

## Formation and Characterization of Paint Based on Alkyd Resin Derivative of *Ximenia americana* (Wild Olive) Seed Oil

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Received: March 18, 2013 Accepted: June 26, 2013 Online Published: June 29, 2013

doi: 10.5539/enrr.v3n3p52

URL: <http://dx.doi.org/10.5539/enrr.v3n3p52>

### Abstract

Alcoholysis-polyesterification method was used in the investigation of utilization of *Ximenia americana* seed oil in the formulation of alkyd resins. The extracted oilseed gave an oil yield of 45.7% (w/w) and the physicochemical characterization indicated it is semi-drying in nature with iodine value of 152.3 g I<sub>2</sub> 100 g<sup>-1</sup>. The fatty acid analysis of the oil carried out earlier revealed oleic and linolenic as dominant fatty acids, having values of 72.1 and 10.3% respectively. Four grades of alkyds were formulated at 40% (I), 50% (II), 60% (III) and 70% (IV) 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. Kinetic studies showed that the reaction was second-order with values of 3.12 x 10<sup>-4</sup>, 2.44 x 10<sup>-4</sup>, 2.3 x 10<sup>-4</sup> and 2.28 x 10<sup>-4</sup> g (mg KOH)<sup>-1</sup> min<sup>-1</sup> for samples I, II, III and IV respectively. The extent of reaction (% P<sub>av</sub>) determined at the initial stage of reaction ranged from 63.3 to 78.6%, indicating an appreciable degree of conversion. The corresponding average degree of polymerization (D<sub>p</sub>) ranged from 2.7 to 4.7 and this indicated the formation of high molecular weight alkyd. Characterization of the alkyd gave iodine value of 70.1 ± 0.74, 76.1 ± 1.05, 81.2 ± 1.0 and 86.3 ± 0.8 g I<sub>2</sub> 100 g<sup>-1</sup> 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<sup>-1</sup>. The 40 and 50% oil length alkyd films were resistant to acid, brine and water with little resistance to alkali. Characterization of paint based on two alkyd resin derivatives, 40 and 50% oil lengths, gave values for surface drying and tack-free property of less than 2 and 5 hours respectively in respect of the 40% oil length.

**Keywords:** alkyd resin, polymer binder, condensation, polymerization, alcoholysis

### 1. Introduction

Paints could be described as colloidal mixture of chemical substances which when spread over a surface in a thin layer, form a solid, cohesive and adherent film. They are used in our daily life for decorative purposes as well as for protecting surfaces against various environmental effects like UV-radiation, chemical invasion and mechanical stresses. A conventional paint consists of binder, pigment, solvent and additives. The polymer-binding material (alkyd resin) with a large extent of variations is responsible for the formation of continuous film that adheres to the substrate and holds the other substances together (Wicks et al., 1994).

The preparation of alkyd resins is carried out by condensation polymerization of polyhydric alcohol (e.g. glycerol) and polyfunctional acid or polybasic acids (e.g. phthalic anhydride and isophthalic acid) modified by fatty acid or their triglyceride. The alkyd resins produced this way are referred to as oil-modified alkyd resins and contribute about 70% to the conventional binders used in surface coating (Bajpai & Seth, 2000). They determine the performance quality of surface coatings such as the rate of drying, gloss, durability of the dry film and resistance of the dry film to abrasion and chemicals. However, classification of alkyd resins is based on the oil length and oil type (Micciche, 2005). The vegetable oils used in oil-modified alkyd resins are usually extracted either by mechanical press or solvent extraction (Abulude et al., 2007). The natural oil in the oil-modified alkyds reacts with atmospheric oxygen leading to the formation of network of polymers cross-linked through the C = C bond. The oxidative drying of the oil brings about the formation of film that shows improved properties with drying time, hardness or water resistance (Akintayo, 2004). The oils used in

surface coatings contain linolenic and conjugated acid groups, such oils include linseed, perilla and tung oils and possess pronounced drying abilities (Aigbodion et al., 2003).

There has been tremendous increase in the demand for alkyd resin production for use in the Nigerian surface coating industry due to the rapid growth of the economy. Consequently, large quantities of oil are needed for the production of alkyds. Hence, there is need to investigate indigenous oilseeds in order to find other sources of drying oils with comparable properties to those currently being imported for resin production for paint formulation; notably *Ximenia americana* seed oil (XASO).

*Ximenia americana* (Linn) is a shrubby tropical plant of the family Olacaceae. It grows in many tropical African countries such as Nigeria, Senegal, Sudan and Angola (Storrs, 1995) to a height of about 5m on the average. It produces a small, yellow plum fruits which are edible with oily seed kernel. It grows in the savannah region of Nigeria and has different local names: Hausa-Tsada; Fulani-Chabbuli; Tiv-Anomadze; Yoruba-Igo (Keay, 1989). In this work, *Ximenia americana* seed oil had been examined via physicochemical analyses for its practical application as alkyd resin base material for industrial paint formulation.

## 2. Materials and Methods

The seeds of *Ximenia americana* (Wild Olive) plant were collected in Yola, Adamawa State, Nigeria. The seeds were shelled by cracking to remove the embryos. The embryos were sun-dried for two weeks before milling into granular form. Oil was extracted from the seeds with petroleum ether (40-60 °C) using soxhlet extraction method (Eromosele et al., 1994). The aliquot of the extract obtained was freed from petroleum ether by evaporation in a rotary evaporator to yield the oil. The physicochemical properties of *Ximenia americana* seed oil were assayed using the American Oils Chemists Society Methods (AOCS, 1996).

Table 3 shows the formulation of four grades of alkyd resin prepared with glycerol, phthalic anhydride and *Ximenia americana* seed oil. Monoglyceride of each grade was first prepared by heating a mixture of oil, glycerol and small quantity of CaO (Catalyst) in a 2-litre three necked round bottom flask fitted with a Dean and Stark having necessary accessories that will allow the reaction progress (Aigbodion & Okieimen, 1996). This mixture was heated by heating mantle to 200 °C and maintained at this temperature for 2 hours after which a small quantity of the aliquot was taken to check for solubility in methanol indicating formation of the monoglyceride. At the onset of the second phase, the temperature was lowered to about 180 °C and measured quantity of phthalic anhydride was added, followed by addition of xylene (10% of total weight charged) into the reaction mixture to remove the water of esterification by forming an azeotrope (Onukwli & Igbokwe, 2008; Ikhuoria et al., 2007). The temperature was increased to 230-250 °C while the reaction lasted. Aliquots were withdrawn from the reaction mixture at intervals of 30 minutes to determine drop in acid value and volume of water evolved. The reaction was stopped when the acid value attained the value of about 10 mg KOH g<sup>-1</sup> and the alkyd resin allowed to cool. The acid value of in-process samples taken at intervals were determined by titrating with a 0.1M KOH solution to the phenolphthalein end point after dissolution in a mixture of toluene and ethanol (1:1) (Bobalek et al., 1964). The acid value was related to the extent of the reaction  $P_{av}$  and the average degree of polymerization  $D_p$  thus:

$$P_{av} = \frac{(C_0 - C_t)}{C_0}, \quad D_p = (1 - P_{av})^{-1}$$

The rate equation for the reaction is expressed as:  $(1 - P_{av})^{-1} = C_0(kt + 1)$

where  $C_0$  is the initial acid value,  $C_t$  is the acid value after time,  $t$ , of the reaction,  $k$  is the rate constant and  $t$  is the time of reaction.

Some physicochemical properties (colour, iodine value, saponification value and acid value) of the alkyd resins prepared were determined using standard method (AOCS, 1996). The alkyd samples were thinned to 50% with xylene and applied on thin glass panels at room temperature (Ikhuoria et al., 2007). The drying schedule of the sample in terms of time to set-to-touch and drying through was determined. The resistance of the dried films to different solvent media was also determined (ASTM, 1994).

The gloss paint formulation is shown in Table 10. The first six ingredients were mixed thoroughly using high speed shearing technique for about 30 min. The premix base was then subjected to a milling process to produce a refined dispersion. The remaining ingredients of the formulation were then added under controlled conditions to make up the overall volume (Essien et al., 2012). The paint produced was stored in a container.

## 3. Results and Discussion

The physicochemical properties of *Ximenia americana* seed oil is shown in Table 1. The acid value of 16.13 mg

KOH g<sup>-1</sup> suggests low in-vivo lipolytic activities in the seed, and indicates a good non-degraded state of the oil and falls within limits for industrially useful oils (Oyedeji & Oderinde, 2006). However, it is high in comparison with the values for linseed oil and low comparing with rubber seed oil i.e. 1.0 mg KOH g<sup>-1</sup> and 19.18 mg KOH g<sup>-1</sup> respectively (Majumder, 1990; Ikhuoria & Okieimen, 2005). Williams (1966) reported that low acid values for oils are useful in the manufacture of paints and varnishes. The free fatty acid concentration of 8.07% for *Ximenia americana* is high, consistent with the high acid value observed. The saponification value of the XASO is 178.5 mg KOH g<sup>-1</sup> and is lower in comparison with the corresponding values for rubber seed, castor seed and linseed oils i.e. 181.14, 182 and 185-194 mg KOH g<sup>-1</sup> respectively (Onukwli & Igbokwe, 2008; Majumder, 1990; Ikhuoria & Okieimen, 2005). Eromosele et al. (1994) reported the saponification value of *Ximenia americana* seed oil as 182.3 mg KOH g<sup>-1</sup>. This suggests that the seed oil may be suitable for preparation of soap. The iodine value of 152.28 g I<sub>2</sub> 100 g<sup>-1</sup> is comparable to the one for rubber seed 136.2 g I<sub>2</sub> 100 g<sup>-1</sup> (Ikhuoria & Okieimen, 2005). Also, Folarin et al. (2011) reported the value of *Ximenia americana* seed oil as 158.30. By this value, *Ximenia americana* seed oil is semi-drying although it has much lower value than that of linseed oil (188 g I<sub>2</sub> 100 g<sup>-1</sup>) (Majumder, 1990). Semi-drying oils can be used for synthesis of alkyd resins, formulation of liquid soap and hair shampoo while non-drying oil is suitable for use as plasticizer (Fasina, 1989). The seed oil appeared highly susceptible to oxidative rancidity, it has peroxide value of 31.25 mEq kg<sup>-1</sup>. The viscosity of the seed oil is 900 cp, this indicates that the oil is highly viscous at ambient temperature. The specific gravity is 0.912 g cm<sup>-3</sup>, it is the lowest in comparison with linseed oil, crude castor seed oil and rubber seed oil having values of 0.93-0.98, 0.93 and 0.93 g cm<sup>-3</sup> respectively (Onukwli & Igbokwe, 2008; Ikhuoria et al., 2007; Majumder, 1990). The refractive index of the seed oil is 1.435, it is lower comparing with the range of refractive indices of drying oils which are comparatively narrow from 1.46 to 1.54 and this suggests that it can be used as a test for purity and as an aid to identification (BS 6900).

Table 1. Physicochemical properties of *Ximenia americana* seed oil (XASO) compared with castor seed oil, rubber seed oil and linseed oil

Properties	XASO	Castor seed oil*	Rubber seed oil**	Linseed oil***
Colour	Dark	-	Brown	Yellow
Oil yield (%)	45.7	44.69	-	-
Specific gravity (g cm <sup>-3</sup> , 30 °C)	0.912	0.93	0.93	0.931- 0.98
Refractive index (30 °C)	1.467	-	1.477	1.479-1.48
Viscosity (cp, 30 °C)	900	-	-	-
Saponification value (mg KOH g <sup>-1</sup> )	178.5	182.0	181.14	185.0-194.0
Iodine value (g I <sub>2</sub> 100 g <sup>-1</sup> )	152.28	82.8	136.2	188.0
Acid value (mg KOH g <sup>-1</sup> )	16.13	2.89	19.18	1.0
Free fatty acids (%)	8.07	1.45	9.54	-
Peroxide value (mEqkg <sup>-1</sup> )	31.25	6.7	-	-
Average molecular weight (g mol <sup>-1</sup> )	314.34	307.6	-	-

Onukwli and Igbokwe (2008)\*, Ikhuoria & Okieimen (2005)\*\* , Majumder (1990)\*\*\*.

The fatty acid composition of *Ximenia americana* seed oil is shown in Table 2. Previous results (Eromosele & Eromosele, 2002; Folarin et al., 2011) indicate that the seed oil contains twelve fatty acids of which nine are unsaturated, yielding a total unsaturation of 92.92% and this is slightly higher than that of linseed oil (91.3%) (Tarandjiiska et al., 1996). The concentrations of the dominant fatty acids are 72.09 and 10.31% for oleic and linolenic acid respectively. The oil may have nutritional value due to the presence of essential fatty acids such as linoleic (1.34%), linolenic (10.31%) and arachidonic (0.60%). Linoleic acid in particular plays an important role in the biosynthesis of prostaglandins (Al-Jassir et al., 1995). The level of linolenic acid is significant, albeit a factor of five less than the value in linseed oil (Tarandjiiska et al., 1996). However, the presence of erucic acid in the oil makes toxicological analysis imperative to ascertain its edibility. From the level of unsaturation, its distribution and the presence of fatty acids with up to four double bonds, *Ximenia americana* seed oil appears to be a suitable base material for alkyd resin synthesis and paints formulation. Furthermore, the presence of stearic

acid shows that the oil could be used for pharmaceutical preparations (Okieimen & Eromosele, 1999).

Table 2. Fatty acid composition of *Ximenia americana* seed oil

Fatty acid	Composition (%)
Caprylic	0.55
Palmitic	3.31
Stearic	3.47
Oleic	72.09
Linoleic	1.34
Linolenic	10.31
Eicosatrienoic	2.39
Gadoleic	1.58
Arachidonic	0.60
Erucic	2.46
Nervonic	1.23
Stearolic	0.92
Total unsaturation	92.92

Eromosele and Eromosele, 2002; Folarin et al., 2011.

Table 3. Recipe for the formation of alkyd samples

Ingredient (100g)	Alkyd Samples			
	I	II	III	IV
<i>Ximenia americana</i> seed oil (XASO) (%)	40	50	60	70
Phthalic anhydride (%)	36.31	30.2	24.09	17.98
Glycerol (%)	23.69	19.8	15.91	12.02
Mole Ratio (XASO : Glycerol)	1 : 2	1 : 1.4	1 : 0.9	1 : 1.06
Alkyd Constant (K)	1.02	1.02	1.02	1.02

Table 4. Variation in Acid Value (AV) of in-process samples (I, II, III and IV) with the corresponding extent of reaction (%P<sub>av</sub>)

Time (Min)	Alkyd Samples							
	I		II		III		IV	
	AV	%P <sub>av</sub>	AV	%P <sub>av</sub>	AV	%P <sub>av</sub>	AV	%P <sub>av</sub>
0	196.35	-	199.15	-	173.91	-	84.15	-
30	64.52	67.14	86.95	56.34	81.35	53.22	56.10	33.33
60	42.07	78.57	50.91	74.44	51.20	70.56	38.88	53.79
90	14.00	92.87	16.83	91.55	22.44	87.10	30.86	63.33
120	8.42	95.71	12.16	93.89	10.66	93.87	12.44	85.22
150	6.34	96.71	10.37	94.79	7.85	95.49	5.61	93.33
180	-	-	7.01	96.48	-	-	-	-

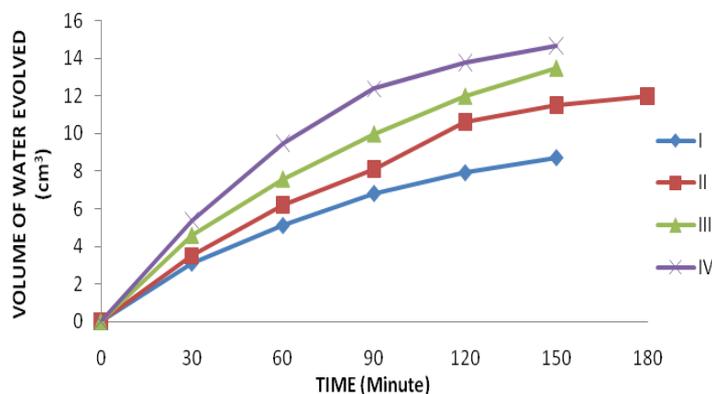


Figure 1. Plots of change in volume of water evolved versus reaction time for varying oil length alkyd resins. I (40%); II (50%); III (60%); IV (70%)

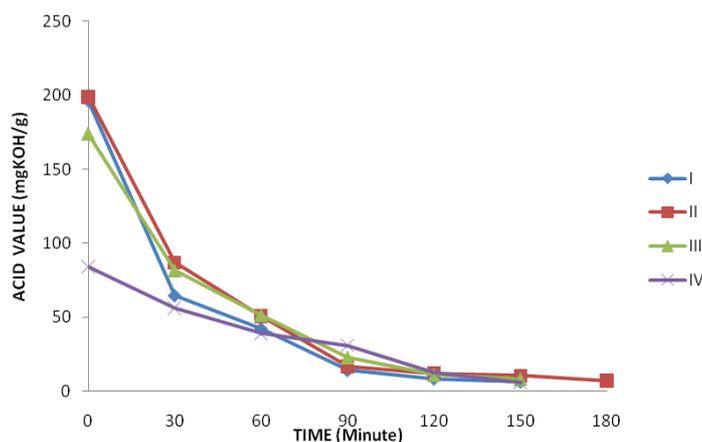


Figure 2. Plots of change in acid values versus reaction time for varying oil length alkyd resins. I (40%); II (50%); III (60%); IV (70%)

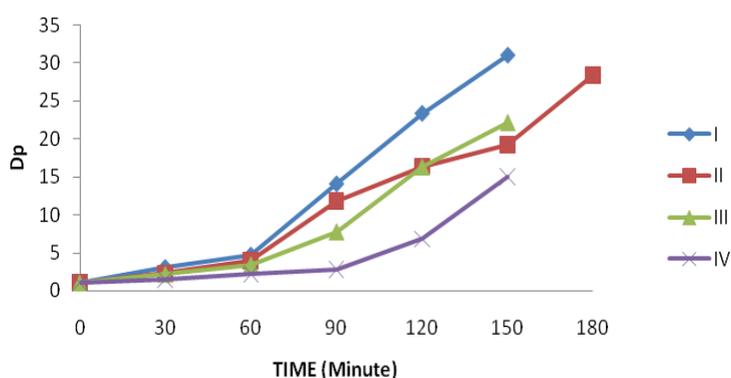


Figure 3. Plots of change in average degree of polymerization ( $D_p$ ) versus reaction time for varying oil length alkyd resins. I (40%); II (50%); III (60%); IV (70%)

Four grades of alkyds were formulated at 40% (I), 50% (II), 60% (III) and 70% (IV) oil length with various amounts of phthalic anhydride and glycerol employing the two-stage alcoholysis-polyesterification method as shown in Table 3. The kinetics of polyesterification reaction was monitored by determining the acid value for the aliquot of the reaction mixture at various time intervals beside the volume of water evolved. The variation of volume of water evolved with reaction time for the alkyd samples is shown in Figure 1. It shows that at the early

stages of reaction, the rate of water evolution was high and this is followed by a lower rate at longer periods of reaction. This may be due to high initial esterification reaction and the attendant reduction in the available functional groups for the condensation reactions. In addition, the increasing viscosity of the medium was reduced as the reaction progressed. It was observed that as the oil length increases, the total volume of water evolved for each alkyd sample increases. This is corroborated by the changes in acid value with reaction time as shown in Table 4 and in Figure 2. In the latter, it is revealed that there is an initial sharp decrease in acid value followed by a more gradual decrease. Similar observations had been reported (Onukwli & Igbokwe, 2008; Ikhuoria et al., 2007). The decrease in acid value is explained as arising from the desperate reactivities of primary and secondary hydroxyl groups of glycerol with carboxyl groups of phthalic anhydride. It is also attributable to incorporation of almost all reactants in the polymer chain at the initial stage of reaction, characteristics of step-growth polymerization. It has been reported that the primary hydroxyl groups of the monoglyceride reacts more rapidly than the secondary hydroxyl groups with carboxyl groups of phthalic anhydride. It is established that at a temperature of about 160 °C, primary hydroxyl groups of glycerol react rapidly with carboxyl groups of phthalic anhydride, while secondary hydroxyl groups react at temperature above 230 °C (Goldsmith, 1948). Thus, the initial marked decrease in acid value observed for all the alkyd samples may be due to increase in the rate of esterification accompanying the rapid increase in temperature to 230 °C. In confirmation of the above, the acid value for all the samples decreased with increase in oil length, consistent with high amounts of di- and triglyceride present in the reaction mixture and the concentration of the acid anhydride (Onukwli & Igbokwe, 2008). However, in polyesterification reactions, the reactivity of the functional group does not depend on the size of molecule to which it is attached (Aigbodion & Okieimen, 1996).

The variation in the average degree of polymerization ( $D_p$ ) with reaction time is shown in Figure 3. The first region of these plots shows the period when the primary hydroxyls of glycerol reacted with carboxyl groups of phthalic anhydride leading to formation of linear chains. Immediately the primary hydroxyl groups are esterified, there is an abrupt drop in acid value and the reaction slackens until a temperature is reached when the secondary hydroxyl groups begin to react (Aigbodion & Okieimen, 1996). Thus, the increasing  $D_p$  of the alkyd chains results in increasing viscosity of the reaction medium.

The average molecular weight ( $M_{av}$ ) with respect to the acid value at different stages of the reaction was calculated using the equation:

$$M_{av} = W / (k - P_{av}) \ell_A \text{ (Bobalek et al., 1964; Bobalek & Chiang, 1964)}$$

where  $W$  is the total weight of all the reactants;  $k$  is the ratio of the total moles of all reactants to total equivalent of the acid ( $m_o/\ell_A$ ); and  $\ell_A$  is the total equivalent of the acid. It was adduced that there is no reasonable increase in the molecular size of the reaction mixture at the earliest stages of the reaction. However, there is appreciable increase as the reaction progressed (Table 5). The low molecular weight observed at the beginning of the reaction is attributed to the low rate of polymerization. Increase in polymerization rate results in corresponding increase in molecular weight. This trend continues until the gelation point, at which structural changes begin to occur in the polymer size of the molecule in solution. The molecular weight of the alkyd decreases with increase in the oil lengths. This is consistent with earlier report by Aigbodion and Pallai (2001). An increase in oil length from 40-70% is accompanied by a decrease in the XASO: Glycerol ratio in the range 1: 2-1: 0.6. Consequently, the effective concentration of monoglyceride produced in-situ decreases resulting in lower  $D_p$  and molecular weight of alkyd resin. This is corroborated by the extent of reaction ( $P_{av}$ ) calculated at the region of deviation from second-order as shown in Table 6.

The extent of reaction ( $\%P_{av}$ ) and average degree of polymerization ( $D_p$ ) calculated for alkyd sample at the region of deviation from second order reaction is shown in Table 6. The result shows that the extent of reactions at this region varies from 63.33 to 78.57% for samples IV - I. Although these values are relatively lower than the range 75-80% obtained for reaction between phthalic anhydride and glycerol (Nagata, 1969; Carothers 1936), they indicate a significant degree of conversion. However, sample I (78.57%) falls within the range of the reactivity of phthalic anhydride and glycerol, with appreciable degree of conversion consistent with the ideal ratio of 1:2 for XASO: Glycerol for the alcoholysis reaction. The corresponding average degree of polymerization ( $D_p$ ) ranges from 2.73 to 4.67 and this suggests the formation of high molecular weight species. The second-order rate constant,  $k$ , calculated from the linear portion of Figure 3 for the alkyd samples is represented in Table 7.

Table 5. Variation in Acid Value (AV) of in-process samples (I, II, III, and IV) with the corresponding average molecular weight ( $M_{av}$ )

	Alkyd Samples							
	I		II		III		IV	
Time (Min)	(AV)	( $M_{av}$ )	(AV)	( $M_{av}$ )	(AV)	( $M_{av}$ )	(AV)	( $M_{av}$ )
0	196.35	-	199.15	-	173.91	-	84.15	-
30	64.52	464.5	86.95	386.3	81.35	361.7	56.1	312.8
60	42.07	691.1	50.91	640.1	51.2	561.2	38.88	445.6
90	14	1773.5	16.83	1688	22.44	1184	30.86	555.5
120	8.42	2574.5	12.16	2175.1	10.66	2170.1	12.44	749.3
150	6.34	3095.9	10.37	2446.6	7.85	2710	5.61	2477.8
180	-	-	7.01	3195.6	-	-	-	-

Table 6. Extent of reaction (%  $P_{av}$ ) and average degree of polymerization ( $D_p$ ) in the region of deviation from second order reaction

Parameter	Alkyd Samples			
	I	II	III	IV
Time (Min)	60	60	60	60
% $P_{av}$	78.57	74.44	70.56	63.33
$D_p$	4.67	3.91	3.40	2.73

Table 7. Value of second-order rate constant (k), calculated from the linear portion of plots ( $D_p$ ) versus reaction time for the alkyd samples

Alkyd sample	Mole Ratio (XASO: Glycerol)	$k \times 10^4 \text{ g (mg KOH)}^{-1} \text{ min}^{-1}$
I	1: 2	3.12
II	1: 1.4	2.44
III	1: 0.9	2.30
IV	1: 0.6	2.28

The rate of esterification reaction is expressed as;

$$(1 - P_{av})^{-1} = C_0(kt + 1)$$

where  $C_0$ ,  $k$ ,  $t$  and  $P_{av}$  have been defined previously. From the slopes of the plots, the second-order rate constant is in range,  $2.28\text{-}3.12 \times 10^{-4} \text{ g (mg KOH)}^{-1} \text{ min}^{-1}$ , the highest value corresponding to sample I i.e. 40% oil length. It has been established that the rate constant for esterification reaction is dependent on the proportion of reactants, speed of agitation of the reaction mixture, changes in temperature and removal of water of esterification (Aigbodion et al., 2001; Akintayo & Adebawale, 2004). In addition, the rate constant for a second-order reaction depends on the initial concentration of the reactants monitored for the reaction. From the results above, the rate constants for all the samples are within the same order of magnitude, albeit higher for sample I. This is attributed to the mole ratio of XASO: Glycerol used in the formulations. The mole ratio of XASO: Glycerol of 1:2 for 40% oil length alkyd suggests higher initial concentration of  $\alpha$ -monoglyceride formed in-situ and decreases as the oil length increases. Aigbodion and Okieimen (1996) reported that the rate constants for rubber seed oil range from  $1.92\text{-}4.08 \times 10^{-5} \text{ g (mg KOH)}^{-1} \text{ min}^{-1}$  for oil length of 20-60%. Similarly, for locust bean seed oil,  $k$  values were in the range,  $5.98\text{-}12.51 \times 10^{-5} \text{ g (mg KOH)}^{-1} \text{ min}^{-1}$  (Aigbodion et al., 2001). *Ximenia americana*-oil base alkyd resin has rate constants higher than the ones reported for locust bean oil and rubber seed oil. This may be due to difference in experimental conditions.

Table 8. Properties of the finished alkyds

Property	Alkyd Samples			
	I	II	III	IV
Colour	Dark brown	Dark brown	Dark brown	Dark brown
Acid Value (mgKOHg <sup>-1</sup> )	6.34±0.61	7.01 ±0.72	7.85±1.00	5.61±1.90
Saponification Value (mgKOHg <sup>-1</sup> )	297.5±1.48	332.5±1.21	378.1 ±1.10	420.2 ±1.32
Iodine Value (gI <sub>2</sub> 100g <sup>-1</sup> )	70.06 ±0.74	76.14 ±1.05	81.22±0.97	86.30±0.81
Drying Time (hour)				
Surface Dry	<2	<2	<3	<4
Dry Through	Over night	Over night	Over night	Over night

Table 9. Resistance of the alkyd resin

Alkyd Samples	Medium			
	Distilled H <sub>2</sub> O	5% NaCl	0.1M H <sub>2</sub> SO <sub>4</sub>	0.1M KOH
I	a	a	a	c
II	a	a	a	c
III	a	a	b	c
IV	a	a	b	c

a- no effect, b-wrinkle, c-film removed.

Table 10. A typical gloss paint formulation

Component	Amount (g)
Alkyd resin	200
Titanium dioxide (TiO <sub>2</sub> )	160
Dispersant (Soya lecithin)	1.1
Kerosine	30
White spirit	20
Alkyd resin	400
Kerosine	70
White spirit	140
Anti-skin	1.1

Table 11. Properties of the paints

Parameter	Paint samples	
	40%	50%
Oil Length	40%	50%
Colour	Cream	Cream
Specific Gravity (gcm <sup>-3</sup> )	1.01± 0.14	1.07± 0.12
Viscosity (cp)	130	110
Surface Dry (hour)	<2	<2
Tack Free (hour)	<5	<6
Dry Through (hour)	Overnight	Overnight

The properties of the finished alkyd resins are presented in Table 8. The dark colour of the alkyds is attributed to the colour of the oil. The iodine value is, as expected low, in the understanding that the reactive diol contains only one fatty acid moiety. However, as the oil length increases, the iodine value increases. The high saponification values of  $297.5 \pm 1.48$ ,  $332.5 \pm 1.21$ ,  $378 \pm 1.10$  and  $420 \pm 1.32$  mg KOH g<sup>-1</sup> for alkyd samples I, II, III and IV respectively are expected since they are oligomeric and are composed of ester links. These results confirm earlier reports (Aigbodion & Pillai, 2001; Aigbodion et al., 2001). Another important property of alkyds, which of course, is the most critical to their application as binders, is the drying schedule. This is the ability of the alkyd to dry to a hard and durable film by the process of autoxidation. This is related to the amount of the double bonds present in the oil as measured by the iodine value (Muizebelt et al., 1998; Agbenyega et al., 1991). The results in Table 8 also show the effect of alkyd resin oil length on the drying time. It shows that the 40 and 50% oil lengths reached the surface-dry conditions faster at less than 2 hours while 60 and 70% oil length attained the same conditions less than 3 and 4 hours respectively. This is attributed to the decrease of the solubility of the alkyd in the solvent (xylene) as oil length decreases, increasing the amount of solvent embedded in the alkyd resin. It has been reported that higher oil content of long and medium oil alkyds gave slower initial drying due to more thermosetting of long oil alkyd as compared to short oil alkyd (Singh, 2009). Subsequently, gloss retention is more pronounced in long oil alkyd compared to the medium and short oil alkyd.

Table 9 presents the results of the resistance of the alkyds in different service media. It shows that the water and brine media have no effect on the alkyds, while they are affected to varying degrees by acid and alkali media. Thus, the 40 and 50% oil length alkyd films are highly resistant to acid, brine and water but fairly resistant to alkali. This may be due to the fact that alkyds are essentially polyesters that are susceptible to hydrolysis. The properties of the paints formulated is presented in Table 11. The cream colour of the paints is attributed to the initial colour of the alkyds and the amount of white pigment used in the formulation. The result shows that the 40 and 50% oil length alkyd paints gave values for surface drying and tack-free property of less than 2 and 5 hours respectively in respect of the 40% oil length, while it was less than 2 and 6 hours for 50% oil length.

#### 4. Conclusion

The suitability of *Ximenia americana* seed oil in the preparation of alkyd resin and gloss paint formulation was investigated. The extracted oilseed gave an oil yield of 45.7% (w/w), this suggests the possibility of classifying *Ximenia americana* as oilseed plant. The physicochemical characterization of the oil indicated it is semi-drying in nature based on the iodine value and suitable for alkyd resin preparation. Four grades of alkyd resin were prepared via alcoholysis-polyesterification method and the kinetics of the reaction indicated it is second order. The extent of reaction and the corresponding average degree of polymerization determined revealed the formation of high molecular weight alkyd. The alkyd resins exhibited excellent resistance to acid, brine and water, but fairly resistant to alkali in respect of 40 and 50% oil length based on the degree of conversion of the reactant with the reaction time. Their resistance to different service media is consistent with observable resistance of oil-paint to these media when applied as surface coating. Characterization of paint based on alkyd resin derivatives gave values for surface drying and tack-free property of less than 2 and 5 hours respectively in respect of the 40% oil length. Thus, *Ximenia americana* seed oil-modified alkyd resin is a suitable base material for oil paint formulation.

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