https://doi.org/10.1016/S0960-8524(99)00025-5. 11 March, 2014.

Hasmukh, S. P. & Amel, M. N.(2011).Surface coating studies of [(alkyd) – (epoxy resin treated castoroil)]: [maleated/tetrahydrophthalated cyclohexanoneformaldehyde resin[-[epoxy resin] condensate. *Journal of chemical and pharmaceutical research*, **3**(1),770-783.

Haveren, J.V., Oostveen, E. A., Miccichè, F., Noordover, B.A.J, Koning, C.E., Benthem, R.A., Frissen, A. E. & Weijnen, J.G.J.(2007).Resins and additives for powder coatings and alkyd paints, based on renewable resources. *Journal of coatings technology and research,* 177-186.

Ibanga, O. I. & Edet, W., N. (2015). Studies in Molecular Weight Determination of Cottonseed and Melon Seed Oils Based Biopolymers. *Advances in Chemical Engineering and Sciences,* 05(01), 43-50. DOI: 10.4236/aces.2015.51005. 11 March, 2015.

Ibanga, O., I. & Nyeneime, W., A. (2014). Physicochemical characteristics of fumarized and maleinized cottonseed oil. T*he international journal of engineering and science (IJES*), **3**(12), 01-04. Retrieved from www.theijes.com. 11 March, 2015.

Ibanga, O. I., Okon, D. E., & Udofot, J. E.(2014). Extraction, characterization of african pear (*dacryodes edulis*) oil and its application in synthesis and evaluation of surface coating driers. *International journal of advanced research in chemical science,***1**(4), 14-22. Retrieved from www.arcjournals.org. 11 March 2015.

Ibanga, O., I. & Edet, W. N. (2013). Influence of polybasic acid type on the physicochemical and viscosity properties of cottonseed oil alkyd resins. *The international journal of engineering and science (IJES),* **2**(5), 01-14.

Idiaghe, J.A., Aguele, F.O & Ekebafe, L.O.(2012). Preparation of low voc hybrid binder for surface coating applications..I*nternational journal of basic and applied sciences*, **1**(4), 280-282.

Igbo, U.E.; Igwe, C.C.; Akubueze, E.E., Ishola, O. R., Odusote, A. O & Oyewole, A.O. (2014). Utilisation of beniseed oil for the production of alkyd resin. *journal of applied chemistry (IOSR-JAC),***7**(5),104-106.

Ilkhani, A., R. (2012). Comparison of chemical nano structure, rheological and mechanical properties of long oil alkyd resin synthesized using polybasic acids catalyst. *Tanz. J. Sci*. **38**(2),177 -183

Ikhuoria, E.U., Okieimen, F.E., Obazee, E.O. & Erhabor, T.(2011). Synthesis and characterization of styrenated rubber seed oil alkyd. *African journal of biotechnology,***l** (10),1913-1918.

Ikhuoria, E., U., Aigbodion I., & Felix, E.,O.(2004). Enhancing the quality of alkyd resins using methyl esters of rubber seed oil. *Tropical journal of pharmaceutical research*, **3**(1),311-317. Retrieved from http//dx.doi.org/10.4314/tjpr.v.3i1/14615. 10 January, 2015.

ISO 11890-1(2007). *Paints and varnishes – Determination of volatile organic compound (VOC) content - Part 1: Difference method*. Retrieved from http: www.ec.gc.ca on 10 Jan, 2017.

Isaac, I. & Nsi, E.(2015). Studies in molecular weight determination of cottonseed and melon seed oils based biopolymers. *Advances In Chemical Engineering and Science*, **5**, 43-50.

Issam, A. M., & Cheun, C. Y.(2009). A study of the effect of palm oil on the properties of a new alkyd resin. *Malaysian Polym. J.*, 4,42-49.

Jamal, A. (2012). Rheological behavior of polyacrylamide/laponite nanoparticle suspensions in electrolyte media. *Journal of Macromolecular Science, Part B: Physics*.51:1139-1147. Doi:10.1080/00222348.2011.625903. 10 May, 2019.

Jem S. L., Issam A. M., Arniza G., Melati K.,(2014). Novel poly(alkyd-urethane)s from vegetable oils: Synthesis and properties. *Industrial Crops and Products*, 52, 74– 84.

Jenifer, G. (2018). *Environmentally friendly, non toxic paint - sustainable build*. Retrieved from www.sustainablebuild.co.uk. 10 Jan, 2019.

Jovicic, M. C., Radicevic, R. Z. & Simendic, V. B.(2009). *Synthesis and curing of enamel based on ricinoleic acid*. Retrieved from https://core.au.uk. 10 March, 2015.

Kienle, R.H., & Race, H.H.(1934).The Electrical, Chemical and physical properties of alkyd resins. *Journal of Electrochemical Society*, **65**(1), 87-107.

Kong, F., & Singh, R. P. (2011). Advances in instrumental methods to determine food quality deteriotation. Food and Beverage Stability and shell life. Retrieved from sciencedirect.com. 4 March, 2020.

Kontogiogors V., Biliaderis C. G., Kiosseoglou V. & Doxastakis G.(2004). Stability and rheology of egg yolk stabilized concentrated emulsions containing cereal β-glucans of varing molecular size. *Food Hydrocolloids*, 18, 987-998.

Lane, K. R., & Wilhelmi, M.A. (1994). Zero-VOC alkyd emulsions: a route to low-VOC architectural coatings. (volatile organic compounds) (special report: clean air compliance). A*merican Paint and Coatings Journal.*

Larsson, M., & Duffy, J.(2013). An overview of measurement techniques for determination of yield stress. A*nnual Transactions of the Nordic Rheology Society*, **21.**

Lewandowska, K. (2012). Rheological properties of chitosan blends with partially hydrolysed polyacrylamide in different solvents. *Progress On Chemistry and Application of Chitin and Its Derivatives*. 17, 53-57.

Lewandowska, K.(2006).Comparative study on rheological properties of polyacrylamide and partially hydrolyzed polyacrylamide solutions.*Journal of Applied Polymer Science*. 103: 2235-2241.Doi: 10.1002/App.25247. 10 May, 2019.

Lietuvos, M. (2016). Selected problems. *54th Lithuanian National Chemistry Olympiad,* 1-6.

Lin, C.,C. & Hsieh, K., H. (1977). The kinetics of polyesterification. I. Adipic acid and ethylen glycol. *J. Appl. Polym. Sci.*, 21, 2711–2719.

Lin, G., Xiujuan, Z., Ying, L., & William, A.(2008). Some nanocomposites based on a glycerol-derived alkyd resin and layered silicates. *Mol. Cryst. Liq. Cryst.*, **483**, 33–48.

Lopez, J. A.B., Alvarado, T. M., Coyt, G.G., Diosdado,M. A. & Reyes, D. J.(2013). Thermal characterization of vegetable oils by means of photoacoustic techniques**.** *Revista Mexicana de F´ısica*, **59** (1), 168–172.

Loius, H. M., Barminas, J. T., Fidelis, T. T., Joseph, O., O. & Bismong E., A.(2015). Formulation of alkyd based polymer coating from treated seed of tsada (Ximenia Americana) seed oil: Physiochemical and mechanical characterisation. *The International Journal of Science and Technology*, **3**(8), 112-119.

Malvern instruments white paper(2017). *Understanding yield stress measurements*. Retrieved from http://www.malvern.com/en/support/resource-center/whitepapers. 20 Aug, 2018.

Malvern Instruments. (2015). *Optimizing rheology for paint and coating applications*. White paper, 12. Retrieved from: http://www.malvern.com/en/support/resource-center/whitepapers. 22 May, 2017.

Malvern instrument (2005). *Predicting performance of paints using rheological measurements and equipment*. Retrieved from http://www.malvern.com/en/support/resource-center. 22 May, 2017.

McClements D. J.(2005). Food emulsion: principle, practice and techniques. Boca Raton FL: CRC press.

Menkiti, M.C., & Onukwuli, O.D.(2011). Utilization potentials of rubber seed oil for the production of alkyd resin using variable base oil lengths. *New York Science Journal*, **4**(2), 51-59. Retrieved from http://www.sciencepub.net/newyork. 12 Feb, 2015.

Mevy, J.P., Bessiere, J.M., Greff, S., Zombre, G. & Viano, J. (2006). Composition Composition of the volatile oil from the leaves of *Ximenia americana L. Biochem. Syst. Ecol*., 34, 549-553.

Alkyd Resins (Short, Medium And Long) Based On Sunflower Oil And Linoleic Acid As Binder For Paints. *International Journal Of Chemical & Petrochemical Technology (Ijcpt)*, **7 (**1): 1-16. Retrieved from www.tjprc.org. 10 Dec, 2017.

Monika, G., Reyes, Y., de Las Heras Alarcón, C., Minari, R., J., Beristain, I., Paulis, M., Barandiaran, M., Keddie, J., L., Asua, J., M.(2012).Transformation of waterborne hybrid polymer particles into films: Morphology development and modeling. *Polymer,* 53 (5)1, 1098-1108. Doi.org/10.1016/j.polymer.2012.01.021. 10 March, 2015.

Muhammad, R. I., Mohammad, D. H. B. & Saidul, S. J.(2014). Alkyd based resin from non-drying oil. *Procedia Engineering*, 90:78 – 88. Doi: 10.1016/j.proeng.2014.11.818. 10 March, 2015.

Murillo, E.A., Betty L. Lo´pez & Witold Brostow. (2014). Obtaining and properties of structurally-dyed alkyd resin. *Technology Audit and Production Reserves*, **3**(5),17.

Mukhtar, A., Ullah, H. & Mukhtar, H. (2007).Fatty acid composition of tobacco seed oil and synthesis of alkyd resin. *Chinese Journal of Chemistry*, **25**,705–708. Doi: 10.1002/cjoc.200790132. 22 Jan, 2015.

Nader, Z. S., Bahram, L., Elaheh, S. S. & Anahita, (2013). Synthesis and improvement of activity of cobalt organic salts as drier. *International Scholarly Research: Inorganic Chemistry,* **20**, 4.

Nikola, T., & Donka,T. (2014). Research on the possibility to utilize crude glycerol and waste polyethylene terephthalate for production of alkyd resins. *International Journal of Scientific Research***, 3**(10).

Njoku, O. U., & Ononogbo, I. C.(1995). Alkyd resin from rubber seed oil. *Indian Journal of Natural Rubber Research*, **8** (1), 63 – 65.

Njuku, F.W, Mwangi, P.M &Thiong'o, G. T.(2014). A comparison of cardanol and its derivatives as reactive diluents in alkyd coatings. *Chemistry and Materials Research*,**6(**3),50. Retrieved from: www.iiste.org. 10 March, 2015.

Nway, N. H., & Mya, M. O.(2008). Manufacture of alkyd resin from castor oil. *World Academy of Science, Engineering and Technology,* **24**,155 -156.

Nwafor, P. (2018, Sept 1) Air pollution: Nigeria ranks 4th deadliest globally. *Vanguard* Retrieved from https://www.vangardngr.com, on 10 Oct, 2018.

Nzikou, J. M., Mvoula-Tsieri, M. & Matos, L.(2007). "*Solanum nigrum l.* seeds as an alternative source of edible lipids and nutriment in Congo Brazzaville," *Journal of Applied Sciences*, 7(8),1107–1115.

Odetoye, T. E., Ogunniyi, D. S. & Olatunji, G. A.(2010). Preparation and evaluation of Jatropha curcas Linneaus seed oil alkyd resins. *Ind. Crops & Products*, 32, 225 – 230.

Oil and Colour Chemists' Association (1993). *Water-Reducible Resins In: Surface Coatings.* Springer, Dordrecht. Doi:10.1007/978-94-011-1220-8_17 on 01/15/2015.

Okon. D. E. & Ibanga, O. I.(2013). Fatty acid composition of melon (*Colocynthis vulgaris* Shrad) seed oil and its application in synthesis and evaluation of alkyd resins. *Journal of Applied Chemistry (IOSR-JAC)*.4 (4),30-41.

Oladipo, O.G., Gabriel, O., Ighodalo, C. E., & Olujinmi, M. F. (2013). Formation and characterization of paint based on alkyd resin derivative of ximenia americana (wild olive) seed oil**.** *Environment and Natural Resources Research*, **3**, 3.

Olakunle M. S., Abdulhamid, M., J. & Nebo, A., C.(2014). Kinetics and thermodynamics of oil extraction from water-melon seeds. *International Journal of Applied and Natural Sciences*, **3** (4):93-102.Retrieved from www.iaset.us. 15 March, 2019.

Omya, G.,A.(2005). Alkyd resin emulsion gives primers anti-corrosive properties. *European Journal of Coatings*,11, 68. Retrieved from www.europeans-coatings.com on 10 March, 2015.

Onukwuli,O.D, & Obodo, N. J.(2015). Optimization of high performance styrenatedalkyd resin for surface coating using response surface methodology . *International Journal of Novel Research In Physics Chemistry & Mathematics*, **2** (2), 33-40.9.

Orchard, S.E.(1962). On surface levelling in viscous liquids and gels. *Applied Science Research*, **11,**451-464.

Osemeahon, S..A, Nkafamiya, I. I., Maitera, O.N. & Akinterinwa, A.(2015). Synthesis and characterization of an emulsion paint binder from a copolymer composite of dimethylol urea/polystyrene. *Journal of Polymer & Composites*, **3**(2),11–21.

Osemeahon, S. A., Barminas, J.T. & Aliyu, B.A., (2007). Effect of Urea formaldehyde Viscosity on some Physical Properties of a Composite from Reactive Blending of Urea formaldehyde with Natural Rubber. *Int. J. Phys. Sci*., **2**(9), 242-248.

Patel, D.P., Nimavat, K.S., & Vyas, K.B.(2012). Surface coating studies of polyurethane derived from [(alkyd)-(epoxy resin treated castor oil)] using isophorene diisocynate ii *International journal for pharmaceutical research scholars (IJPRS),* **5**(1),I-3.

Ramakant, V., Nimbalkar,V., & Vilas, D. A.(2010). Synthesis and characterization of canola oil alkyd resins based on novel acrylic monomer (ATBS). *Journal of The American Oil Chemists Society*, **87**(8), 947-954.

Rao, M. A.,(2007). *Rheology of food and semisolids: Principle and application.* New York, Springer, 2nd ed.

Resene C.P.D. (2005, Aug).*Volume Solids, PVC, Hiding Power*. Retrieved from https://www.resene.co.nz/archspec/cpd_earn_points/pdfs/CPD_volumesolidspvchiding, on 10 Feb, 2015,

Ronald, W. M., Charles, A. M., & Bradley, A. S. (1999). *Introduction to chemical reaction engineering and kinetics.* New York, John Wiley & sons Inc.

Rossseau, D. (2000). Fat crystals and emulsion stability - a review. *Food Research International*, 33, 3 – 14.

Satheesh, K.M.N., Zahira, Y., Siti, M.S., & Abdullah, S.R.S.(2010). Synthesis of alkyd resin from non-edible jatropha seed oil. J*ournal of Polymers and The Environment*, **18**(4), 539-544.

Santosh, K. U. (2006). *Chemical kinetics and reaction dynamics.* New Delhi: India, Anamaya Publisher.

Shirley, C., Valeria, J., G.& Jorge, C., T.(2017). Rheological properties in aqueous solution for hydrophobically modified polyacrylamides prepared in inverse emulsion polymerization. *International Journal of Polymer Science*. 2017:1-13. Doi:10.1155/2017/8236870. 10 May, 2019.

Sorensen K. (2008). Route to VOC compliant alkyd coatings. S*urface Coating International*,6, 312-318. Retrieved from: https//www.persorp.com. 10 March, 2015

Sharma P., Singh, L. & Dilbaghi, N.(2009). Optimisation of process variables for decolorization of disperse yellow 211 by Baciillus subtilis using Box-Behnken design. *Journal of Harzard Mater*, **164**, 1024 -1029.

Spyros, A.(2002). Characterization of unsaturated polyester and alkyd resins using one- and two-dimensional NMR spectroscopy. *Journal of Applied Polymer Science*, **88**,1881– 1888.

Strivens T.A. (1999). The rheology of paints. *In* R Lambourne & TA Strivens(Eds.) *Paints and Surface Coatings.* Woodhead Publishers, 575-597.

Tapahenho, H., H.(2014).Obtaining and properties of structurally dyed alky resin. *Technology Audict and Production Reserves*. **3**(5) 17.

T.A.Instruments (2016). Understanding rheology of structured fluids. *TA Instruments* Retrieved from http://www.tainstruments.com , on 28 July, 2018.

T.A.Instruments (2015, Sept). Rheology characterisation of paints and coatings. *Azo Materials.*Retrieved from https://www.azom.com/article.aspx?, on 28 July, 2018.

Tim, D. (2016). Inconsistent viscosity measurements. *Product finishing magazine*. Retrieved from http//www.pf.epubxp.com, on 28 July, 2018.

Trumbo, D.L., Mote, B.E. & Rasoul, H.A.A. (2001). Synthesis of copolymers of a linoleic derivative and properties of the copolymer films. *Journal of AppliedPolymer Science*,80: 261-267.

Uche, I. C., Chukwujike, I. C., & Nwanonenyi, S. C.(2016). Synthesis, characterization and performance evaluation of breadfruit seed oil modified alkyd resin. *European Journal of Advances In Engineering and Technology*, **3**(9), 5-11.

Umeobika U.C., Onuegbu T.U., Iloamaeke M.I., & Ekwueme I.J.(2013). Synthesis and evaluation of performance characteristics of rubber seed oil-modified short and medium alkyd resins. *International Journal of Science Innovations and Discoveries*, **3** (1), 86-92. Retrieved from www.ijsidonline.info, on 10 March, 2015.

Uzoh C. F.,Onukwuli, O. D., Emeka, M.(2015). Kinetics of castor oil alkyd resin polycondensation reaction. *J. Chem Eng Process Technol* 6:240. Doi:10.4172/2157-7048.1000240. 20 March, 2017.

Uzoh, C.F., Obodo, N.J., & Onukwuli, O.D. (2015). Kinetic study on the polyesterification and copolymerisation process of unstyrenated and styrenated palm kernel oil based alkyd resin. *Journal of Chem Eng Process Technology*, **6**, 242. Doi:10.4172/2157-7048.1000242. 20 March, 2017.

Uzoh C. F., Onukwuli, O.D., Odera, R.S. & Ofochebe, S. (2013).Optimization of polyesterification process for production of palm oil modified alkyd resin using response surface methodology. *Journal of Environmental Chemical Engineering*, 1, 777–785.Retrieved from https://www.journals.elsevier.com/journal-of-environmental-chemical-engineering, on 20 March, 2017.

Valerie, S.(2017, Oct). Measuring the hardness of applied coatings. *KTA*. Retrieved from https://kta.com/kta-university/measuring-hardness-applied-coatings, on 11 Feb, 2018.

Vance, R.G., Morris, N. H. & Olson C. M.(1991). Coupling solvent effect on water reducible alkyd resins. *Journal of Coating Technolog*,63(802),47-54.

Viguerie, L., Guylaine, D., François, L., Thierry, M. M., Philippe, W.(2009). Historical evolution of oil painting media: A rheological study. *C. R. Physique*. 10: 612–621. Doi:10.1016/j.crhy.2009.08.006. 11 March, 2015.

Volatile organic compound (2018, April 30). Retrieved from https://en.wikipedia.org/wiki/Volatile_organic_compound, on 30 April, 2018.

Vikkasit, A., Siripon, D., & Wiwut, T.(2006). Effect of oil type on the properties of short oil alkyd coating materials. *Korean Journal of Chemical Engineering*, **23**(4), 672-677.

Walstra P., V., & Berestyn C.(1975). Characterisation of milk fat in the emulsified state. *Netherlands Milk and Diary Journal*,29,35-65.

Wright, M.R., (2004). *An Introduction to Chemical Kinetics*. England:John Wiley and Sons Ltd.,

Zeno, W.W., Frank, N. J., Socrates, P. P.& Douglas, A. W(2007).Synthetic procedure for alkyd resins. *In Organic Coatings: Science and Technology*. Retrieved from, https//book.google.com.ng/books, on 20 March, 2015.

APPENDICES

APPENDIX A: COMPUTATION FOR OIL EXTRACTION AND CHARACTERIZATION

(A1) Oil Extraction

Oil was extracted from three different species of palm kernel oil which include;

Osukwu specie *(Eleasis guineensis pisifera)*

Weight of A = B = C = 2kg

Weight of crude palm kernel oil = 0.7kg

Weight of palm kernel cake = 1.29kg

Losses 2kg – (0.7 + 1.29)kg = 0.01kg

$$\text{Moisture content}\% = \text{weight of moisture}/\text{weight of oil sample} \qquad (3.3b)$$

For moisture content

Weight of potassium hydroxide = 1g

Weight of oil sample = 1g

Weight of KOH and Oil after evaporation = 1.7g

Weight of moisture % = (2 –1.7)g = 0.3g

Moisture content = 0.3/1 = 0.3%

Weight of oil (kg) = 0.7 – (0.3% of 0.7) = 0.698kg

$$yeild = \frac{weight\ of\ oil}{weight\ of\ kernel}\ x\ 100 \qquad (3.3c\ )$$

$$yeild = \frac{0.7}{2}\ x\ 100 = 35\%$$

Ojukwu specie *(Eleasis guineensis tenera)*

Weight of crude palm kernel oil = 0.79kg

Weight of palm kernel cake = 1.2kg

Losses 2kg – (0.79 + 1.2)kg = 0.01kg

For moisture content

Weight of potassium hydroxide = 1g

Weight of oil sample = 1g

Weight of KOH and Oil after evaporation = 1.66g

Weight of moisture % = (2 –1.66)g = 0.34g

Moisture content = 0.34/1 = 0.34%

$$yeild \frac{0.79}{2}\ x\ 100 = 39.5\%$$

Okporoko specie *(Eleasis guineensis dura)*

Weight of crude palm kernel oil = 0.74kg

Weight of palm kernel cake = 1.25kg

Losses 2kg – (0.74 + 1.25)kg = 0.01kg

For moisture content

Weight of potassium hydroxide = 1g

Weight of oil sample = 1g

Weight of KOH and Oil after evaporation = 1.68g

Weight of moisture % -= (2 –1.68)g = 0.32g

Moisture content = 0.32/1 = 0.32%

$$yeild = \frac{weight\ of\ oil}{weight\ of\ kernel}\ x\ 100 \qquad (3.4)$$

$yeild = \frac{0.74}{2}\ x\ 100 = 37\%$

Moisture conent of jatropha seed *(jatropha curcas)* oil

W_1 = 32.34g, W_2 = 35.66g, W_3 = 40.27g, W_4 = 40.25g.

Weight of moisture = $W_3 - W_4$ = 40.27 – 40 25 = 0.02

$$\%\ \text{moisture} = \frac{Weight\ of\ moisture}{weight\ of\ oil}\ x\ 100 \quad = \frac{0.02}{5}\ x\ 100\ =\ 0.4\%$$

(A2) Computation For Oil Characterisation

Density

Weight of beaker = W_B = 104.22g

Weight of beaker and oil = W_{BO} = 139.92g

Weight of oil = W_O

Weight of oil A =W_{OA}

Weight of oil B = W_{OB}

Weight of oil C = W_{OC}

Weight of beaker and water = W_{BW} = 143.52g

Volume of oil = $V_{O\,=}$ V = 5oml

Volume of water = V_W = 5oml

$$\text{Density, } \rho = \frac{m}{v} \tag{3.1}$$

Density of A = ρ_A

Density of B = ρ_B

Density of C = ρ_C

Mass m = W

Specific gravity = SPG

Density

Osukwu specie *(Eleasis guineensis pisifera)*.

The same beaker was used for the three species.

W_{OA} = W_{BO} - $W_{B;}$ 139.92g - 104.22g = 35.7g

$\rho_{A\,=}$ 0.714g

Ojukwu specie *(Eleasis guineensis tenera)*.

$W_{OB} = W_{BO} - W_{B;}$ 140.55g – 104.22g = 36.31g

ρ_B = 0.7262g

Okporoko specie *(Eleasis guineensis dura)*.

$W_{OC} = W_{BO} - W_B$; 139.71g – 104.22g = 39.71g

ρ_C = 0.7098g

Density of jatropha seed *(jatropha curcas)* oil

W_B = 95.97g, W_{Bo} = 127.08g, $W_O = W_{BO} - W_B$; 130.08g – 95.97g = 34.17g

ρ = 0.6834g

Water

W_{BW} = 143.52g

$W_W = W_{BW} - W_B$ = 143.52g – 104.22g =39.30g

ρ_W = 0.786g

Specific Gravity (SPG)

$$SPG = \frac{mass\ of\ oil}{mass\ of\ equal\ vol\ of\ water} \qquad 3.2$$

Osukwu specie *(Eleasis guinnensis pisifera)*.

$\frac{35.7}{39.3} = 0.908$

Ojukwu specie *(Eleasis guineensis tenera)*.

$\frac{36.31}{39.3} = 0.924$

Okporoko specie *(Eleasis guineensis dura)*.

$\frac{35.49}{39.3} = 0.903$

Density of jatropha seed*(jatropha curcas)* oil

$\frac{34.17}{39.3} = 0.8695$

Acid Value

$$Acid\ value = \frac{56.1MV}{W} \qquad (3.7)$$

Mass of oil = W = 1g; Mass of ethanol = 15.62g; Molarity of NaOH = M = 0.1M

Volume of ethanol = 20ml

Osukwu specie *(Eleasis guinnensis pisifera)*

V = Volume of NaOH = 1.5ml

$$Acid\ value = \frac{56.1x1.5x0.1}{1} = 8.42mgNaOH/g$$

Ojukwu specie *(Eleasis guineensis tenera)*

V is volume of NaOH = 1.42ml

$$Acid\ value = \frac{56.1x1.42x0.1}{1} = 7.95mgNaOH/g$$

Okporoko specie *(Eleasis guineensis dura)*

V is volume of NaOH = 1.40ml

$$Acid\ value = \frac{56.1x1.40x0.1}{1} = \ 7.84mgNaOH/g$$

Acid value of jatropha seed*(jatropha curcas)* oil

V is volume of NaOH = 2.5ml

$$Acid\ value = \frac{56.1x2.5x0.1}{1} = 14.025mgNaOH/g$$

Free Fatty Acid (FFA)

$$FFA = \frac{AV}{\,}2 \tag{3.4}$$

Osukwu specie *(Eleasis guineensis pisifera)*.

$$FFA = \frac{8.42}{2} \ = 4.21mgNaOH/g$$

Ojukwu specie *(Eleasis guinnensis tenera)*.l

$$FFA = \frac{7.95}{2} \ = 3.98mgNaOH/g$$

Okporoko specie *(Eleasis guineensis dura)*.

$$FFA = \frac{7.84}{2} = 3.92mgNaOH/g$$

FFA of jatropha seed*(jatropha curcas)* oil

$$FFA = \frac{14.025}{2} = 7.02mgNaOH/g$$

Iodine Value (IV)

$$\frac{12.69M(X-V)}{W} \tag{3.6}$$

M is molarity of NaOH used for the titration = 0.1M

X is volume of NaOH used for the titration

V is volume of NaOH used for the blank titration = 29ml

W is mass of oil sample used for the titration = 1g

Osukwu specie *(Eleasis guinnensis pisifera)*

X = 46.5ml

$$\frac{12.69x0.1(46.5-29)}{1} = 22.208mgNaOH/g$$

Ojukwu specie *(Eleasis guinnensis tenera)*

X = 46.4ml

$$\frac{12.69x0.1(46.4-29)}{1} = 22.081mgNaOH/g$$

Okporoko specie *(Eleasis guinnensis dura)*

X = 46.4ml

$$\frac{12.69x0.1(46.4-29)}{1} = 22.081mgNaOH/g$$

I V For Jatropha Seed *(jatropha curcas)*Oil

X = 112ml

$$\frac{12.69x0.1(112-29)}{1} = 105.327mgNaOH/g$$

Peroxide Value (PV)

$$PV = \frac{(S-B)M10}{W} \tag{3.5}$$

M is molarity of sodium thiosulphate used for the titration = 0.1M

S is volume of sodium thiosulphate used for the titration

B is volume of sodium thiosulphate used for the blank titration = 20ml

W is mass of oil sample used for the titration = 5g

Osukwu specie *(Eleasis guinnensis pisifera)*

S = 70ML

$$PV = \frac{(70-20)0.1x10}{5} = 10mEq/kg$$

Ojukwu specie *(Eleasis guinnensis tenera)*

S = 80ml

$$PV = \frac{(80-20)0.1x10}{5} = 12mEq/kg$$

Okporoko specie *(Eleasis guineensis dura)*

S = 78ml

$$PV = \frac{(78-20)0.1x10}{5} = 11.6mEq/kg$$

P V For Jatropha Seed *(jatropha curcas)*Oil

S = 40ml

$$PV = \frac{(40-20)0.1x10}{5} = 4mEq/kg$$

APPENDIX B:

B1 Volatile Content Calculation for Latin Square Plan

WAl is weight of aluminium; WAR is weight of aluminium and resin.

WAfter is weight of aluminium and resin after drying.

Sample 1

WAl = 4.80g; WAR = 5.8g; WAfter = 5.47g

VC = 5.8 - 5.47 = 0.33g;

%VC = $\frac{0.33}{1} x100 = 33\%$

Sample 2

WAl = 4.97g; WAR = 5.97g; WAfter = 5.55g

VC = 5.97 - 5.55 = 0.42g;

%VC = $\frac{0.42}{1} x100 = 42\%$

Sample 3

WAl = 5.97g; WAR = 5.97g; WAfter = 5.71g

VC = 5.97 - 5.71 = 0.26g

%VC = $\frac{0.26}{1} x100 = 26\%$

Sample 4

WAl = 4.80g; WAR = 5.8g; WAfter = 5.65g

VC = 5.8 - 5.65 = 0.15g

%VC = $\frac{0.15}{1} x100 = 15\%$

Sample 5

WAl = 5.20g; WAR = 6.20g; WAfter = 5.74g

VC = 6.2 - 5.74 = 0.46g

%VC = $\frac{0.46}{1}x100 = 46\%$

Sample 6

WAl = 4.94g; WAR = 5.94g; WAfter = 5.78g

VC = 5.94 - 5.78 = 0.16g

%VC = $\frac{0.16}{1}x100 = 16\%$

Sample 7

WAl = 5.36g; WAR = 6.36g; WAfter = 5.83g

VC = 6.36 - 5.83 = 0.53g

%VC = $\frac{0.33}{1}x100 = 53\%$

Sample 8

WAl = 4.80g; WAR = 5.8g; WAfter = 5.31g

VC = 5.8 - 5.31 = 0.49g

%VC = $\frac{0.49}{1}x100 = 49\%$

Sample 9

WAl = 5.30g; WAR = 6.3g; WAfter = 5.8g

VC = 6.3 - 5.8 = 0.5g

%VC = $\frac{0.5}{1}x100 = 50\%$

(B2) Latin square calculation

Table B.1: Latin square plan of experiment with responses

Oil type/Temperature	230 °C	240 °C	250°C	U_i	U_i^2
A	22.29	28.97	17.09	68.25	4671.72
B	8.90	31.95	9.65	50.5	2550.25
C	37.15	34.18	34.92	106.25	11289.06
V_j	68.34	95.10	61.66	**225**	**18511.03**
V_j^2	4670.36	9044.01	3801.96	**17516.33**	

Table B .2 Sum of W (water to alkyd ratio) used in the experiment

	W_1	W_2	W_3	Total
W_k	50	75	100	225
W_k^2	2500	5625	10000	18125

The total sum of square for all the experimental results is determined as follow;

$$Q1 = \sum_{i=1}^{n} \sum_{yi} 2 \qquad (B.1)$$

$Q1 = 22.29^2 + 28.97^2 + 17.09^2 + 8.90^2 + 31.95^2 + 9.65^2 + 37.15^2 + 34.18^2 + 34.92^2 = 6583.85$

$$Q2 = \frac{1}{n} \sum_{Ui} 2 \qquad (B.2)$$

$$Q2 = \frac{1}{3}\,(4671.72 + 2550.25 + 11289.06) = \frac{18511.03}{3} = 6170.34$$

$$Q3 = \frac{1}{n}\sum_{Vi} 2 \qquad (B.3)$$

$$Q3 = \frac{1}{3}\ (4670.36 + 9044.01 + 3801.96) = \frac{17516.33}{3} = 5838.78$$

$$Q4 = \frac{1}{n}\sum_{Wi} 2 \qquad (B.4)$$

$$Q4 = \frac{1}{3}\ (2500 + 5625 + 10000) = \frac{18125}{3} = 6041.67$$

To determine the quantity G,

$$G = \sum_{i=1} Ui\ = \sum_{i=1} Vi = \sum_{i=1} Wi\ = 225 \qquad (B.5)$$

$$Q5 = \frac{G^2}{n^2} = \frac{225^2}{3^2} = \frac{50625}{9} = 5625 \qquad (B.6)$$

Total sum of square $Q = Q1 - Q5$ $\qquad (B.7)$

$$Q = 6583.85 - 5625 = 958.85$$

Sum of squares connected to the effect of the factors x_1, x_2, x_3

$$Q(\mathrm{x}1) = Q2 - Q5\ \ = 6170.34 - 5625 = 545.34 \qquad (B.8)$$

$$Q(\mathrm{x}2) = Q3 - Q5\ \ = 5838.78 - 5625 = 213.78 \qquad (B.9)$$

$$Q(\mathrm{x}3) = Q4 - Q5\ \ = 6041.67 - 5625 = 416.67 \qquad (B.10)$$

$$Q\mathrm{res} = \ Q(\mathrm{x}1) - \ Q(\mathrm{x}2) - \ Q(\mathrm{x}3) \qquad (\mathrm{B.11})$$

$$Q\mathrm{res} = \ 958.85 - 545.34 - 213.78 - \ 416.67\ \ = -216.94$$

Number of degrees of freedom corresponding to the sums $Q\mathrm{res}, Q(\mathrm{x}1), Q(\mathrm{x}2)\ and\ Q(\mathrm{x}3)$

$$v = n^2 - 1 = 9 - 1 = 8 \qquad (B.12)$$

$$v_1 = v_2 = v_3 \qquad (B.13)$$

$$v_{res} = (n-1)(n-2) = (3-1)(3-2) = 2 \qquad (B.14)$$

$$check;\ v = v_1 + v_2 + v_{3+} \quad v_{res} \quad {\scriptstyle =2+2+2+2=8} \qquad (B.15)$$

Estimates of variance

$$s_1^2 = \frac{Q_{x1}}{v_1} = \frac{545.43}{2} = 272.67 \qquad \text{(B.16)}$$

$$s_2^2 = \frac{Q_{x2}}{v_2} = \frac{213.78}{2} = 106.89 \qquad \text{(B.17)}$$

$$s_3^2 = \frac{Q_{x3}}{v_3} = \frac{416.67}{2} = 208.34 \qquad (B.18)$$

$$s_{res}^2 = \frac{Q_{res}}{v} = \frac{216.92}{2} = -108.46 \qquad \text{(B.19)}$$

$$f_1 = \frac{s_1^2}{s_{res}^2} = \frac{272.67}{108.46} = 2.51 \qquad (B.20)$$

$$f_2 = \frac{s_2^2}{s_{res}^2} = \frac{106.89}{108.46} = 0.98 \qquad (B.21)$$

$$f_3 = \frac{s_3^2}{s_{res}^2} = \frac{208.34}{108.46} = 1.92 \qquad \text{(B.22)}$$

At 0.05 level of significance and $v_1 = v_2 = v_{3=}$ 2 and $v_{r\,=\,2}$

$$F_{table}(0.05,2,2) = 19.00 \qquad (\ B.23)$$

$$F_1 < F_{table}\ \ ie\ 2.51\ < 19.00 \qquad (B.24)$$

$$F_2 < F_{table} \ \ ie \ 0.98 \ < 19.00 \qquad (B.24)$$

$$F_3 < F_{table} \ \ ie \ 1.92 < 19.00 \qquad (B.25)$$

$X_{1,}$ X_2, X_3 are not significant .

At 0.01 level of significance and $v_1 = v_2 = v_{3=}$ 2 and $v_{r\ =\ 2}$

$$F_{table}(0.01,2,2) = 99.00 \qquad (B.26)$$

$$F_1 < F_{table} \ \ ie \ 2.51 \ < 99.00 \qquad (B.27)$$

$$F_2 < F_{table} \ \ ie \ 0.98 \ < 99.0 \qquad (B.28)$$

$$F_3 < F_{table} \ \ ie \ 1.92 < 99.00 \qquad (B.29)$$

$X_{1,}$ X_2, X_3 are also not significant .

This means that the percentage of Volatile organic component does not substantially depend on oil type, reaction temperature, and water to alkyd ratio.

Table B.3: Latin square plan of experiment with responses

Oil type/Temperature	230 °C	240 °C	250°C	U_i	U_i^2
A	25.6	24.65	23.25	73.5	5402.25
B	21.39	19.53	17.21	58.13	3379.09
C	32.55	31.63	29.29	93.47	8736.64
V_j	79.54	75.81	69.75	**225**	**17517.98**
V_j^2	6326.61	5747.16	4865.06	**16938.83**	

The total sum of square for all the experimental results is determined as follow; using equation B.1- B.4.

Q1 = $25.6^2 + 24.65^2 + 23.25^2+21.39^2+ 19.53^2+ 17.21^2+ 32.55^2+ 31.63^2+29.29^2 = 5856.53$

$$Q2 = \frac{1}{3}\ (5402.25 + 3379.09 + 8736.64) = \frac{17517.98}{3} = 5839.33$$

$$Q3 = \frac{1}{3}\ (6326.61 + 5747.16 + 4865.06) = \frac{16938.83}{3} = 5646.28$$

$$Q4 = \frac{1}{3}\ (2500 + 5625 + 10000) = \frac{18125}{3} = 6041.67$$

The quantity G is determined using equation B.5.

$$G = \sum_{i=1} Ui\ = \sum_{i=1} Vi = \sum_{i=1} Wi\ = 225$$

Q5 is determined using equation B.6

$$Q5 = \frac{G^2}{n^2} = \frac{225^2}{3^2} = \frac{50625}{9} = 5625$$

Total sum of square is determined using equation B.7 $Q = 5856.53 - 5625 = 231.53$

Sum of squares connected to the effect of the factors x_1, x_2, x_3 are determined using equations B.8 – B.11

$$Q(\mathrm{x1}) = Q2 - Q5\ \ = 5839.33 - 5625 = 214.33$$

$$Q(\mathrm{x2}) = Q3 - Q5\ \ = 5646.28 - 5625 = 21.28$$

$$Q(\mathrm{x3}) = Q4 - Q5\ \ = 6041.67 - 5625 = 416.67$$

$Q\text{res} = \ Q(\text{x}1) - \ Q(\text{x}2) - \ Q(\text{x}3)$

$Q\text{res} = \ 231.53 - 214.33 - 21.28 \ - \ \ 416.67 \ \ = \ -420.75$

Number of degrees of freedom corresponding to the sums $Q\text{res}, Q(\text{x}1), Q(\text{x}2)\ and\ Q(\text{x}3)$ .where determined as shown below using equation B.12 – B.15

$v = n^2 - 1 = 9 - 1 = 8$

$v_1 = v_2 = v_3$

$v_{res} = \ (n-1)(n-2) = (3-1)(3-2) = 2$

$check;\ v = \ v_1 + v_2 + v_{3+}\ \ v_{res}$ =2+2+2+2=8

Estimates of variance where determined as shown below using equation B.16 –B.22

$s_1^2 = \frac{Q_{x1}}{v_1} = \ \frac{214.33}{2} = 107.17$

$s_2^2 = \frac{Q_{x2}}{v_2} = \ \frac{21.28}{2} = 10.64$

$s_3^2 = \frac{Q_{x3}}{v_3} = \ \frac{416.67}{2} = 208.34$

$s_{res}^2 = \frac{Q_{res}}{v} = \ \frac{-420.67}{2} = -210.38$

$f_1 = \frac{s_1^2}{s_{res}^2} = \frac{107.17}{210.38} = 0.51$

$f_2 = \frac{s_2^2}{s_{res}^2} = \frac{10.64}{210.38} = 0.05$

$f_3 = \frac{s_3^2}{s_{res}^2} = \frac{208.34}{210.38} = 0.99$

At 0.05 level of significance and $v_1 = v_2 = v_{3=}$ 2 and $v_{r\,=\,2}$

$F_{table}(0.05{,}2{,}2) = 19.00$

$F_1 < F_{table}\ \ ie\ 0.51\ < 19.00$

$F_2 < F_{table}\ \ ie\ 0.051\ < 19.00$

$F_3 < F_{table}\ \ ie\ 0.99\ < 19.00$

$X_{1,}$ X_2, X_3 are not significant .

At 0.01 level of significance and $v_1 = v_2 = v_{3=}$ 2 and $v_{r\,=\,2}$

$F_{table}(0.01{,}2{,}2) = 99.00$

$F_1 < F_{table}\ \ ie\ 0.51\ < 99.00$

$F_2 < F_{table}\ \ ie\ 0.051\ < 99.00$

$F_3 < F_{table}\ \ ie\ 0.99\ < 99.00$

$X_{1,}$ X_2, X_3 are also not significant .

This means that the acid value does not substantially depend on reaction temperature, oil type and water to alkyd ratio.

(B4) Volatile Content Computations For RSM Designed Experiment

Wal = weight of aluminium, War = weight of aluminium and resin

Wafter = weight of aluminium and resin after drying

VOC = Volatile organic component.

Table B4: Volatile organic content calcuation for RSM designed experiment for PKOBAE.

Run % Volatile Organic Content

1 Wal = 5.30g,War = 6.3g,Wafter = 6.05g

VOC = 6.3 – 6.05 = 0.25g, %VOC = $\frac{0.25}{1} x100 = 25\%$

2 Wal = 5.47g,War = 6.47g,Wafter = 6.41g

VOC = 6.47 – 6.41 = 0.06g, %VOC = $\frac{0.06}{1} x100$ =6%

3 Wal = 5.50g,War = 6.5g,Wafter = 6.4g

VOC = 6.5 – 6.4 = 0.1g, %VOC = $\frac{0.1}{1} x100 = 10\%$

4 Wal = 5.52g,War = 6.52g,Wafter = 6.44g

VOC = 6.52 – 6.44 = 0.08g, %VOC = $\frac{0.08}{1} x100 = 8\%$

5 Wal =5.47g,War = 6.47g,Wafter = 6.4g

VOC = 6.47 – 6.40 = 0.07g, %VOC = $\frac{0.07}{1} x100 = 7\%$

6 Wal = 5.52g,War = 6.52g,Wafter = 6.46g

VOC = 6.52 – 6.46 = 0.06g, %VOC = $\frac{0.06}{1} x100 = 6\%$

7 Wal = 5.30g,War = 6.30g,Wafter = 6.10g

VOC = 6.30 – 6.10 = 0.2g, %VOC = $\frac{0.20}{1} x100 = 20\%$

8 Wal = 5.52g,War = 6.52g,Wafter = 6.47g

VOC = 6.52 – 6.47 = 0.05g, %VOC = $\frac{0.05}{1} x100 = 5\%$

9 Wal = 5.60g,War = 6.60g,Wafter = 6.53g

VOC = 6.60 – 6.53 = 0.07g, %VOC = $\frac{0.07}{1} x100 = 7\%$

10 Wal =5.47g,War = 6.47g,Wafter = 6.31g

VOC = 6.47 – 6.31 = 0.16g, %VOC = $\frac{0.16}{1} x100 = 16\%$

11 Wal = 5.33g,War = 6.33g,Wafter = 6.29g

VOC = 6.33 – 6.29 = 0.04g, %VOC = $\frac{0.04}{1} x100 = 4\%$

12 Wal = 5.40g,War = 6.4g,Wafter = 6.32g

VOC = 6.4 – 6.32 = 0.08g, %VOC = $\frac{0.08}{1}x100 = 8\%$

13 Wal = 5.70g,War = 6.7g,Wafter = 6.65g

VOC = 6.7 – 6.65 = 0.05g, %VOC = $\frac{0.05}{1}x100 = 5\ \%$

14 Wal = 5.40g,War = 6.4g,Wafter = 6.3g

VOC = 6.4 – 6.3 = 0.10g, %VOC = $\frac{0.10}{1}x100 = 10\%$

15 Wal = 5.33g,War = 6.33g,Wafter = 6.28g

VOC = 6.33 – 6.28 = 0.05g, %VOC = $\frac{0.05}{1}x100 = 5\%$

16 Wal = 5.33g,War = 6.33g,Wafter = 6.25g

VOC = 6.33 – 6.25 = 0.08g, %VOC = $\frac{0.08}{1}x100 = 8\%$

17 Wal = 5.30g,War = 6.34g,Wafter = 6.3g

VOC = 6.34 – 6.28= 0.06g, %VOC = $\frac{0.06}{1}x100 = 6\%$

Table B5: Volatile organic content calcuation for RSM designed experiment for JSOBAE.

Run % Volatile organic content

1 Wal = 4.65g,War = 5.68g,Wafter = 5.56g, Wr = 5.68 – 4.65 = 1.03

VOC = 5.68 – 5.56 = 0.12g, %VOC = $\frac{0.12}{1.03}x100 = 11.7\%$

2 Wal = 5.19g,War = 6.19g,Wafter = 6.13g, Wr = 6.19- 5.19 = 1

VOC = 6.19 – 6.13 = 0.06g, %VOC = $\frac{0.06}{1}x100 = 6\%$

3 Wal = 6.18g,War = 7.18g,Wafter = 7.14g, Wr = 7.18- 6.18 =1g

VOC = 7.18 – 7.14 = 0.04g, %VOC = $\frac{0.04}{1}x100 = 4\%$

4 Wal = 4.25g,War = 5.35g,Wafter = 5.21g, Wr =5.35-4.25 = 1.10

VOC = 5.35- 5.21 = 0.14g, %VOC = $\frac{0.14}{1.1}x100 = 12.73\%$

5 Wal = 5.38g,War = 6.41g,Wafter = 6.22g, Wr = 6.41-5.38 = 1.03g

VOC = 6.41 – 6.22 = 0.19g, %VOC = $\frac{0.19}{1.03}x100 = 18.45\%$

6 Wal =4.68g,War = 5.74g,Wafter = 5.67g, Wr =5.74- 4.68 =1.06

VOC = 5.74 – 5.67 = 0.07g, %VOC = $\frac{0.07}{1.06}x100 = 6.60\%$

7 Wal = 5.38g,War = 6.41g,Wafter = 6.26g, Wr 6.41-5.38 = 1.03g

VOC = 6.41 – 6.26 = 0.15g, %VOC = $\frac{0.15}{1.03}x100 = 14.56\%$

8 Wal =4.68g,War = 5.74g,Wafter = 5.66g, Wr =5.74- 4.68 =1.06

VOC = 5.74 – 5.66 = 0.08g, %VOC = $\frac{0.08}{1.06}x100 = 7.5\%$

9 Wal = 6.08g,War = 7.1g,Wafter = 7.02g, Wr = 7.1- 6.08 = 1.02g

VOC = 7.08 – 7.02 = 0.06g, %VOC = $\frac{0.06}{1.02}x100 = 5.9\%$

10 Wal = 4.33g,War = 5.35g,Wafter = 5.24g, Wr = 5.35- 4.33 = 1.02g

VOC = 5.35 - 5.24 = 0.11g, %VOC = $\frac{0.11}{1.02}x100 = 10.78\%$

11 Wal = 5.59g,War = 6.70g,Wafter = 6.65g, Wr = 6.7 -5.59 =1.11

VOC = 6.70 – 6.65 = 0.05g, %VOC = $\frac{0.05}{1}x100 = 4.5\%$

12 Wal = 4.20g,War = 5.22g,Wafter = 5.15g, Wr = 5.22- 4.21 = 1.01g

VOC = 5.22 – 5.15= 0.07g, %VOC = $\frac{0.07}{1.01}x100 = 6.96\%$

13 Wal = 6.08g,War = 7.08g,Wafter = 7.03g, Wr = 7.08- 6.08 = 1g

VOC = 7.08 – 7.03 = 0.05g, %VOC = $\frac{0.05}{1}x100 = 5\%$

14 Wal = 6.18g,War = 7.18g,Wafter = 7.10g, Wr = 7.18- 6.18 =1g

VOC = 7.18 – 7.10 = 0.08g, %VOC = $\frac{0.08}{1}x100 = 8\%$

15 Wal = 6.16g,War = 7.18g,Wafter = 7.10g, Wr = 7.18- 6.16 =1.02g

VOC = 7.18 – 7.10 = 0.08g, %VOC = $\frac{0.08}{1.02}x100 = 7.8\%$

16 Wal =4.84g,War = 5.88g,Wafter = 5.83g, Wr = 5.88-4.84 = 1.04g

VOC = 5.88 – 5.83 = 0.05g, %VOC = $\frac{0.05}{1.04}x100 = 14.42\%$

17 Wal = 5.21g,War = 6.22g,Wafter = 6.16g, Wr = 6.22-5.21= 1.01g

VOC = 6.22 – 6.16 = 0.06g, %VOC = $\frac{0.06}{1.01}x100 = 5.95\%$

Appendix C: Calculation For Kinetic Study Of Alkyd Resin Production

C1: Reaction rate

Table C1: Calculation for acid value against time for polycondensation reaction of PKO*BAR*

Time(mins)	Volume of NaOH(ml)	Mass of resin(g)	Acid value = $5.61\frac{v}{m}$(mgNAOH/g)
0	21.23	0.6	$5.61\frac{21.23}{0.6} = 198.5$
20	17.90	0.65	$5.61\frac{17.9}{0.65} = 154.50$
40	14.40	0.70	$5.61\frac{14.4}{0.7} = 115.30$
60	10.43	0.70	$5.61\frac{10.43}{0.7} = 83.60$
80	7.40	0.70	$5.61\frac{7.4}{0.7} = 59.30$
100	4.05	0.50	$5.61\frac{4.05}{0.5} = 45.44$
120	3.64	0.50	$5.61\frac{3.64}{0.5} = 40.80$
140	2.75	0.50	$5.61\frac{2.75}{0.5} = 30.90$
160	2.13	0.50	$5.61\frac{2.13}{0.5} = 24.00$
180	2.35	0.70	$5.61\frac{2.35}{0.7} = 18.89$
200	1.6	0.55	$5.61\frac{1.6}{0.55} = 16.33$
220	1.4	0.63	$5.61\frac{1.4}{0.63} = 12.47$
240	0.87	0.5	$5.61\frac{0.87}{0.5} = 9.76$

Using equation 3.16

$$f = pav = \frac{c_{0-c}}{c_0} \quad or\ c = c_0(1-f) \qquad (3.16)$$

From table C1,
at t = 0mins, co = 198.5(mgNaOH/g),

at t = 20mins, c = 154.5(mgNaOH/g),

$$f = \frac{198.5 - 154.5}{198.5} = 0.2217$$

For percentage conversion

$$\% \, pav_{20} = 22.17\%$$

Substuting f into equation 3.16b

$$k = \frac{1}{tc_0}(\frac{1}{1-f} - 1) \qquad (3.16b)$$

$k = \frac{1}{20x198.5}\left(\frac{1}{1-0.223} - 1\right) = 0.000252(0.287) = 7.22 \, x \, 10^{-5}$

Hence k_{20} = 7.22 x 10^{-5}g(mgNaOH)min^{-1}

At time t = 40mins, c = 115.30(mgNaOH/g)

$$f = \frac{198.5 - 115.3}{198.5} = 0.419$$

For percentage conversion, $\% \, pav_{40} = 41.9\%$

Substuting f into equation 3.16b

$k = \frac{1}{40x198.5}\left(\frac{1}{1-0.419} - 1\right) = (0.000126 \, x \, 0.7212) = 9.08 \text{ x } 10^{-5}$

Hence k_{40} = 9.08 x 10^{-5}g(mgNaOH)min^{-1}

At time t = 60mins, c = 83.6.00(mgNaOH/g)

$$f = \frac{198.5 - 83.6}{198.5} = 0.5788$$

For percentage conversion, $\% \, pav_{60} = 57.88\%$

Substuting f into equation 3.16b

$k = \frac{1}{60x198.5}\left(\frac{1}{1-0.579} - 1\right) = (8.396\ x\ 10^{-5}\ x\ 1.375) = 0.0001155,$

Hence k_{60} = 1.15 x 10^{-4}g(mgNaOH)min^{-1}

At t = 80mins, c = 59.7(mgNaOH/g)

$$f = \frac{198.5 - 59.7}{198.5} = 0.6992$$

For percentage conversion, $\%\ pav_{80} = 69.92\%$

Substuting f into equation 3.13b
$k = \frac{1}{80x198.5}\left(\frac{1}{1-0.699} - 1\right) = 6.297\ x\ 10^{-5}\ x\ 2.3222 = 0.0001462,$

Hence k_{40} = 1.46 x 10^{-4}g(mgNaOH)min^{-1}

At t = 100mins, c = 45.44(mgNaOH/g)

$$f = \frac{198.5 - 45.44}{198.5} = 0.7761$$

For percentage conversion, $\%\ pav_{100} = 77.61\%$

Substuting f into equation 3.16b
$k = \frac{1}{100x198.5}\left(\frac{1}{1-0.761} - 1\right) = 5.037\ x\ 10^{-5}\ x\ 3.464 = 0.000174,$

Hence k_{100} = 1.74 x 10^{-4}g(mgNaOH)min^{-1}

At t = 120mins, c = 40.8(mgNaOH/g)

$$f = \frac{198.5 - 40.8}{198.5} = 0.7945$$

For percentage conversion, $\%\ pav_{120} = 79.45\%$

Substuting f into equation 3.16b
$k = \frac{1}{120x198.5}\left(\frac{1}{1-0.795} - 1\right) = 4.198\ x\ 10^{-5}\ x\ 3.878 = 0.0001628,$

Hence k_{120} = 1.63 x 10^{-4}g(mgNaOH)min^{-1}

At t = 140mins, c = 30.9(mgNaOH/g)

$$f = \frac{198.5 - 30.9}{198.5} = 0.8443$$

For percentage conversion, $\% \, pav_{140} = 84.43\%$

Substuting f into equation 3.16b
$k = \frac{1}{140x198.5}\left(\frac{1}{1-0.8443} - 1\right) = 3.598 \, x \, 10^{-5} \, x \, 5.422 = 0.0001951,$

Hence k_{140} = 1.95 x 10^{-4}g(mgNaOH)min^{-1}

At t = 160mins, c = 40.8(mgNaOH/g)

$$f = \frac{198.5 - 24}{198.5} = 0.8791$$

For percentage conversion, $\% \, pav_{160} = 87.91\%$

Substuting f into equation 3.16b
$k = \frac{1}{160x198.5}\left(\frac{1}{1-0.8791} - 1\right) = 3.1489 \, x \, 10^{-5} \, x \, 7.271 = 0.0002289,$

Hence k_{160} = 2.29 x 10^{-4}g(mgNaOH)min^{-1}

At t = 180mins, c = 18.89(mgNaOH/g)

$$f = \frac{198.5 - 18.89}{198.5} = 0.9048$$

For percentage conversion, $\% \, pav_{180} = 90.48\%$

Substuting f into equation 3.16b
$k = \frac{1}{180x198.5}\left(\frac{1}{1-0.9048} - 1\right) = 2.7987 \, x \, 10^{-5} \, x \, 9.504 = 0.0002659,$

Hence k_{180} = 2.66 x 10^{-4}g(mgNaOH)min^{-1}

At t = 200mins, c = 16.33(mgNaOH/g)

$$f = \frac{198.5 - 16.33}{198.5} = 0.9177$$

For percentage conversion, $\% \, pav_{200} = 91.77\%$

Substuting f into equation 3.16b

$k = \frac{1}{200x198.5}\left(\frac{1}{1-0.9177} - 1\right) = 2.519 \; x \; 10^{-5} \; x \; 11.151 = 0.0002809,$

Hence $k_{200} = 2.81 \times 10^{-4}$g(mgNaOH)min^{-1}

At t = 220mins, c = 12.5(mgNaOH/g)

$$f = \frac{198.5 - 12.5}{198.5} = 0.9370$$

For percentage conversion, $\% \, pav_{220} = 93.70\%$

Substuting f into equation 3.16b

$k = \frac{1}{220x198.5}\left(\frac{1}{1-0.937} - 1\right) = 2.2899x \; 10^{-5} \; x \; 14.898 = 0.0003411,$

Hence $k_{220} = 3.41 \times 10^{-4}$g(mgNaOH)min^{-1}

At t = 240mins, c = 9.78(mgNaOH/g)

$$f = \frac{198.5 - 9.78}{198.5} = 0.9507$$

For percentage conversion, $\% \, pav_{240} = 95.07\%$

Substuting f into equation 3.16b

$k = \frac{1}{240x198.5}\left(\frac{1}{1-0.951} - 1\right) = 2.0991x \; 10^{-5} \; x \; 19.284 = 0.000405,$

Hence $k_{240} = 4.05 \times 10^{-4}$g(mgNaOH)min^{-1}

Table C2: Calculation for acid value against time for polycondensation reaction of JSOBAR

Time(mins)	Volume of NaOH(ml)	Mass of resin(g)	Acid value = $5.61\frac{v}{m}$(mgNAOH/g)
0	15.73	0.5	$5.61\frac{15.73}{0.5} = 176.5$
20	14.48	0.6	$5.61\frac{14.48}{0.6} = 135.4$
40	8.48	0.5	$5.61\frac{8.48}{0.5} =95.2$
60	8.10	0.6	$5.61\frac{8.1}{0.6} = 79.8$
80	4.94	0.5	$5.61\frac{4.94}{0.5} = 55.4$
100	4.29	0.6	$5.61\frac{4.29}{0.6} = 40.02$
120	2.50	0.45	$5.61\frac{2.5}{0.45} = 31.1$
140	2.60	0.6	$5.61\frac{2.6}{0.6} = 24.3$
160	2.1	0.39	$5.61\frac{2.1}{0.6} = 19.6$
180	1.50	0.5	$5.61\frac{1.72}{0.5} = 16.83$
200	1.20	0.49	$5.61\frac{1.2}{0.49} = 13.7$
220	1.15	0.6	$5.61\frac{1.15}{0.6} = 10.8$
240	0.53	0.5	$5.61\frac{0.53}{0.5} = 5.9$

From table C2,
At t = 0mins, co = 176.5(mgNaOH/g),

at t = 20mins, c = 135.4(mgNaOH/g),

$$f = \frac{176.5 - 135.4}{176.5} = 0.2329$$

For percentage conversion, $\% \, pav_{20} = 23.29\%$

Substuting f into equation 3.16b

$k = \frac{1}{20x176.5}\left(\frac{1}{1-0.2329} - 1\right) = 0.000283(0.3036) =$ 8.59 x 10^{-5}

Hence k_{20} = 8.59 x 10^{-5}g(mgNaOH)min^{-1}

at t = 40mins, c = 95.2(mgNaOH/g)

$$f = \frac{176.5 - 95.2}{176.5} = 0.4606$$

For percentage conversion, $\% \, pav_{40} = 46.06\%$

Substuting f into equation 3.16b
$k = \frac{1}{40x176.5}\left(\frac{1}{1-0.4606} - 1\right) = 0.0001416(0.8543) = 0.000121$

Hence k_{40} = 1.21 x 10^{-4}g(mgNaOH)min^{-1}

at t = 60mins, c = 79.8(mgNaOH/g)

$$f = \frac{176.5-79.8}{176.5} = 0.5479$$

For percentage conversion, $\% \, pav_{60} = 54.79\%$

Substuting f into equation 3.16b
$k = \frac{1}{60x176.5}\left(\frac{1}{1-0.5479} - 1\right) = 9.44\, x10^{-5}(1.21180) = 0.000114$

Hence k_{60} = 1.14 x 10^{-4}g(mgNaOH)min^{-1}

at t = 80mins, c = 55.4(mgNaOH/g)

$$f = \frac{176.5 - 55.4}{176.5} = 0.6861$$

For percentage conversion, $\% \, pav_{80} = 68.61\%$

Substuting f into equation 3.16b
$k = \frac{1}{80x176.5}\left(\frac{1}{1-0.6861} - 1\right) = 7.08\, x10^{-5}(2.1859) = 0.0001548$

Hence k_{80} = 1.55 x 10^{-4}g(mgNaOH)min^{-1}

at t = 100mins, c = 40.02(mgNaOH/g)

$$f = \frac{176.5 - 40.02}{176.5} = 0.7733$$

For percentage conversion, % $pav_{100} = 77.33\%$

Substuting f into equation 3.16b
$k = \frac{1}{100x176.5}\left(\frac{1}{1-0.7733} - 1\right) = 5.6657\,x10^{-5}(3.4111) = 0.0001933$

Hence k_{100} = 1.93 x 10^{-4}g(mgNaOH)min^{-1}

at t = 120mins, c = 31.1(mgNaOH/g)

$$f = \frac{176.5 - 31.1}{176.5} = 0.8238$$

For percentage conversion, % $pav_{120} = 82.38\%$

Substuting f into equation 3.16b
$k = \frac{1}{120x176.5}\left(\frac{1}{1-0.8238} - 1\right) = 4.7214\,x10^{-5}(4.67537) = 0.0002207$

Hence k_{120} = 2.21 x 10^{-4}g(mgNaOH)min^{-1}

at t = 140mins, c = 24.3(mgNaOH/g)

$$f = \frac{176.5 - 24.3}{176.5} = 0.8623$$

For percentage conversion, % $pav_{140} = 86.23\%$

Substuting f into equation 3.16b
$k = \frac{1}{140x176.5}\left(\frac{1}{1-0.8623} - 1\right) = 4.0469\,x10^{-5}(6.31145) = 0.0002554$

Hence k_{140} = 2.55 x 10^{-4}g(mgNaOH)min^{-1}

at t = 160mins, c = 19.6(mgNaOH/g)

$$f = \frac{176.5 - 19.6}{176.5} = 0.8889$$

For percentage conversion, $\% \, pav_{160} = 88.89\%$

Substuting f into equation 3.16b
$k = \frac{1}{160x176.5}\left(\frac{1}{1-0.8889} - 1\right) = 3.54107\, x10^{-5}(8.00576) = 0.0002835,$

Hence $k_{160} = 2.84 \times 10^{-4}$g(mgNaOH)min^{-1}

at t = 180mins, c = 16.5(mgNaOH/g)

$$f = \frac{176.5 - 16.5}{176.5} = 0.9065$$

For percentage conversion, $\% \, pav_{180} = 90.65\%$

Substuting f into equation 3.16b
$k = \frac{1}{180x176.5}\left(\frac{1}{1-0.9065} - 1\right) = 3.1476\, x10^{-5}(9.69747) = 0.0003052,$

Hence $k_{180} = 3.05 \times 10^{-4}$g(mgNaOH)min^{-1}

at t = 200mins, c = 13.7 (mgNaOH/g)

$$f = \frac{176.5 - 13.7}{176.5} = 0.9224$$

For percentage conversion, $\% \, pav_{200} = 92.24\%$

Substuting f into equation 3.16b
$k = \frac{1}{200x176.5}\left(\frac{1}{1-0.9224} - 1\right) = 2.83286\, x10^{-5}(11.8832) = 0.0003366,$

Hence $k_{200} = 3.37 \times 10^{-4}$g(mgNaOH)min^{-1}

at t = 220mins, c = 10.8(mgNaOH/g)

$$f = \frac{176.5 - 10.8}{176.5} = 0.9388$$

For percentage conversion, $\% \, pav_{220} = 93.88\%$

Substuting f into equation 3.16b

$k = \frac{1}{220x176.5}\left(\frac{1}{1-0.9388} - 1\right) = 2.57532\ x10^{-5}(15.3399) = 0.0003951,$

Hence k_{220} = 3.95 x 10^{-4}g(mgNaOH)$\min^{-1}$

at t = 240mins, c = 5.9(mgNaOH/g)

$$f = \frac{176.5 - 5.9}{176.5} = 0.9665$$

For percentage conversion, % $pav_{240} = 96.65\%$

Substuting f into equation 3.16b
$k = \frac{1}{240x176.5}\left(\frac{1}{1-0.9665} - 1\right) = 2.360717\ x10^{-5}(28.9222) = 0.0006827,$

Hence k_{240} = 6.83 x 10^{-4}g(mgNaOH)$\min^{-1}$

C2: Degree of polymerisation (Dp)

Dp for PKOBAR production

$$Dp = (1 - Pav)^{-1} \qquad D4$$

$$Dp_{20} = (1 - 0.2217)^{-1} = 1.2849$$

$$Dp_{40} = (1 - 0.4119)^{-1} = 1.7004$$

$$Dp_{60} = (1 - 0.5788)^{-1} = 2.3742$$

$$Dp_{80} = (1 - 0.6992)^{-1} = 3.3244$$

$$Dp_{100} = (1 - 0.7761)^{-1} = 4.4663$$

$$Dp_{120} = (1 - 0.7945)^{-1} = 4.8662$$

$$Dp_{140} = (1 - 0.8443)^{-1} = 6.4226$$

$$Dp_{160} = (1 - 0.8791)^{-1} = 8.2713$$

$$Dp_{180} = (1 - 0.9048)^{-1} = 10.5042$$

$$Dp_{200} = (1 - 0.9177)^{-1} = 12.1507$$

$$Dp_{220} = (1-0.937)^{-1} = 15.8730$$

$$Dp_{240} = (1-0.9507)^{-1} = 20.2840$$

Dp for JSOBAR production

$$Dp_{20} = (1-0.2329)^{-1} = 1.3036$$

$$Dp_{40} = (1-0.4606)^{-1} = 1.8539$$

$$Dp_{60} = (1-0.5479)^{-1} = 2.2119$$

$$Dp_{80} = (1-0.6861)^{-1} = 3.1857$$

$$Dp_{100} = (1-0.7733)^{-1} = 4.4111$$

$$Dp_{120} = (1-0.8238)^{-1} = 5.6754$$

$$Dp_{140} = (1-0.8623)^{-1} = 7.2621$$

$$Dp_{160} = (1-0.8889)^{-1} = 9.0009$$

$$Dp_{180} = (1-0.9065)^{-1} = 10.6952$$

$$Dp_{200} = (1-0.9224)^{-1} = 12.8866$$

$$Dp_{220} = (1-0.9388)^{-1} = 16.3399$$

$$Dp_{240} = (1-0.9665)^{-1} = 29.850$$

Appendix D: Calculations for thermodynamic study of the alkyd emulsions

For PKOBAR

$$y = 0.124x - 2.491 \tag{4.8}$$

$\frac{E}{R} = -0.124$, E = R x -0.124 = -1.03J/mol

$$In\eta_o = -2.491$$

$$\eta_o = e^{-2.491} = 0.2273$$

For JSOBAR

$$y = 0.125x - 2.609 \tag{4.9}$$

$\frac{E}{R} = -0.125$, E = R x -0.125 = -1.039J/mol

$$In\eta_o = -2.609$$

$$\eta_o = e^{-2.609} = 0.1093$$

Solving $\Delta S^{\#}$ for PKOBAR using equation 3.24

$$0.2273 = \frac{8.314\ x\ 532}{6.0221 \text{ X } 10^{23}\ x\ 6.62607 \text{ X } 10^{-34}} e^{\frac{\Delta S^{\#}}{8.314}} =$$

$$e^{\frac{8.314}{\Delta S^{\#}}} = \frac{8.314\ x\ 532}{6.0221 \text{ X } 10^{23}\ x\ 6.62607 \text{ X } 10^{-34}}\ x\ \frac{1}{0.2273} =$$

$$= \frac{4423.048}{3.9896\ x 10^{-10}}\ \frac{1}{0.2273} = 4.877\ x\ 10^{-7}$$

$$e^{\frac{8.314}{\Delta S^{\#}}} = 4.877\ x\ 10^{-7}$$

$$e^{8.314} e^{-\Delta S^{\#}} = 4.877\ x\ 10^{-7}$$

$$e^{-\Delta S^{\#}} = \frac{4.877\ x\ 10^{-7}}{22.599} = 2.158\ x\ 10^{-8}$$

$$-\Delta S^{\#} = e^{2.158\ x\ 10^{-7}} = 5.866x\ 10^{-7}$$

$\Delta S^{\#} = -5.866x\ 10^{-7}$J/molK

Activation enthalpy is solved using equation 3.25

$$\Delta H^{\#} = -1.03 - 8.314 \text{ x } 523 = -4349.25\text{KJ/mol}$$

Activation Gibbs free energy is solved using equation 3.26

$$\Delta G^{\#} = 4349.25 - 523\ x - 5.866x\ 10^{-7}$$

$$\Delta G^{\#} = 4349.25KJ/mol$$

For Jatropha based resin activation entropy, equation is applied 3.24

$$0.1093 = \frac{8.314\ x\ 523}{6.0221 \text{ X } 10^{23}\ x\ 6.62607 \text{ X } 10^{-34}} e^{\frac{\Delta S^{\#}}{8.314}} =$$

$$e^{\frac{8.314}{\Delta S^{\#}}} = \frac{8.314\ x\ 523}{6.0221 \text{ X } 10^{23}\ x\ 6.62607 \text{ X } 10^{-34}}\ x\ \frac{1}{0.1093} =$$

$$= \frac{4423.048}{3.9896\ x 10^{-10}}\ x\ \frac{1}{0.1093} = 1.01\ x\ 10^{-6}$$

$$e^{\frac{8.314}{\Delta S^{\#}}} = 1.01\ x\ 10^{-6}$$

$$e^{8.314}e^{-\Delta S^{\#}} = 1.01\ x\ 10^{-6}$$

$$e^{-\Delta S^{\#}} = \frac{1.01\ x\ 10^{-6}}{22.599} = 4.488\ x\ 10^{-8}$$

$$-\Delta S^{\#} = e^{4.488\ x\ 10^{-8}} = 1.22x\ 10^{-7}$$

$\Delta S^{\#} = -1.22x\ 10^{-7}$J/molK

Activation enthalpy is solved using equation 3.25

$$\Delta H^{\#} = -1.039 - 8.314 \text{ x } 523 = -4349.26\text{KJ/mol}$$

Activation Gibbs free energy is solved using equation 3.26

$$\Delta G^{\#} = 4349.26 - 523\ x - 1.22x\ 10^{-7}$$

$$\Delta G^{\#} = 4349.26KJ/mol$$

Appendix E: Calculations For PKOBAE And JSOBAE Characterisation

E1: Iodine value (IV) for *PKOBAE* and JSOBAE

M = Molarity of NaOH used for the titration, X = Volume of NaOH used for the titration

V = Volume of NaOH used for the blank titration, W = mass of oil sample used for the titration.

PKO*BAE*

$IV = \frac{12.69M(X-V)}{W}$; M = 0.1M; X = 55ml; V = 29ml; W = 1g

$\frac{12.69x0.1(55-29)}{1} = 32.994mgNaOH/$g

JSOBAE

$IV = \frac{12.69M(X-V)}{W}$; M = 0.1M; X = 55ml; V = 21ml; W = 1g

$\frac{12.69x0.1(55-21)}{1} = 43.146mgNaOH/g$

E2: Density and spg of PKOBAE, JSOBAE and the paint samples.

PKO*BAE* and paint samples

Density(g/m^3) = $\rho = \frac{m}{v}$; m is mass of the sample, v is volume of the sample.

W_B is weight of the empty beaker; W_{BR} is weight of the empty beaker

Vol of water = vol of resin= 50ml; Mass of water = 36.05g

PKOBAE

W_B = 103.68; W_{BR} = 147.18; m = 147.18 - 103.68 = 43.5

$\rho = \frac{43.5}{50} = 0.87gm^3$

$\text{spg} = \frac{mass\ of\ resin}{mass\ of\ equal\ volume\ of\ water} = \frac{43.5}{36.05}$ =1.207

PKOP

W_B = 8.1g; W_{BR} = 58.18g; m = 58.18 – 8.1 = 50.08

$\rho = \frac{52.08}{50} = 1.0016gm^3$

$\text{spg} = \frac{mass\ of\ resin}{mass\ of\ equal\ volume\ of\ water} = \frac{50.08}{36.05}$ =1.389.

JSOBAE and paint samples

JSOBAE

W_B = 95.97g; W_{BR} = 138.03g; m = 138.03 – 95.97 = 42.06g

$\rho = \frac{42.06}{50} = 0.8412gm^3$

$\text{spg} = \frac{mass\ of\ resin}{mass\ of\ equal\ volume\ of\ water} = \frac{42.06}{36.05}$ =1.167

JSOP

W_B = 8.1g; W_{BR} = 60.18g; m = 60.18 – 8.1 = 52.08g

$\rho = \frac{52.08}{50} = 1.0416gm^3$

$\text{spg} = \frac{mass\ of\ resin}{mass\ of\ equal\ volume\ of\ water} = \frac{52.08}{36.05}$ =1.4447.

JOS_2P

W_B = 8.1g; W_{BR} = 61.59g; m = 61.59 – 8.1 = 53.49g

$\rho = \frac{53.49}{50} = 1.0698gm^3$

$\text{spg} = \frac{mass\ of\ resin}{mass\ of\ equal\ volume\ of\ water} = \frac{53.49}{36.05}$ =1.4838

JOS_3P

W_B = 8.1g; W_{BR} = 62.01g; m = 62.01 – 8.1 = 53.91g

$\rho = \frac{53.91}{50} = 1.0782gm^3$

$\text{spg} = \frac{mass\ of\ resin}{mass\ of\ equal\ volume\ of\ water} = \frac{53.91}{36.05}$ =1.4954

PSNA

W_B = 8.1g; W_{BR} = 57.93g; m = 57.93 – 8.1 = 49.83g

$\rho = \frac{49.83}{50} = 0.9966gm^3$

$\text{spg} = \frac{mass\ of\ resin}{mass\ of\ equal\ volume\ of\ water} = \frac{49.83}{36.05}$ =1.3822.

E3: Calculation for drying curve PKOBAE and JSOBAE.

Moisture content calculation for PKOBAE and JSOBAE.

$$Moisture\ content(MC) = \frac{W_{i-}W_f}{W_f}\ x\ 100$$

W_f is final weight of the sample, W_i is initial weight of the sample

Moisture content calculation for PKOBAE

At 20 mins $(MC) = \frac{1.02-0.94}{0.94}\ x\ 100 = 8.51\%$

At 40 mins $(MC) = \frac{0.98-0.94}{0.94}\ x\ 100 = 4.25\ \%$

At 60 mins $(MC) = \frac{0.96-0.94}{0.94}\ x\ 100 = 2.13\%$

At 80 mins $(MC) = \frac{0.95-0.94}{0.94}\ x\ 100 = 1.06\%$

At 100 mins $(MC) = \frac{0.95-0.94}{0.94}\ x\ 100 = 1.06\%$

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At 120 mins $(MC) = \frac{0.94-0.94}{0.94}\ x\ 100 = 0\%$

Moisture content calculation for JSOBAE.

At 20 mins $(MC) = \frac{1.02-0.8}{0.8}\ x\ 100 = 27.5\%$

At 40 mins $(MC) = \frac{0.97-0.8}{0.8}\ x\ 100 = 21.25\%$

At 60 mins $(MC) = \frac{0.94-0.8}{0.8}\ x\ 100 = 14\%$

At 80 mins $(MC) = \frac{0.91-0.8}{0.8}\ x\ 100 = 13.75\%$

At 100 mins $(MC) = \frac{0.88-0.8}{0.8}\ x\ 100 = 10\%$

At 120 mins $(MC) = \frac{0.83-0.}{0.8}\ x\ 100 = 3.75\%$

Drying rate content calculation for PKOBAE and JSOBAE.

Drying rate (DR)= $\frac{M_{t-}\ M_{t+\Delta t}}{\Delta t}$

Where M_t is initial moisture content, $M_{t+\Delta t}$ is moisture content at time t, Δt is change in time

Drying rate content calculation for PKOBAE

DR = $\frac{8.51-4.25}{20} = 0.213$

DR = $\frac{4.25-2.13}{20} = 0.106$

DR = $\frac{2.13-1.06}{20} = 0.054$

DR = $\frac{1.06-1.06}{20} = 0$

DR = $\frac{1.06-0}{20} = 0.053$

Drying rate content calculation for JSOBAE

DR = $\frac{22-21.25}{20}$ =0.038

DR = $\frac{21.25-14}{20} = 0.363$

DR = $\frac{14-13.75}{20} = 0.613$

DR = $\frac{13.75-10}{20} = 0.187$

DR = $\frac{10-3.75}{20} = 0.313$

E4: Volatile organic content computation for PKOBAE and JSOBAE emulsion

PKOBAE and paint samples

WAl is weight of aluminium, VOC is volatile organic content

WAR is weight of aluminium and resin WAfter is weight of aluminium and resin after drying.

PKOBAE

WAl = 5.6g; WAR = 6.63g; WAfter = 6.61g

VOC = 6.63 - 6.61 = 0.02g %VOC = $\frac{0.02}{1} x100 = 2\%$

PKOP

WAl = 0.07; WAR = 0.40g; WAfter = 0.33g; VOC = 0.4 – 0.33 = 0.07

%VOC = $\frac{0.07}{1} x100 = 7\%$

JSOBAE and paint samples

JSOBAE

WAl = 0.07; WAR = 0.39; WAfter = 0.36; VOC = 0.39 – 0.36 = 0.03g

$$\%VOC = \frac{0.03}{1} x100 = 3\%$$

JSOP

WAl = 0.06; WAR = 0.39.; WAfter = 0.35; VOC = 0.39 – 0.35 = 0.04g

$$\%VOC = \frac{0.04}{1} x100 = 4\%$$

JOS$_2$P

WAl = 0.06; WAR =0.39.; WAfter = 0.32; VOC = 0.39- 0.32 = 0.07

$$\%VOC = \frac{0.09}{1} x100 = 7\%$$

JOS$_3$P

WAl = 0.06; WAR =0.39.; WAfter = 0.30; VOC = 0.39 – 0.30 = 0.09

$$\%VOC = \frac{0.09}{1} x100 = 9\%$$

PSNA

WAl = 0.08; WAR =0.41.; WAfter = 0.39; VOC = 0.41- 0.39 = 0.02

$$\%VOC = \frac{0.02}{1} x100 = 2\%$$

E5 Calculation of PVC for the paint samples

$$PVC\% = \frac{volume\ of\ pigment}{volume\ of\ pigment + volume\ of\ binder}\ x100\ = \frac{30}{80}\ x100 = 37.5\%$$

Volume of pigment = 30g; volume of binders = 50g;

Appendix F: Rheology calculations

F1: Shear stress calculation

$$\boldsymbol{Shear\ stress = (shear\ rate\ x\ viscosity)} \qquad \textbf{(F1)}$$

To calculate shear stress from shear rate, rpm is converted to sec^{-1}

1 rpm = 1.7; therefore; 60 rpm = 1.7 x 60 = 102 sec^{-1}.

06rpm = 06 x 1.7 = 10.2sec^{-1}, 12rpm = 12 x 1.7 = 20.4sec^{-1}, 30rpm = 30 x 1.7 = 51sec^{-1}

60rpm = 60 x 1.7 = 102 sec^{-1}

For JSOP

10.2 x 1061 = 10822.2 mPa

20.4 x 533.5 = 10883.4 mPa

51 x 214 = 10914 mPa

102 x 107.1 = 10924.2 mPa

For JOS$_2$P

10.2 x 1031 = 10516.2 mPa

20.4 x 518 = 10567.2 mPa

51 x 209.1= 10664.1 mPa

102 x 107.1= 10924.2 mPa

For JOS$_3$P

10.2 x 1052 = 10730.4 mPa

20.4 x 530 = 10812 mPa

51 x 212.7 = 10847.7 mPa

102 x 106.8 = 10893.6 mPa

For PKOP

10.2 x 1054 = 10750.8 mPa

20.4 x 530.5 = 10822.2 mPa

51 x 213 = 10863 mPa

102 x 106.8 = 10893.6 mPa

For PSNA

10.2 x 1055.9 = 10770.18 mPa

20.4 x 528.3 = 10777.32 mPa

51 x 211.8 = 10801.8 mPa

102 x 106.7 = 10883.5 mPa

For CP

10.2 x 5149 = 52519.8 mPa

20.4 x 2597 = 52978.8 mPa

51 x 1040 = 53040 mPa

102 x 522.5 = 53295 mPa

F2: Power law model

The equation is given by $\eta = k\gamma^{n-1}$ (2.6)

Equation 3.7 is converted to a linear equation by taking log of both sides

$$\log\eta = n - 1\log\gamma + logk \quad (3.14)$$

Slope = n-1; intercept = antilog

n = power law index; k = consistency

Value of k and n were calculated from similar equations for each of the samples

JSOP sample:

y = -0.338x + 3.370

n-1 = -0.338; n = 1- 0.338 = 0.662

k = antilog 3.370 = 2344.23

JOS_2P sample:

$$y = -0.343x + 3.386$$

n-1 = -0.343; n= 1-0.343 = 0.657

k = antilog 3.386 = 2432.20

JOS_3P sample:

$$y = -0.342x + 3.383$$

n-1 = -0.342; n = 1-0.342 = 0.658

k = antilog 3.383 = 2415.46

PKOP sample:

$$y = -0.346x + 3.395$$

n-1 = -0.346; n = 1 -0.346 = 0.654

k = antilog 3.395 = 2483.13

CP sample:

$$y = -0.336x + 4.049$$

n-1 = -0.336; n = 1-0.336 = 0.664

k = antilog 4.049 = 11194.37

PSNA sample:

$$y = -0.341x + 3.379$$

n-1 = -0.341; n = 1- 0.341 = 0.659

k = antilog 3.379 = 2393.3

APPENDIX G: Tables and graphs for the Results

Table G1: Drying performance of PKOBAE and JSOBAE

Time (mins)	Weight of PKOBAE(g)	Moist cont (%) for PKOBAE	PKOBAE drying rate (kg/minm^2)	Weight of JSOBAE(g)	Moist cont (%) for JSOBAE	JSOBAE drying rate (kg/minm^2)
0	1.02	-	-	1.02	-	-
20	0.98	8.51	0.21	0.97	27.5	0.04
40	0.96	4.25	0.11	0.94	21.25	0.36
60	0.95	2.13	0.05	0.91	14.00	0.61
80	0.95	1.06	0.00	0.88	13.75	0.19
100	0.94	1.06	0.05	0.83	10.00	0.31
120	0.94	0.00	-	0.80	3.75	-

Table G2: Variation of Viscosity with Shear Rate

γ(rpm)	JSOP η (mPa.s)	JOS$_2$P η(mPa.s)	JOS$_3$P η(mPa.s)	PKOP η(mPa.s)	PSNA η (mPa.s)	CP η (mPa.s)
06	1061	1031	1052	1054	1055.9	5149
12	533.5	518	530	530.5	528.3	2597
30	214	209.1	212.7	213	211.8	1040
60	107.1	107.1	106.8	106.8	106.7	522.5

γ(rpm) is share rate and η is viscosity (mPa.s)

Table G3: Variation of Shear Rate γ(rpm) with Shear Stress τ (mPa)

	JSOP	JOS_2P	JOS_3P	PKOP	PSNA	CP
γ(rpm)	τ (mPa)	τ (mPa)	τ (mPa)	τ (mPa)	τ (mPa)	τ (mPa)
06	10822.2	10516.2	10730.4	10750.8	10770.18	52519.8
12	10883.4	10567.2	10812	10822.2	10777.32	52978.8
30	10914	10664.1	10847.7	10822.2	10801.8	53040
60	10924.2	10924.2	10893.6	10863	10883.5	53295

Table G 4: Log Of Viscosity (Logη) and Log Of Shear Rate (Log γ)

Log γ	JSOP Logη	JOS_2P Logη	JOS_3P Logη	PKOP Logη	PSNA Logη	CP Logη
0.7782	3.0257	3.0391	3.0358	3.0465	3.0322	3.7058
1.07918	2.7197	2.7254	2.7247	2.7247	2.7229	3.4055
1.47712	2.3181	2.3204	2.3174	2.3159	2.3168	3.0056
1.77815	2.0298	2.0298	2.0286	2.0269	2.0282	2.7180

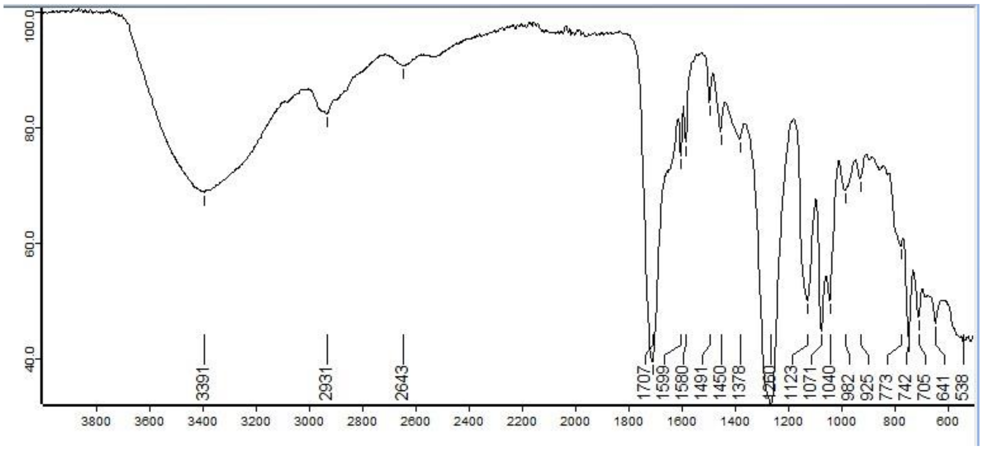

Figure G1: FTIR Spectra for PKOBAE *(Eleasis guineensis dura)*

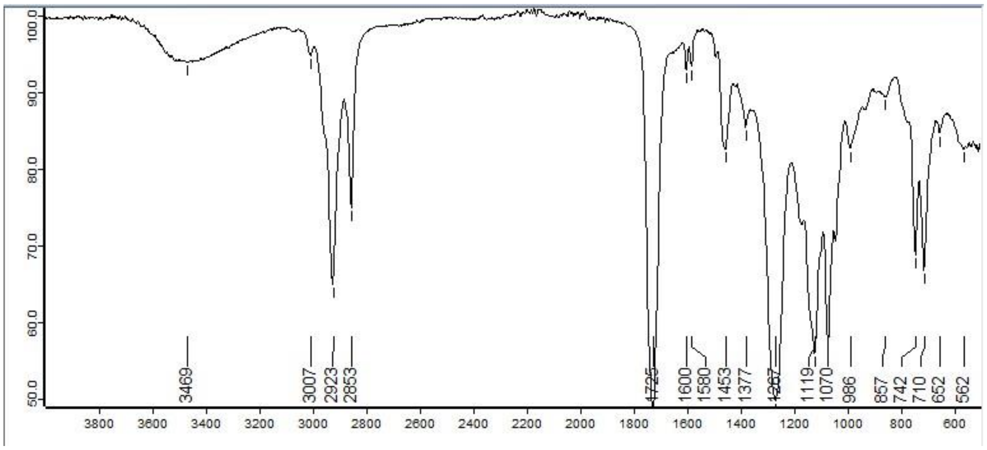

Figure G2: FTIR Spectra for JSOBAE *(Jatropha curcas)*