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Preparation and Characterisation of Alkyd Resins Using Crude and Refined Rubber Seed Oil

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Abstract. Six different alkyds were formulated with crude rubber seed oil 45% **(1)**, 50% **(II)** and 55% **(III)**; refined rubber seed oil 45% **(IV)**, 50% **(V)** and 55% **(VI)**; phthalic anhydride and glycerol. All the alkyds were formulated to alkyd constant of about 1.0. The alcoholysis method was used. Refining enhanced the quality of rubber seed oil in alkyd resin manufacture. The properties of the finished alkyd resins such as viscosity, number average molecular weights, drying schedule, chemical resistance and film hardness were determined. The intrinsic viscosity (η) was observed to be proportional to the number average molecular weight of the two sets of alkyd resins. However, samples **I-III** exhibited higher intrinsic viscosity in toluene than samples **IV-VI**. On the contrary, the films of samples **IV-VI** were harder, dried faster, and were more chemically resistant than those of samples **I-III**. The practical implications of these results are discussed.

Keywords: alkyd resins, rubber seed oil, refining, surface coatings, coating binders

Introduction

Generally, surface coatings are composed of binders, solvents and pigments. Binders are film-forming components of the coatings. They are responsible for the performance quality of the coatings such as the rate of drying, gloss, durability of the dry film, and resistance of the dry film to abrasion and chemicals. Alkyds are examples of binders. They constitute over 70% of binders currently used in surface coatings due to their unique qualities like gloss and gloss retention, exterior durability, and compatibility with other film formers for purposes of cost reduction (Bajpai and Seth, 2000). They are essential products of condensation reaction between polyols and polybasic acids modified with fatty acids or triglyceride oils. Glycerol and phthalic anhydride, respectively, are examples of polyols and polybasic acids commonly employed in the preparation of alkyds because of their relative abundance and low cost. They form the main alkyd backbone chain to which fatty acids are attached thereby terminating the growth of the alkyd chain in that direction. Vegetable oils are now most commonly employed in alkyd formation due to their low cost. Drying oils are among the oldest binders used in coating formulations because of their ability to form hard and solid films upon exposure to air (Patel *et al.,* 2000).

The nature of the drying oil used governs the physical and chemical properties such as rate of drying, film hardness, colour and gloss retention, flexibility, and adhesiveness of the alkyd film, thereby making drying oil the most important component of alkyd resins (Wick *et al.,* 1999). Natural forms of the oils seldom fulfil the technical requirements for film properties like resistance to weathering, chemicals, acid, water, alkali and abrasion (OCCAA, 1983). Thus, to enhance their initial quality, several physical and chemical modifications of the oils have been evolved over the years. Examples of such modification techniques include acrylation (Akintayo and Adebowale, 2004a), catalytic and thermocatalytic polymerization (Patel *et al.,* 2000), interesterification (Athawale and Joshi, 2001), phosphorylation, expoxidation (Zhong *et al.,* 2001), copolymerization (Trumbo *et al.,* 2001), dehydration (Thames *et al.,* 1997), and chlorination (Akintayo and Adebowale, 2004b).

Various physical and chemical modifications of rubber seed oil, such as heat treatment (Aigbodion and Pillai, 2001) and monomer-modification (Aigbodion *et al.,* 2003) have been previously reported. In this study, we report on the quality of alkyd resins modified with crude rubber seed oil (RSO) compared with the quality of those modified with refined rubber seed oil. Rubber seed oil has been found to have strong potential for use in the production of alkyd resins with quality comparable to that of commercial alkyd resins (Aigbodion *et al.,* 2001; Aigbodion and Okieimen, 1995). Like other vegetable oils, crude rubber seed oil is composed of a mixture of triglycerides and minor constituents like free fatty acids, which are extraneous to the neutral oil and contaminants. It was then hoped that removal of these minor constituents would enhance the quality of rubber seed oil in the manufacture of alkyd resins.

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Materials and Methods

Materials. Rubber seeds were collected from the plantation of Rubber Research Institute of Nigeria, Iyanomo, Benin City. The seeds were dried in oven at 50 °C for 72 h and shelled. Kernels were ground and oil was extracted from the milled kernels with *n*-hexane (40-60 °C) using Soxhlet extractor.

Refining. Rubber seed oil was refined according to the method adopted by Protein Oil Starch Pilot Plant Corporation, Canada (Cocks and Rede, 1966). In a typical batch, a known weight of the pre-heated oil (60 °C) was treated with 10% (w/w) of 0.8 M sodium hydroxide by stirring for 5 min, after which it was allowed to stand or centrifuged to separate the aqueous layer. The oil phase was washed with water for about 3 times until neutral. The physicochemical properties of refined rubber seed oil and those of the crude rubber seed oil are compared with those of linseed and soybean oils in Table 1.

Preparation of alkyds. Six different alkyd samples were prepared with crude and refined rubber seed oil, glycerol, and phthalic anhydride using lead (II) oxide as catalyst according to the recipe in Table 2. The preparation was carried out in a three-necked round bottom flask fitted with a motorized stirrer, a Dean and Stark trap carrying water cooled condenser and nitrogen inlet tube. Reaction temperature ranged from 230-250 °C. Xylene was employed as the azeotropic solvent (Aigbodion *et al.,* 2003). Following two stages were involved.

Stage 1. Alcoholysis. In the alocholysis stage, the mono-glyceride was first prepared by reacting glycerol with rubber seed oil at a temperature of 230-250 °C (Aigbodion and Pillai, 2000; Athawale *et al.,* 2000). Alcoholysis was completed when one part of the reaction mixture dissolved in three parts of anhydrous methanol and formed a clear solution. The reaction was cooled to 140 °C.

Stage 2. Calculated amount of phthalic anhydride was added to the reaction mixture and temperature was quickly raised to about 230 °C and maintained at a range of 230-250 °C. The water of condensation was drained into a Dean and Stark trap where water of condensation was removed and the xylene returned to the reaction flask through an overflow point. The reaction was monitored by periodic determination of the acid value of the mixture until acid value dropped to below 10.

Physicochemical characterisation of crude and refined rubber seed oil. Physicochemical properties of the crude and refined rubber seed oils (colour, specific gravity, refractive index, acid value, free fatty acids, saponification value, iodine value and solid content) were determined according to ASTM standard methods. These properties were compared with those of conventional drying oils (soybean and linseed oils) commonly used in surface coatings (Table 1).

Physicochemical characterisation of alkyd resins. The physicochemical properties of the alkyd resins (colour, specific gravity, refractive index, acid value, free fatty acids, saponfication value, iodine value and non-volatile matter) were determined according to ASTM standard methods (ASTMD 1541-50, 1979; 1639-90, 1963-4, 1979; 1959-69, 1979).

Viscosity measurements. Viscosity measurements were carried out with solutions of the alkyds in toluene using Ubbelohde 50 viscometer. Three additional dilutions were made in the viscometer, allowing reflux time to be measured at concentration of 2.5, 2.0, 1.5, 1.0 and 0.5 g/100 cm^3. Viscosity measurements were carried out at temperature of 30±0.5 °C. Another 10 ml of the solution was evaporated to dryness and weighed to determine the exact concentration of the solution. Intrinsic viscosities were determined by extrapolation of the plots of η_{sp}/C against concentration to zero concentration, where C is the concentration (g/100 ml) and η_{sp} is the specific viscosity. Fig. 1 shows typical plots of η_{sp}/C versus concentration (C). The values of the Huggin's constant, K_H, were calculated as follows from the Huggin-Kreamer viscosity relationship.

$$\eta_{sp}/C = [\eta] + K_H[\eta]^2C \qquad (1)$$

Table 1. Physicochemical properties of crude and refined rubber seed oils (RSO) compared with soybean and linseed oils

Properties	Crude RSO	Refined RSO	Soybean oil*	Linseed oil**
Colour	brown	yellow	yellow	yellow
Specific gravity (at 30 °C)	0.930	0.920	0.932	0.931 – 0.980
Refractive index	1.477	1.472	1.475	1.479 – 1.480
Acid value (KOH, mg/g)	19.18	8.96	4.78	1
Free fatty acids (%, as oleic acid)	9.54	4.48	2.39	
Saponification value (KOH, mg/g)	181.14	178.75	190.00	185.00 – 194.00
Iodine value, Wijs (I_2, g/100 g)	136.2	148.6	140.0	188.0

*Cocks and Rede (1966); **Majumder (1990)

Table 2. Recipe of the alkyd resins prepared with crude (samples **I-III**) and refined (samples **IV-VI**) rubber seed oils

Ingredients	**(I)**	**(II)**	**(III)**	**(IV)**	**(V)**	**(VI)**
Rubber seed oil (g)	136.18	151.13	164.87	136.18	151.13	164.87
Phthalic anhydride (g)	101.02	91.28	83.31	101.40	91.28	83.31
Glycerol (g)	62.78	57.60	51.60	62.78	57.60	51.60
Alkyd constant	1.00	1.00	1.00	1.00	1.00	1.00

Determination of molecular weights. Molecular weights of the alkyds were determined using the Rast method (Furniss *et al.,*1978). The technique involves melting point depression of camphor in the presence of the alkyd sample.

Performance characteristics of the alkyd resins. The drying schedule and resistance of the alkyd films to different service media were determined using the methods described in ASTM 1647-89 and 1640-83 (1994) , respectively. Pencil hardness was also determined according to ASTM (1979).

Results and Discussion

Table 1 compares the properties of crude and refined rubber seed oils with those of soybean and linseed oils commonly used in alkyd production. The colour of the crude rubber seed oil was observed to be brown. Although colour is a useful characteristic of oils and an important parameter commonly employed in quality grading of oils and their sales appeal (Wick *et al.,* 1999), it is not necessarily the sole determinant of the potential end-use of the oil in industrial applications. However, refining was observed to lighten the colour of rubber seed oil, thereby enhancing its utilization in the formulation of light coloured coatings. The yellow colour observed with the refined oil was found to be the same as that of soybean and linseed oils commonly used in surface coatings. The specific gravity of rubber seed oil of 0.930 compares well with the value of 0.932 for soybean oil and 0.931 for linseed oil. The refractive index of 1.478 obtained for rubber seed oil in this study compares well with the values of 1.475 and 1.470 reported for soybean and linseed oils, respectively. The acid value of rubber seed oil (19.18 mg KOH/g) is relatively high compared to the value of (1.0 mg KOH/g) for linseed oil and (4.78 mg KOH/g) for soybean oil. A comparatively high acid value had earlier been reported for rubber seed oil (Aigbodion and Pallai, 2000). The saponification value of rubber seed oil (181.14 mg KOH/g) was found to be close to the value of soybean seed oil (190 mg KOH/g) and linseed oil (185-194 mg KOH/g). The iodine value of rubber seed oil (136 g I_2/100 g) was found to be somewhat lower than that of soybean oil (140 g I_2/100 g) and much lower than linseed oil (188 g I_2/100 g). Refining also increased the iodine value of rubber seed oil to 148.6 g I_2/100 g.

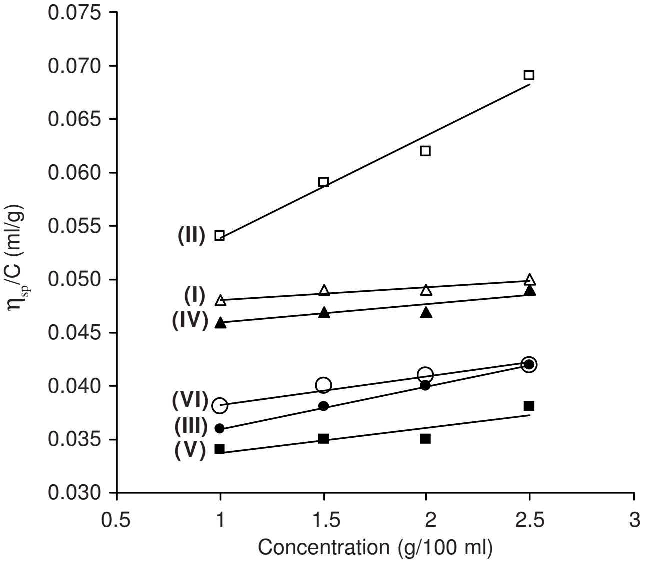

Fig. 1. Plots of reduced viscocity (η_{sp}/C) against concentration (C) of alkyd samples from crude rubber seed oil of 45% **(I)**, 50% **(II)**, 55% **(III)** oil content and refined rubber seed oil of 45% **(IV)**, 50% **(V)**, 55% **(VI)** oil content.

Physicochemical properties of the finished alkyds are shown in Table 3. All the alkyd resins were of good colouration with acid value below 4 mg KOH/g. Saponification values of the alkyd samples **I-VI** were relatively higher than those of unrefined and refined rubber seed oils. This is probably so, as they are essentially polyesters. Generally, the iodine value of the finished alkyd resins increases with the oil length of the samples. However, samples **I-III** modified with unrefined rubber seed oil were found to have lower iodine values than the corresponding alkyd samples modified with the refined oil. This implies that samples **IV-VI** were of higher degree of unsaturation. The percent solid content of samples **IV-VI** was higher than that of samples **I-III**. This may imply that refined rubber seed oil could be suitable in formulating high solid alkyd resins for use as binders in environmentally friendly coatings. Scratch/gouge pencil hardness tests for samples **I-III**, respectively, were HB/4H, HB/3H and H/4H, and for

Table 3. Phyiscochemical properties of finished alkyd resins

Properties	(I)	(II)	(III)	(IV)	(V)	(VI)
Specific gravity (at 30 °C)	0.945	0.938	0.933	0.943	0.037	0.930
Colour	brown	brown	dark brown	brown	ash brown	ash brown
Acid value (KOH, mg/g)	2.41	1.11	0.74	2.60	1.95	3.61
Saponification value (KOH, mg/g)	345.10	326.29	322.60	335.14	337.04	315.37
Iodine value (I_2, g/100 g)	65.64	72.21	83.30	53.84	60.34	72.59
Solid content (%)	62	60	64	76	85	82
Pencil hardness (scratch)	HB	HB	H	H	H	H
(gouge)	4H	3	H	H	4H	3H 4H

samples **IV-VI,** respectively, were 2H/4H, 3H/4H and HB/2H. The films of samples **IV-VI** formulated with refined rubber seed oil were observed to be the hardest films.

Table 4 shows the drying schedule of the alkyd resins in terms of the times of set-to-touch and dry-through. The result showed that the time of set-to-touch and dry-through were about 30 min and 1440 min, respectively, for the alkyd resins from the crude rubber seed oil samples **I-III**. In the case of refined alkyd resin samples **IV-VI**, the time of set-to-touch and dry-through was found to be about 20 min and 1200 min, respectively. The results indicate that alkyd samples formulated with refined oil showed faster drying rates than the resins formulated with crude oil. This trend is in agreement with the level of unsaturation as indicated by the iodine values of the samples as shown in Table 3. The higher the level of unsaturation, the faster was the rate of drying. Drying is believed to occur through the process of auto-oxidation, which involves the adsorption of oxygen at the double bonds of the unsaturated fatty acids (Wick *et al.,* 1999).

Table 5 shows the chemical resistance of the resins. All the alkyd samples seemed to be highly resistant to brine while they were poorly resistant to alkali. This poor resistance to alkali was probably due to alkaline hydrolysis. Samples **IV-VI** were virtually unaffected by water and acid while samples **I-III** can be said to be fairly resistant to water and acid. Based on these results, it can be deduced that refining improved the chemical resistance of alkyd film.

Table 6 shows the intrinsic viscosity and number average molecular weight determined for the alkyd sample. Dilute solution properties such as intrinsic viscosity and number average molecular weight are important for characterizing alkyds (Okieimen and Aigbodion, 1998; 1997). The intrinsic viscosity was observed to be proportional to the molecular weight, whereas intrinsic viscosity decreased with increase in oil length for the two sets of alkyds samples **I-III** and samples

Table 4. Drying schedule of the alkyd resins

Alkyd sample	Set-to-touch time (min)	Dry-through time (min)
I	30	1440
II	30	1440
III	31	1440
IV	20	1200
V	20	1200
VI	22	1200

Table 5. Chemical resistance of the alkyd resins

Alkyd sample	Medium			
	Distilled H_2O	NaCl (50% solution)	H_2SO_4 0.1 M	KOH 0.1 M
I	c	a	b	d
II	b	a	b	d
III	c	a	b	d
IV	a	a	a	e
V	a	a	a	e
VI	a	a	a	e

[a] no effect; [b] whitening; [c] shrinkage of film; [d] shortening of film; [e] removal of film

Table 6. Estimated solution parameters of the alkyd samples

Alkyd sample	Intrinsic viscosity [η] (cm^3/g)	Huggin's constant (K_H)	Number average molecular weight (M)
I	0.0469	0.546	899.87
II	0.0442	4.914	412.06
III	0.0320	3.906	316.97
IV	0.0441	0.926	486.52
V	0.0313	2.450	500.17
VI	0.0359	2.040	571.63

IV-VI, except for sample **V**. Values of the Huggin's constant (K_H) do not show regular order of variation.

Conclusion

Alkyd resins from crude samples **I-III** and refined samples **IV-VI** of rubber seed oils have been prepared. In addition to the yield of bright coloured oil, refining also decreased the level of acidity by over 50%, increased the level of unsaturation as estimated by iodine value, and increased the solid content of the finished alkyds. The alkyd samples formulated with the refined oil were observed to produce harder films. The drying time and chemical resistance of the alkyd films were greatly enhanced by refining. Therefore, refining of rubber seed oil intended for alkyd production may be explored further.

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