

Comparative Analysis on the Physico-Chemical and Mechanical Properties of Agricultural Seeds Oil Modified Alkyd Resin

Abstract- Alkyd resins are important raw materials utilized in the surface coatings and paints industry. However, in Nigeria today, alkyd resins are still largely imported partly due to the non-availability of some of the conventional seed oils that are used for alkyd production. The choice of oil is one of the important considerations in alkyd resin preparation. This paper considers the prospects of utilizing non-conventional seed oils of oilbean seed oil from our locally-available tropical plants of oilbean, compares it with breadfruit and the most widely utilized soybean seed oil for alkyd resin production. The physico-chemical and mechanical properties of the alkyd resins synthesized by alcoholysis process gave better results when compared with conventional alkyd resin. The use of oilbean and breadfruit seed oils for alkyd resin synthesis has established new process that utilizes locally available raw materials for alkyd production both for industrial and architectural coatings and thus enhances the Nigerian economy.

Key words: *Alkyd resin, alcoholysis, oilbean seed oil, agricultural oils, conventional oil, phthalic anhydride.*

1. Introduction

The development in organic chemistry, due to better and improved analytical equipment, has made it possible to perform comprehensive examination of chemical composition, the structure and the property of natural products like vegetable oils. Modification and application of improved consumer-based products has continuously evolved (Osagie and Oriji, 2015). This gradual increase in various applications of fats and oils has triggered the expansion of planted areas of these crops. Recently, cultivation by means of genetic engineering to develop high oleic acid soy bean and rapeseed oil as well as new oil seeds, is continuously being investigated and developed to meet growing demands (Scott, 2007; Warwel et al, 2001). In Nigeria, vegetable oil dependent industries rely mostly on imported oils like linseed and soybean oil which are very expensive. The locally available oils like oilbean seed oil, breadfruit seed oil (Uche et al, 2016), palm oil, palm kernel oil, groundnut oil and coconut oil are in short supply. (Akintayo et al, 2002).

The use of petroleum based monomers in manufacturing of petroleum based products is expected to decline in coming years because of the continuous rise in petroleum products and the high rate of oil depletion of known oil reserves (Chukwujike et al, 2016). This coupled with strict governmental legislation all over the world on environmental protection against degradation, has inspired the investigation of renewable natural resources as a viable alternative. (Aigbodion et al. 2003; Chukwujike et al, 2016). Because of this, plants and animals oils have long been identified as possible substitute for petrochemical derivatives in the production of polymers such as resins, paints and vanishes (Chukwujike et al, 2016).

Recently, production has been intensified due to the possibility of utilization of these agricultural materials as a biodiesel. Most of the vegetable oils can be utilized in the alkyd resin formulation. Among them, the most explored is the soybean oil in the alkyd resins formulation. The choice of seed oils used for production of alkyd resins is influenced by

specific desirable properties of the alkyd resin to be produced. The reason being that performance of the alkyd resin produced largely depends on the choice of oil used for its production. The main desirable properties include; the speed of drying, gloss retention, colour retention, abrasion resistance and hardness (Uche et al, 2016). Alkyd resins have remained the most widely used group of binders in surface coatings because of their unique properties such as gloss retention, colour, film flexibility, durability and compatibility with other resin systems (Kynege et al, 2012).

The level of unsaturation of the oil is an important consideration in the production of drying alkyds. The higher the presence of unsaturation, the higher will be the drying performance of the corresponding alkyds prepared from the oil. Alkyd resins are not only the major important binders but also they are the largest volume based coatings and paints utilized especially for decoration (Khalid et al, 2014) both for interior and exterior applications (Chukwujike et al, 2016). The type or class of alkyd resin to be produced is another main consideration for the choice of modifying oil. (Odetoye et al, 2013).

In a bid to enhance sustainable production of alkyd resin in Nigeria, there is a need to increase the production of locally available conventional oils such as oilbean oil seeds which serves the dual purpose of food and non-food uses, and supplement the existing supplies by establishing other lesser-known non-conventional oilseeds that possess similar properties, as raw materials. This will go a long way to encourage the limited indigenous alkyd resin industries.

The utilization of oil depends mainly on its characteristics which are determined by its composition (Usman et al, 2009). The conventional oil used for alkyd resins in the industry today is based on the fatty acid composition of the semi-drying and drying oils. The oils include linseed oil, soya oil, sunflower oil and dehydrated castor oil. Linseed oil is predominantly grown overseas in temperate climates while the utilization of soya oil as an industrial raw material actually competes with food source.

Breadfruit seed oil modified alkyd resin was reported by Uche et al (2016). The result showed low acid value and iodine value of 107.30 mg I/g an indicative of semi-drying oil. Cassava seeds have been reported (Popoola, 2009) to be a potential raw material (semi-drying oil) for alkyd resin preparation. The dominant fatty acid content being linoleic fatty acids with its content up to 47%. The iodine value of 141 g I₂ /100 g (Popoola, 2009) suggests cassava seed oil as good oil for alkyd resin preparation. The oil was reported to have good oxidative stability as the peroxide value was not more than 6.3mequiv/kg.

Furthermore, sandbax seed oil has been reported to have a good potential as industrial raw material for solvent based paints (Okolie et al, 2012) and surface coatings (Obidiegwu et al, 2016). The iodine value of 177g I₂ /100 g was reflective of the relatively high level of unsaturation (66.5 %) of the fatty acid found in the oil. The most abundant unsaturated fatty acid present in the oil is oleic acid (63.2%). The percentage oil yield of 53.6% (Okolie et al, 2012) obtained for Hura crepitans is also encouraging towards its utilization as industrial oil. Obidiegwu et al, (2016) also reported iodine value of 20.928 mmg Iodine/g for sandbax seed oil which suggests a non-drying oil.

2. Materials and Methods

2.1 Materials

The vegetable seed oils, oilbean seed oil (*Pentaclethra Macrophylla* Sedinst) used in this work was sourced locally from Ideato South Local Government Area, within the South-Eastern region of Nigeria. Soyabean Oil (*Glycine Soja*) was obtained from Taraku Mills Limited, Benue State, Nigeria. The Fuller's Earth was a product of Fulmont Ltd, England

which consists mainly of alumina silica ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) impregnated with iron, magnesium and calcium. Metallic Driers used were obtained from Ebony Paints (Nig.) Ltd, within the south east. The following analytical grade solvents and chemicals Xylene (MERCK), Benzene (MERCK), N-hexane (Qualikems, India), Conc. H_2SO_4 (Qualikems, India), Na_2CO_3 , NH_3 (Qualikems), NaOH , Glacial acetic acid (Qualikems), $\text{Na}_2\text{S}_2\text{O}_3$, $\text{K}_2\text{Cr}_2\text{O}_7$, Paraffin oil, Methanol (Qualikems), Phenolphthalein, Iodine trichloride, Iodine crystal, Starch (Qualikems, India), Toluene (MERCK), Glycerol (BDH) were used without further purification. The oilbean seed oil was compared with breadfruit (*Treculia Africana*) and soybean seed oils (Uche et al, 2016)

2.2 Extraction of the Vegetable Oils

The method used by Uche et al (2016) was employed. In this method, the vegetable oils were extracted from their oil bearing seeds by soxhlet extraction using n-hexane. The oil-bearing seeds were shelled, and sun dried. The dried seeds were ground to fine meal using a grinder. Weighed quantities of ground vegetable seeds were placed in a 500 cm^3 round-bottomed flask. 150 cm^3 of n-hexane was poured into the flask which was later placed on a heating mantle. The soxhlet apparatus was set-up for the extraction of oil from the ground seeds. The extracted oil was weighed, and the oil yield was noted.

2.3 Alkali Refining of Oils

The extracted oils were alkali refined to reduce the percentage of free fatty acids they contain. The method of Cocks and Rede (1966) was adopted for the alkali refining of the oils. The amount of NaOH used in the refining process was in 10% excess of that actually required to neutralize the Free Fatty acids in the oils. This was calculated using the Cocks and Rede formula.

$$\text{1M NaOH required} + 10\% \text{ excess} = \frac{\text{Weight of oil taken} \times \% \text{ FFA} \times 1.1 \times 1000 \text{ cm}^3}{100 \times \text{Mw} \times 1 (\text{molarity of NaOH})} \quad (1)$$

Where Mw = weight average molecular weight of oil, %FFA = Percentage of free fatty acid present in the oil.

Purification of the Alkali Refined Oils: The oil obtained from the alkali refining process was impure as it contains some soap residues and un-reacted NaOH . The oil was purified by dissolving it in a reasonable amount of petroleum benzene (b.pt $60-80^\circ\text{C}$) and filtered using Buckner funnel to remove the soap and other impurities. The oil solution was then subjected to vacuum distillation at a temperature of 50°C in a heating mantle to remove the solvent from the oil. The recovered oil was washed severally with boiling water in a separating funnel under careful shaking to avoid emulsification of the oil. The washing was stopped when the aqueous extract was clear and neutral to litmus. The washed oil was subjected to vacuum distillation at 70°C to remove any traces of water in the oil.

2.4 Bleaching of Oils

In this method, 400 g each of the alkali refined oil was mixed with 60 g of Fuller's earth (15 wt % based on oil) in a three-necked round bottomed flask. The flask with its content was immersed in an oil bath maintained at a constant temperature of 80°C , and heated under vacuum. The mixture was stirred continuously with an electrical stirrer, and the bleaching lasted for 40 minutes. At the end of the bleaching, the contents of the flasks were filtered hot under vacuum using a Buckner funnel. Filtration was repeated with a Whatman Grade 1 filter paper to obtain optically clear oil.

2.5 Characterization of Oils.

2.5.1 Acid Value: This was determined using ASTM method (ASTM D 1639 -61, 1966). In order to aid acid value determination, alcoholic Potassium Hydroxide Solution (0.1M) was

first prepared. In this method, 5.61 g of KOH was dissolved in 1 litre of Methanol. The solution was then standardized using a standard 0.1M HCl to a phenolphthalein endpoint. Neutral Solvent was prepared by mixing equal volume of 2-propanol and toluene in a 1000 cm³ conical flask. The mixture was titrated with 0.1M KOH solution using phenolphthalein as indicator until a pink colour which persisted for about one minute was obtained. Phenolphthalein indicator was prepared by dissolving 1 g of phenolphthalein in 100 cm³ of methanol.

Acid Value Determination: In this method, 0.5 g of the oil sample was dissolved in 50 cm³ of neutral solvent in a conical flask. 1-3 drops of phenolphthalein indicator was added and the mixture was then titrated with 0.1 M KOH until a pink colour which persisted for about 1 minute was obtained.

This was calculated using the formula;

$$\text{Acid Value} = \frac{MV \times 56.1}{W} \quad (2)$$

Where: M = Molarity of KOH solution, V = Volume of KOH solution used in titration (cm³), 56.1 = Molecular weight of KOH, W = Weight of oil used in grams.

2.5.2 Iodine Value: The iodine value was determined using ASTM method (ASTM D1959 – 69). The solutions used in iodine value determination were prepared as follows: Potassium Iodide Solution was prepared by dissolving 150 g of potassium iodide (KI) in water and diluting to one liter. Sodium Thiosulphate Solution (0.1M) was also prepared. In this method, 24.8 g of sodium thiosulphate (Na₂S₂O₃·5H₂O) was dissolved in water, and diluted to one liter. Starch indicator solution was prepared by homogenizing paste of 5 g of soluble starch in cold water and adding 500 cm³ of boiling water. The solution was stirred rapidly, and cooled. WIJ's Solution (0.2M KI solution) was also prepared. In this method, 8.67 g of iodine was dissolved in 100 g of methanol. A solution of 7.96 g of iodine trichloride (ICl₃) dissolved in a quantity of glacial acetic acid was also prepared. The two solutions were warmed over a water bath ensuring that the solutions did not mix. The solutions were then mixed in a one litre flask and made up to mark with glacial acetic acid.

Standardization of Sodium Thiosulphate Solution: The method employed by Uche et al 2016 was applied. In this method, 25 cm³ of standard potassium dichromate solution (containing 4.904 g K₂Cr₂O₇/litre of diluted water) was pipette into a conical flask and diluted with 50 cm³ distilled water. 10% KI was added followed by 10 cm³ concentrated hydrochloric acid (HCl sp.gr. 1.19), and the solution was shaken to mix. The liberated iodine was titrated with Na₂S₂O₃ solution while shaking constantly until the yellow colour had almost disappeared. 1 – 2 cm³ of starch indicator solution was added, and titration continued until the blue colour had disappeared. The molarity of the Na₂S₂O₃ was calculated as follows;

$$(\text{Vol. of Na}_2\text{S}_2\text{O}_3) \times (\text{Molarity of Na}_2\text{S}_2\text{O}_3) = (\text{Vol. of K}_2\text{Cr}_2\text{O}_7) \times (\text{Molarity of K}_2\text{Cr}_2\text{O}_7) \quad (3)$$

Iodine value determination: In this method, 0.15 g of the oil was introduced into a clean conical flask. 20 cm³ of carbon tetrachloride was added into the flask containing the oil and shaken thoroughly to dissolve the oil. Similar amounts of CCl₄ were added into two additional flasks which served as blanks. 25 cm³ of Wij's solution was pipette into the flask containing the oil sample, and also into the blanks. The flasks were stoppered and the flask containing the oil sample was swirled to ensure an intimate mixing. The flasks were stored in a dark place for one hour at room temperature. At the expiration of one hour, the flasks were removed from storage and 20 cm³ of KI solution and 100 cm³ of distilled water was added into each flask. The contents of each flask were titrated with Na₂S₂O₃ solution with constant and vigorous shaking until the yellow colour had almost disappeared. 1-2 cm³ of starch indicator solution was added, and the titration was continued until the disappearance of blue colour. Iodine value was calculated using the formula;

$$\text{Iodine Value} = \frac{12.69N (V_2 - V_1)}{W} \quad (4)$$

Where M = Molarity of $\text{Na}_2\text{S}_2\text{O}_3$ solution, V_2 = Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used in blank titration (cm^3), V_1 = Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used in sample titration (cm^3), W = Weight of sample (oil) used in grams.

2.5.3 Saponification Value: This was determined using the AOCS (American Oil Chemist Society) method (AOCS Cd 3-25, 1966). In this method, 2g of the oil sample was introduced into a conical flask. 25cm^3 of 0.5 M alcoholic potassium hydroxide was added. A blank was also prepared, by putting 25 cm^3 of the alcoholic potassium hydroxide in another conical flask. Condensers were fitted to both flasks and the contents were boiled for one hour in a water bath, while swirling the flasks from time to time. The flasks were then allowed to cool a little and the condensers were washed down with a little distilled water. The excess potassium hydroxide was titrated with 0.5M hydrochloric acid using phenolphthalein indicator.

The saponification value was calculated as follows;

$$\text{Saponification Value} = \frac{28.05 \times (\text{blank titration} - \text{sample titration})}{\text{Weight of Oil}} \quad (5)$$

Where 28.05 = the number of milligrams of KOH in 1 cm^3 of 0.5M KOH

2.6 Synthesis of Alkyd Resins

The formulations used in the synthesis of long and medium oil length of oilbean seed oil modified alkyd resins are shown in Table 1.

Table 1: Formulations for the Synthesis of Alkyd Resin

S/N	Ingredients(g)	Long Oil Length Alkyd Resin	Medium Oil Length Alkyd Resin
1	Vegetable Oil	153.6	103.4
2	Litharge (PbO)	3.84	2.54
3	Glycerol	30.7	30.7
4	Phthalic Anhydride	74	74

In this method, 750 cm^3 three necked round bottomed resin kettle heated with a heating mantle was equipped with a variable speed stirrer, a dean and stark water collector, reflux condenser, nitrogen inlet tube, a thermometer and a sampling device. The kettle which had been flushed with nitrogen was charged 153.6g of the refined oil for the synthesis of the long oil modified alkyd resins or 103.4 g of the refined oil for the synthesis of the medium oil alkyd resins. The oil was heated to the reaction temperature of $245 \pm 2^\circ$, 3.84 g of the catalyst, litharge (PbO), was added immediately for the synthesis of the long oil alkyds or 2.59 g (PbO) for the synthesis of medium oil alkyds, followed by 30.7 g of glycerol which was added slowly from a dropping funnel over a period of 2 minutes with vigorous agitation. Samples were withdrawn at intervals for methanol tolerance test. The alcoholysis stage was completed when 1 volume of the alcoholysis mixture was soluble in 2 volumes of anhydrous methanol.

At the end of the alcoholysis stage, 74 g phthalic anhydride was added all at once, and the nitrogen flow was increased. The mixture was heated and stirred at the reaction temperature. The progress of the reaction was followed by a frequent check on the acid number of the reaction mixture. The reaction was stopped on attainment of acid number of less than 10, and the contents allowed cooling by dropping the reaction kettle in a bath of cold paraffin oil.

2.7 Performance Evaluation of Synthesized Alkyd Resins

Drying Studies:

I. Preparation of Resin – Drier Mixture; 119 g of the synthesized long oil alkyd resin and 84 g of the synthesized medium oil length alkyd resin were accurately weighed out into a 500 cm³ beaker and dissolved in 70 g and 139 g by weight of xylene respectively. This gives a resin solution of 64% and 38% solid respectively. 1.75 g lead naphthanate and 0.9 g cobalt naphthanate driers for long oil length alkyd resin and 1.2 g lead naphthanate and 0.6 g cobalt naphthanate driers for medium oil length alkyd resin were added. The resin – drier mixture was mixed thoroughly using a mechanical stirrer. The amount of driers added represent 0.50 wt. % Pb and 0.05 wt. % Co which are the amounts of these metals normally used in the surface coatings industry.

II. Preparation of Coating Surfaces; Glass was used as the coating surface for the casting of resin – drier mixtures. Four glass plates were cut to dimensions of approximately 16 cm x 9 cm. and were taped to various thicknesses for the casting of the resin drier-mixtures depending on the film thickness of resin-drier mixture required. Tape thicknesses ranged from 0.10 mm to 1.0 mm, obtained by applying one or more layers of tape of thickness, 0.10 mm. The resin drier wet film thickness was assumed the same as the thickness of tape layer(s) used.

Property Determination: The alkyd resins synthesized were evaluated for their drying times, resistance to chemicals using the following codes, 0: no change, 1: very slight change, 2: light effect, 3: definite and 4: bad effect (Chukwujike et al, 2016), adherence to surface, mildew formation using international standard methods.

3. Results and Discussion

3.1 Characterization of the oils

Oil Yields: The oil yields of oilbean and breadfruit seed are presented in Table 2.

Table 2: Oil Yields of Oilbean and Breadfruit Seeds

Vegetable Seed	Yield (%)	
	Experimental	Literature
Oilbean Seed	42.61	53.66 (Akindahunsi, 2004) 7.50 (Bwai et al, 2013) 32.0 (Amadi et al, 2012) 47.90 (Ikhuoria et al, 2008) 12.23 (Eze, 2012) 46.30 (Ogueke et al, 2010)
Breadfruit	25.73 (Uche et al, 2016)	18.95 (Berezi et al, 2012) 9.71 (Eze, 2012) 20.83 (Ajiwe et al, 1995) 25.73 (Uche et al, 2016)

Differences in oil yields arise because these oil seeds are natural products which are subject to variations in properties as a result of factors such as temperature, soil variety, seed variety and maturity, post-harvest storage, among the other factors.

Acid Value: Acid value is a property that is very useful in assessing the quality of oilseeds at the time of extraction. Therefore, good storage of oilseeds and sun-drying prior to extraction of oil is very important to prevent the oilseeds from deterioration, and minimize the production of free fatty acids in oilseeds.

Table 3: Acid Values of Oils

Oil	Acid Value (mg KOH/g Oil)		Literature
	Crude	Refined	
Oilbean	2.82	0.40	3.62 (Amadi et al, 2012) 7.01 (Odoemelam, 2005) 3.25 (Ikhuoria et al, 2008)
Breadfruit	2.26 (Uche et al, 2016)	0.32(Uche et al, 2016)	7.7 (Bwai et al, 2013)
Soyabean	-	0.16	0.34 (Kyenge et al, 2012) 2.81 (Eze, 2012)

Some literature values of the acid values of the oils are shown in table 3. The observed variations in acid values could have arisen from a number of factors, notably, seed variety and post-harvest storage, age of the oil seeds prior to oil extraction.

Iodine Value: The iodine values of the oils shown in table 4 shows that both oilbean, breadfruit and soybean seed oils are in the category of semi-drying oils having fallen in the range of 90 -130 mg I/g as reported in the literature for semi-drying oils.

Table 4: Iodine Value of Oils

Oil	Refined	Literature
Oilbean	110.10	121.80 (Amadi et al, 2012) 86.30 (Eze, 2012) 57.60 (Ikhuoria et al, 2008)
Breadfruit	107.30 (Uche et al, 2016)	164.97 (Eze, 2012) 52.64 (Bwai et al, 2013) 44.80 (Berezi et al, 2012)
Soyabean	128.40	123.42 (Eze, 2012)

The literature values cited above for the oils differed considerably from the values obtained in this study, and this can be attributed to the fact that these oils are natural products which are subject to variations in composition brought about by a number of factors such as botanical variety, climatic conditions, soil composition, rainfall, temperature and other environmental factors. The table shows that no linolenic acid is present in breadfruit seed oil, while the amount present in oilbean seed oil is low. Linolenic acid is the cause of yellowing associated with alkyds prepared from highly unsaturated (oxidizing) oils. It is expected that alkyds prepared from these oils will be colour retentive because of the absence of linolenic acid in breadfruit seed oil, or low linonelic acid in oilbean seed oil.

Saponification Value: Saponification value is used to assess the mean molecular weight (M_w) of the fatty acids present in an oil. Saponification values above 200 indicate the presence of fatty acids of low or fairly, low molecular weight, and values below 190 indicate the presence of high molecular weight fatty acids (Olaniyi et al, 2014; Uche et al, 2016). The saponification values of the oils showed that soyabean oil contained glyceridres with low molecular weight than oilbean and that of breadfruit seed oils as reported by Uche et al (2016). The later observation was consistent with their iodine values. Ikhuoria et al (2008) had reported a saponification value of 171.11 for oilbean seed oil which compared favourably with the value determined for the oil in the study.

Table 5: Saponification Values of the Vegetable Oils

Oil	Refined	Literature
Oilbean Seed	174.0	213.10 (Amadi et al, 2012) 171.11 (Ikhuria et al, 2008) 189.85 (Odoemelam, 2005) 221.59 (Eze, 2012)
Breadfruit Seed	161.30 (Uche, at al, 2016)	246.09 (Bwai et al, 2013) 210.50 (Berezi et al, 2012)
Soyabean Seed	191.50	189-195 (Odoemelam, 2005) 195.63 (Eze, 2012)

3.2 Characterization of Alkyd Resins

Acid Value: The acid value of an alkyd resin is important in assessing the stability of the synthesized resin. The low acid values (<10 mgKOH/g resin) obtained for the resins synthesized in this study is an indication that the resins were synthesized near to completion of the reaction, and therefore very stable.

Table 6: Acid Values of Alkyd Resins

Alkyd Resin	Long Oil Length Alkyd Resin	Medium Oil Length Alkyd Resin
	Acid Value (mg KOH/g resin)	Acid Value (mg KOH/g resin)
OBSOA	3.17	2.50
BFSOA	4.50 (Uche et al, 2016)	5.21 Uche et al, 2016)
SBSOA	1.60	1.01

Abbreviations: OBSOA = Oilbean Seed Oil Alkyd; BFSOA = Breadfruit Seed Oil Alkyd; SBSOA = Soyabean Seed Oil Alkyd

3.3 Performance Evaluation of Synthesized Alkyd Resins

Drying Properties of Synthesized Alkyd Resins: The drying properties of the synthesized long and medium oil length alkyd resin samples are given in Tables 7 and 8. Film thicknesses of resins investigated (in mm) are: 0.10, 0.40, 0.70, and 1.0.

Table 7: Drying Properties of Long Oil Length Alkyd Resins

S/N	Alkyd Resin	Film Thickness (mm)			
		0.10	0.40	0.70	1.0
1	OBSOA	S	S	NS	NS
2	BFSOA (Uche et al, 2016)	S	NS	NS	NS
3	SBSOA	S	S	NS	NS

Table 8: Drying Properties of Medium Oil Length Alkyd Resins

S/N	Alkyd Resin	Film Thickness (mm)			
		0.10	0.40	0.70	1.0
1.	OBSOA	S	NS	NS	NS
2.	BFSOA (Uche et al, 2016)	S	NS	NS	NS
3.	SBSOA	S	NS	NS	NS

Note: S= Satisfactory; NS = Not Satisfactory

The alkyd resins with film thickness of 0.10 dried satisfactorily and compares favourably with that reported by Uche at al, (2016). For the long oil length alkyd resins, oilbean seed and

soyabean seed oil modified alkyd resins dried satisfactorily at film thickness of 0.40 mm while the reverse was the case with those reported in the literature. Whereas for medium oil length alkyd resins, only soyabean oil alkyd dried satisfactorily at film thickness of 0.40, 0.70 and 1.0 mm were comparably with the literature values.

The drying studies show the superiority of soyabean seed oil/oilbean seed. Both oilbean seed oil and soyabean seed oil are semi-drying oils. This result is in agreement with the breadfruit seed oils reported in the literature. The order in the degree of their unsaturation as determined by iodine number is soyabean seed oil > oilbean seed oil. The present study shows that the oil length of the synthesized alkyd resins did not exhibit marked effect on the drying of alkyd resin films.

The thickness of the alkyd resin film was observed to exact a marked effect on the drying of the alkyd resin samples, namely decrease in drying properties of the resins with increase in alkyd resin film thickness. For an alkyd resin film to dry effectively, the oxygen induced crosslinking (drying) reaction should occur throughout the film from the surface to the interior. Since polymerization and drying are related to oxygen contents, the concentration of which is greatest at the surface and least in the interior, then, the thicker the alkyd resin film, the smaller the oxygen concentration in the inner portion of the film which will lead to an overall reduction in the degree of drying.

The Media Resistance Tests on Alkyd Resin Films: The media resistance of dry alkyd resins to distilled water, 2 % NH_3 , 2 % H_2SO_4 , and 2 % Na_2CO_3 are shown in Tables 9 and 10. From Tables 9 and 10, it is evident that the water and acid resistance of the synthesized alkyd resins were generally good. All the synthesized alkyd resins failed the alkali resistance test. This confirms the fact that alkyds generally have low alkali resistance. The poor alkali resistance of the alkyds may be explained on the basis that they contain ester groups, which are known to be susceptible to hydrolysis by alkali (Momodu, 2011, Uche et al, 2016).

Table 9: Media Resistance of Long oil Length Alkyd Resins

Alkyd Type	Resistance to:			
	Distilled wate	2% H_2SO_4	2% H_2SO_4	2% Na_2CO_3
OBSOA	2	1	3	4
BFSOA	2	0	3	4 (Uche et al, 2916)
SBSOA	1	0	3	4

Table 10: Media Resistance of Medium oil Length Alkyd Resins

Alkyd Type	Resistance to:			
	Distilled wate	2% H_2SO_4	2% H_2SO_4	2% Na_2CO_3
OBSOA	1	0	3	4
BFSOA	1	0	4	4 (Uche et al, 2916)
SBSOA	1	0	3	4

The influence of alkyd oil length was not observed to have any effect on alkyd resistance to the media investigated.

Table 11 Mildew Formation and Adhesion Properties of Synthesized Alkyd Resins

Alkyd Type	Long Oil Length Alkyd Resin		Medium Oil Length Alkyd Resin	
	Adhesion Test (%)	Mildew formation	Adhesion Test (%)	Mildew formation

OBSOA	24	Nil	26	Nil
BFSOA	27	Nil	31	Nil
SBSOA	32	Nil	32	Nil (Uche et al, 2016)

Adhesion to Surfaces: The dried alkyd films exhibited good adhesion properties (Table 11), and is an indication that paints formulated with these resins should be able to protect substrates from corrosion, and thus, functions as anticorrosion paints. The order of adhesion of the alkyd films to the substrate is generally, soyabean oil alkyd > oilbean seed oil alkyd both for the long and medium oil length alkyds. The observed order corresponds to the order in the degree of unsaturation of the oils.

The present study shows that the adhesion properties of soyabean oil alkyd are slightly greater than those of oilbean seed both for the long and medium oil alkyds. The oil length of the synthesized alkyds exerted very slight effect on the adhesion properties of soyabean, and oilbean seed oil modified alkyd resins. Generally, the alkyds exhibited good adhesion properties. According to Nigerian Industrial Standards (NIS 268: 1989), a good oil paint should exhibit 50% maximum removal of the dry paint film.

The good adhesion to the substrate of the resins obtained in this study is attributed to the inherent chemical structure and flexibility of the alkyd resins. It should be noted that certain polar groups in a film such as carboxylic groups (-COOH) are very active promoters of adhesion, due to their attraction to the substrate, or by their influence in improving the wetting properties. Thus, good initial wetting of a substrate by a coating and the maintenance of wetting during the process of film formation are essential for good film adhesion (Uche et al, 2016).

Mildew Formation: No mildew was formed on any of the alkyd sample films subjected to mildew test for the period of eight months (Table 11), an indication that the synthesized alkyds will perform well in coatings.

4. Conclusion

Oilbean seed oil and soybean oil have been successfully used in the synthesis of long and medium oil length alkyd resins with improved performance characteristics. These seed oils were comparable with breadfruit seed oil. The present study has highlighted the utility of oilbean, seed oil in the preparation of long and medium oil length alkyd resins. The ultimate usage of these oils in the coatings industry will save the country the enormous resources being spent in importing vegetable oils for the coatings industry, as well as encouraging the cultivation of the trees of the oil-bearing seeds with the farmers being the ultimate beneficiary.

Most agricultural seed oils of the Nigerian flora have long been neglected. Many potential seed oils that have suitable properties for alkyd resin production are still under-utilized. These oils should be well-harnessed so as to expand the present supplies and cater for the growing demands for vegetable oils. Nigeria and other African countries with favourable climate are implored to invest in the plantation of these potential oilseeds and work towards establishing them as new feedstock for the coatings and the chemical industries at large.

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