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# Preparation, characterization and evaluation of jojoba seed oil-modified alkyd resins

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**ABSTRACT**

*Jojoba oil is a source of specially chemicals and its uses for industrial applications are gaining in adaptability and importance. Four different alkyd resins modified by various amount of jojoba seed oil (JSO) were prepared by an alcoholysis-polyesterification process. The effect of oil contents on properties such as the drying performance, thickness of film, solubility, viscosity and color of the alkyd resins was evaluated. The alkyd with the least oil content had the greatest viscosity and lightest colour as well as the most rapid drying property. The jojoba-alkyds were found to be comparable with commercial samples. Their films were resistance to water, alkali, acids and solvents as well as gloss %, adhesion, impact, hardness, bending and flexibility. Incorporation of jojoba oil into alkyd resin prooved to achieve good mechanical characteristics and high chemical resistance to these resins.*

**Keywords:** Jojoba seed oil; Alkyd; Resin, Chemical resistances; Mechanical properties.

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## INTRODUCTION

***Alkyd resins*** have been introduced in the 1930s as binders for paints. Their compatibility with many polymers and the extremely wide formulating latitude made them suitable for the production of a very broad range of coating materials. This includes do-it-yourself paints and varnishes for wood and metal, road marking paints, anticorrosive paints, nitrocellulose lacquers, two-component isocyanate curing coatings, acid curing coatings, stoving enamels, etc. Except for phthalic anhydride, being of petrochemical origin, the other raw materials used in the synthesis of the alkyds are from biologically renewable sources. This, combined with their biological degradability, makes them very interesting binders from an ecological point of view. Solvents which are used to reduce and adjust the paint viscosity are the only concern with respect to the ecological aspects of the alkyds paints. In recent years, however, we witness quite an activity in designing alkyd emulsions and high solids alkyds which can serve as binders for environmentally friendly coatings.[1]

***Alkyd resins*** are the reaction products of polybasic acids, polyhydric alcohols and monobasic fatty acids or oils. It is a chemical combination between oil or oil-derived fatty acids and polyester polymer, thus enhancing the mechanical properties, drying speed durability of these oleoresinous vehicles formed over and above those compared with the oil themselves. These resins, today comprise about half of all resins used in the surface coating industry.

In spite of a large number of other synthetic resins being available for use in paint formulations, the alkyd resins surpassed all of them in versatility and low cost together with a broad spectrum of performance properties.

It is possible to produce alkyds with greatly improved resistance to hydrolysis by the use of acid containing sterically hindered carboxyl groups , such as the “ versatic acids ” . These are a mixture of heavily branched aliphatic acids with 9 to 11 carbon atoms and with most ( > 93% ) of carboxylic groups attached to a quaternary carbonation.

Oil modified alkyd resins are made with drying semidrying and non-drying oils. The type of oil selected depends on the conditions under which the film will be dried and the color retention properties required in the film. Air drying alkyds are made with the good drying oils such as linseed oil and dehydrated castor oil, but semidrying soya bean oil may also be used in medium and short – oil alkyds. In general, soyabean oil – modified alkyds are not satisfactory for air –drying varnishes [2].

Various vegetable oil sources that are used for alkyd preparation include tall oil, soya oil and many others; a common property of these oils is their high degree of unsaturation. Also, examples of polyhydric alcohols are glycerols, ethylene glycol, pentaerythritol and trimethylolpropane while the commonly used acids/anhydrides are phthalic anhydride, isophthalic anhydride and maleic anhydride [3]. The oil chosen for the production of alkyds usually has a profound effect on the properties of the finished alkyds[4], and they are used in an air-drying water-reducible lacquer formulation[5].

Modified alkyd resin lacquers were prepared from Soya oil, pentaerythritol, phthalic anhydride and Dacron by mixing with pigments, talc and a diluent and a drying agent, milled and filtered to form modified alkyd resin - based paints [6] .

In most developing countries, food-grade oils are used in industrial production, leading to a reduction in the amount available for human consumption. In order to reduce the demand for food-grade oils that are used in industrial production, there is a need to explore new sources of oil.[7]

*Jojoba oil* is a natural product extracted from the seeds of a slow-growing perennial desert shrub. This oil is unique compared with commercial oils coming from soybeans, corn, peanuts, and olives, because it contains the esters of fatty acids with straight chain fatty alcohols and not of glycerol with fatty acids. Jojoba oil is mainly composed of the monoesters of $C_{20}$ and $C_{22}$ acids and $C_{20}$ and $C_{22}$ alcohols, with one double bond on each side of the ester bond. The oil has found a wide range of important industrial and cosmetic applications, but one is of special interest, the possibility to replace sperm whale oil.[8-12]

Jojoba plants and jojoba oil are promising for the following reasons:
1. Jojoba seeds contain 50% of its weight as oil.
2. Jojoba raw oil has special distinguishing features compared to other vegetable oils, such as:
(i) It contains a volumetric composition of 97% of waxed ester and 3% of free fatty acids, alcoholic acids and anti-oxidation compounds named Tokofyrole.
(ii) Jojoba oil molecules have a carbon chain containing 20–22 carbon atoms.
(iii) This oil is considered a liquid wax with a pleasant smell, constant viscosity with temperature, very high resistance to rancid and very high resistance to oxidation.[13] The aim of this paper is to prepare and evaluate jojoba seed oil-modified alkyd resins.

## MATERIALS AND METHODS

### 2.1. Materials

Jojoba seed oil was obtained from the local market.Technical grade phthalic anhydride, glycerol, benzoic acid and calcium carbonate were obtained from commercial sources and used in the preparation of alkyds without purification. Also, reference alkyd resins were commercial products from the local market. Potassium hydroxide, sodium sulphate anhydrous, phenolphthalein, glacial acetic acid, pyridine, iodine and sodium hydroxide were chemically pure grade obtained from EL-Fayrouz Int.trading Co. All other reagents and solvents used throughout this study were chemically pure grade.

### 2.2. Physicochemical properties

Physicochemical properties of jojoba seed oil (e.g., acid value, saponification value, iodine value, density and viscosity) were determined according to relevant ASTM standards[14,15]. Table(1)

**Table 1: Physicochemical properties of jojoba seed oil**

| Properties | Result |
|---|---|
| Acid value (mg KOH/g) | 2.0 |
| Saponification value (mg KOH/g) | 100 |
| Iodine value (g I2/100 g) | 95 |
| Density (g/cm3) | 0.94 |
| Viscosity (poise) | 38.6 |

### 2.3. Preparation of alkyds

Four different alkyds having oil contents of 35% (w/w), 47% (w/w), 60% (w/w) and 78% (w/w) were prepared using a two-stage alcoholysis-polyesterification method. [16,17]

The alkyds were labeled as follows: J-AKD 1 (36% oil); J-AKD 2 (47% oil); J-AKD 3 (59% oil); J-AKD 4 (78% oil). In preparing each of the alkyd, a known weight of jojoba seed oil was heated to a temperature between 220°C and 240°C. Glycerol (14.8 g), and 0.2 g calcium carbonate were added while maintaining the temperature at about 240°C.

The completion of alcoholysis was monitored by taking samples of the reaction mixture every 5 min. Each sample was mixed with anhydrous methanol in a 1:1 volume ratio until a clear solution was obtained which indicated the end of alcoholysis process. [18]

After completion of the alcoholysis stage, phthalic anhydride (25g) and benzoic acid (4.8g) were added and the reaction continued at about 240°C. The reaction was moinitored by acid value determination every one hour until a value of 10 was reached, then the reaction was quenched by immersing the reaction vessel in cold water. Benzoic acid was included in the preparation of alkyds to obtain products with reduced drying times, and since it is monofunctional it also acts as chain terminating agent thus preventing the tendency towards gelling. Nitrogen was used to blanket the surface of the reaction mixture during the reaction. The amount of the various ingredients are shown in table 2.

**Table 2: Formulations of the different alkyd resins**

| | J-AKD 1 (36% oil Content) | J-AKD 2 (47% oil content) | J-AKD 3 (59% oil Content) | J-AKD 4 (78% oil Content) |
|---|---|---|---|---|
| JSO (g) | 25.0 | 39.9 | 64.7 | 156.0 |
| Phthalic anhydride(g) | 25.0 | 25.0 | 25.0 | 25.0 |
| Glycerol (g) | 14.8 | 14.8 | 14.8 | 14.8 |
| CaCO3 (g) | 0.2 | 0.2 | 0.2 | 0.2 |
| Benzoic acid (g) | 4.8 | 4.8 | 4.8 | 4.8 |

### 2.4. Evaluation of alkyd resins

The solubility, cure time, acid value, and drying performance tests as well as solidification time and thickness for the products were carried out using standard methods[19]. Moreover, the prepared alkyds as well as two commercial alkyds of unknown compositions were separately formulated and their characteristics were compared. (table 3)

**Table 3: Physicochemical properties of the alkyds**

| Alkyd sample | Colour | Acid value (mg KOH/g) | Iodine value (g $I_2$/100 g) | Viscosity (cp) | Thickness of film (mm) | Solidification time (s) |
|---|---|---|---|---|---|---|
| J-AKD 1 | Yellow | 32.2 | 17.6 | 10.0 | 0.047 | 30 |
| J-AKD 2 | yellow | 33.4 | 11.2 | 14.0 | 0.039 | 40 |
| J-AKD 3 | light brown | 5.40 | 19.0 | 25.0 | 0.042 | 45 |
| J-AKD 4 | light brown | 12.1 | 26.9 | 30.0 | 0.051 | 50 |
| C-AKD | brown | 25.8 | 66.2 | 10.0 | 0.019 | 40 |
| L-AKD | brown | 35.6 | 64.4 | 12.5 | 0.019 | 45 |

#### 2.4.1. Preparation of test panels:

Glass and mild steel plates (50 x 150 mm) were degreased by dipping into petroleum ether, then the surfaces were cleaned by fine cloth, washed and wipped. The plates were washed with ethyl alcohol and allowed to dry in air. Films were applied onto clean plates and left for half an hour to remove slowly the greatest part of the solvent and then stoved at the required temperature for the specified time in a thermostatically controlled well – ventillated oven.

The J-AKD compounds were thinned to brushable consistency and appropriate quantities of cobalt and lead octoate driers were added. Coating were applied on previously prepared mild steel and glass panels with a brush to obtain a uniform coat. Drying on film formation of coatings were carried out at room temperature, 80˚C, 100˚C and 150˚C for one hour (table 4).

Each run was performed in triplicates.

**Table 4 :Drying Characteristics of the alkyds**

| Resins | Air drying (days) | Stoving at 80˚C 1 hr | Stoving at 100˚C 1 hr | Stoving at 150˚C 1 hr |
|---|---|---|---|---|
| J-AKD 1 | >7 | T | D | HD |
| J-AKD 2 | >7 | T | D | HD |
| J-AKD 3 | >7 | T | D | HD |
| J-AKD 4 | >7 | T | D | HD |
| C-AKD | 1 | VST | ST | D |
| L-AKD | 1 | ST | D | HD |

***VST*** *Very Slightly Tackiness* ***ST*** *Slightly Tackiness*
***T*** *Tacky* ***D*** *Dry* ***HD*** *Hard Dry*

### 2.4.2. Evaluation of film characteristics:

#### 2.4.2.1. Film resistance

Water, alkali (10% NaOH) resistance acid (10% HCl, 20% $H_2SO_4$) resistance and solvents (acetone, ethanol, methanol, ethyl methyl ketone, and toluene) resistance were carried out according to standard methods.[20-22](table 5)

**Table 5: Film Resistance of the alkyds**

| *Alkyd resins* | *Water resistance* (monthes) | *Alkali resistance (10% NaOH)* (hours) | *Acid resistance* (monthes) | | *Solvents resistance* (monthes) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | *HCl 10%* | *$H_2SO_4$ 20%* | *Acetone* | *Methanol* | *Ethanol* | *Ethyl methyl ketone* | *Toluene* |
| J-AKD 1 | >3 | 1 | >3 | >3 | >3 | >3 | >3 | >3 | >3 |
| J-AKD 2 | >3 | 3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 |
| J-AKD 3 | >3 | 4 | >3 | >3 | >3 | >3 | >3 | >3 | >3 |
| J-AKD 4 | >3 | 6 | >3 | >3 | >3 | >3 | >3 | >3 | >3 |
| C-AKD | >3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| L-AKD | >3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

#### 2.4.2.2. Mechanical tests:

After tack-free drying, the film properties such as: bending test, adhesion (tape test), impact, gloss and scratch hardness by pencil test, were determined by standard methods.[23-27] (table 6)

**Table 6:Mechanical properties of the alkyds:**

| Alkyd Resins | *Gloss % at 60 ˚* | *Adhesion test* | *Impact* | *scratch hardness* | *Bending test* |
|---|---|---|---|---|---|
| J-AKD 1 | 40 | good | pass | 2H | pass |
| J-AKD 2 | 46 | good | pass | 2H | pass |
| J-AKD 3 | 50 | good | pass | 2H | pass |
| J-AKD 4 | 56 | good | pass | 2H | pass |
| C-AKD | 119 | good | pass | 2H | pass |
| L-AKD | 100 | good | pass | 2H | pass |

## RESULTS AND DISCUSSION

### 3.1. Physicochemical properties of jojoba seed oil

The properties of the JSO are shown in table 2. The iodine value (95) indicates a level of unsaturation that may consider the oil as semi-drying. It is noteworthy that the degree of unsaturation of the oil is directly related to the drying property of the alkyds.

### 3.2. Preparation of jojoba seed oil-modified alkyd resins:

The alcoholysis was carried out by heating jojoba seed oil with glycerol to 240˚C for about 4 hours in the presence of calcium carbonate as catalyst until a clear solution was obtained. The time needed for the alcoholysis step was dependent and is nearly proportional to the percentage of oil contents. Thus the relationship between the percentage of oil used in the alkyd formula and the time taken for alcoholysis may be used to estimate the time taken for the alcoholysis reaction of JSO for different percentage of oil (Fig 1).

Polyesterfication was conducted by heating a mixture of phthallic anhydride and benzoic acid to the product obtained from the alcoholysis step until the acid value was dropped about 10. The change of the acid value during the polyesterfication process is illustrated in Fig 2 which shows that acid value decreases gradually with time of polyesterfication until it reaches a minimum after about 4 hours.

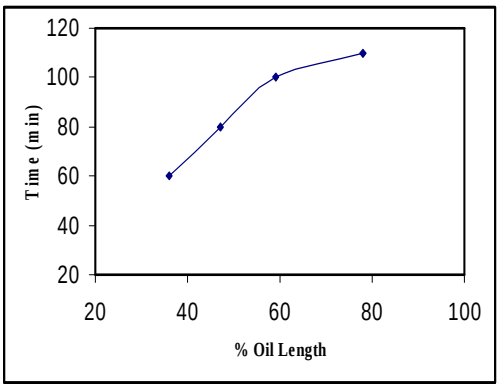


**Fig.1. Percentage oil content versus time of alocholysis**

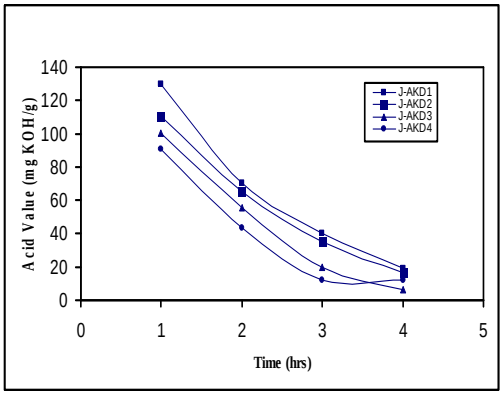


**Fig. 2. Change of acid value during polyesrification.**

### 3.3. Evaluation of alkyd resins prepared:

The alkyd resins were tested for viscosity, thickness and solidification time. J-AKD 1 is more viscous than the other prepared resins this is probably due to a high extent of polymerization in the preparation of this resin.

Physicochemical properties of the alkyds prepared and the commercial standards are shown in Table 3. The acid values, the viscosities and the solidification times of the alkyds are comparable with those of the commercial standards C-AKD and L-AKD. They are lighter in color than those of the commercial standards so they are recommended for special applications. J-AKD 4 has the greatest film thickness owing to its relative high viscosity and a possible high degree of polymerization.

Table 4 shows the drying characteristics of alkyd resin solutions containing cobalt and lead octoate driers in air, at 80˚C, 100˚C and 150˚C for one hour and it is clear that stoving at 100˚C for one hour gives dry films (D) and raising the temperature to 150˚C produces hard dry films (HD).
The alkyd resin films resist water, acid (10% HCl, 20% $H_2SO_4$) and solvents (acetone, ethanol, methanol, ethyl methyl ketone, and toluene) and they show no change for more than three monthes, while alkali (10% NaOH) resistance is poor as ester groups are readily attacked by alkalies and hydrolyzed by acids.(table 5)

The alkyd resin films exhibited good overall mechanical properties, e.g. gloss, adhesion, impact, scratch hardness, bending tests.(table 6)

## CONCLUSION

The jojoba oil plant has been successfully converted to alkyd resins. The alkyds thus obtained gave good drying performance both as clear and pigmented coatings. Also, they are closely comparable with the commercial alkyds samples in their performances.

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