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Physicochemical Characterization of Medium Alkyd Resins Prepared with a Mixture of *Linum usitatissimum* L. and *Plukenetia volubilis* L. Oils

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Abstract**—**Alkyds have become essential raw materials in the coating and paint industry, due to their low cost, good application properties and lower environmental impact in comparison with petroleum-based polymers. The properties of these oil-modified materials depend on the type of polyunsaturated vegetable oil used for its manufacturing, since a higher degree of unsaturation provides a better crosslinking of the cured paint. *Linum usitatissimum* L. (flax) oil is widely used to develop alkyd resins due to its high degree of unsaturation. Although it is intended to find non-traditional sources and increase their commercial value, to authors' best knowledge a natural source that can replace flaxseed oil has not yet been found. However, *Plukenetia volubilis* L. oil, of Peruvian origin, contains a similar fatty acid polyunsaturated content to the one reported for *Linum usitatissimum* L. oil. In this perspective, medium alkyd resins were prepared with a mixture of 50% of *Linum usitatissimum* L. oil and 50% of *Plukenetia volubilis* L. oil. Pure *Linum usitatissimum* L. oil was also used for comparison purposes. Three different resins were obtained by varying the amount of glycerol and pentaerythritol. The synthesized alkyd resins were characterized by FT-IR, and physicochemical properties like acid value, colour, viscosity, density and drying time were evaluated by standard methods. The pencil hardness and chemical resistance behaviour of the cured resins were also studied. Overall, it can be concluded that medium alkyd resins containing *Plukenetia volubilis* L. oil have an equivalent behaviour compared to those prepared purely with *Linum usitatissimum* L. oil. Both *Plukenetia volubilis* L. oil and pentaerythritol have a remarkable influence on certain physicochemical properties of medium alkyd resins.

Keywords**—**Alkyd resins, flaxseed oil, pentaerythritol, *Plukenetia volubilis* L. oil, protective coating.

I. Introduction

ORGANIC coatings have been extensively applied for the protection ,of metal structures against corrosion [1]. Resins or binders are the most important components of a coating, because they agglomerate all nonvolatile components, provide adhesion forces between the protective layer and the substrate, and govern the physicochemical properties of the coating film [2]-[5].

Alkyd resins have become an indispensable class of synthetic polymers in the paint industry [6]. They have increased their popularity due to their cost effectiveness, versatility, and availability of basic raw materials [7]. In most conventional oil-based alkyd synthesis, a polyalcohol and a multi-functional acid react with a rich source of fatty acids to form a polyester backbone [8]. Nowadays, most of their components are biologically renewable sources, which contribute to the replacement of fossil fuels and consequent reduction of the greenhouse effect [9].

Alkyd resins are classified as short (30-42%), medium (43-54%), long (55-68%), and very long (> 68%), based on the percent weight fraction of vegetable oil in the resin [8], [9]. The use of medium-oil chain length alkyd resins is recommended for the manufacture of maintenance paints [10]. Vegetable oils with a high content of unsaturated fatty acids, such as soya bean oil, dehydrated castor oil, linseed oil, and Tung are common sources for alkyd resin formulation [7]. However, other non-traditional sources, such as karanja oil [12] and yellow oleander [13], etc., are being investigated as potential sources for alkyd resins synthesis.

The present study reports the characterization of alkyd resins prepared with *Plukenetia volubilis* L. oil, also known as sacha inchi oil. This seed from the Euphorbiaceae family grows in the Peruvian Amazonian forest [14]. Currently, sacha inchi seeds are used for the production of oils, cakes and protein meals, and as a high quality raw material for the cosmetic, food and medicine industry [15]. Sacha inchi oil contains approximately 36% linoleic acid and 47% linolenic acid [16]. Due to the similarity of the unsaturated fatty acid content of sacha inchi oil with flaxseed oil, the objective of this study is to investigate its use for the manufacture of alkyd resins.

II. Experimental Details

A. Materials

Extra virgin sacha inchi oil was supplied by Amazon Health Products, Peru. Extra virgin flaxseed oil was purchased from a Peruvian local market. Fatty acid composition of both oils is summarized in Table I. The fatty acid content of sacha inchi oil was obtained from the product quality certificate, whereas, flaxseed oil composition, from the product´s nutritional information.

Analytical grade glycerol, phthalic anhydride (≥ 98%) (PA), lithium carbonate (≥ 99%), phenolphthalein, potassium hydroxide, potassium hydrogen phthalate, 2-propanol, ethanol, hydrochloric acid (37%), sodium hydroxide, and sodium chloride were acquired from Merck, Germany. Pentaerythritol

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(98%) was obtained from Sigma-Aldrich, U.S.A. p-Xylene was procured by Avantor Performance Materials S.A. de C.V., Mexico. Cobalt (12%) and zirconium (24%) octoate were procured from Arc Chemicals Private Limited, India.

TABLE I
FATTY ACID COMPOSITION OF VEGETABLE OILS

Fatty acid %	*Plukenetia volubilis* L. oil	*Linum usitatissimum* L. oil
Saturated	7.59	9.80
Polyunsaturated	80.75	68.70
Monosaturated	11.46	20.40
18:0	11.27	19.94
18:2	37.07	19.20
18:3	43.49	49.47

B. Synthesis of Alkyd Resins

Three different medium-oil alkyd resins (54 w.t. % of the total oil) were synthesized by a two stage alcoholysis-polyesterification method with different glycerol (GC): pentaerythritol (PE) weight ratios. A-1 contains 1:0 GC: PE; A-2, 0.5:0.5 GC: PE; A-3, 0.2:0.8 GC: PE. Letter M identifies alkyds prepared with both oils, whereas letter F, pure flaxseed oil-based resins.

The mixture of oils, 50% of *Linum usitatissimum* L. oil and 50% of *Plukenetia volubilis* L. oil, the respective polyalcohol/ mixture of polyalcohol, and lithium carbonate (0.4 wt. % with respect to the oil) were charged into a 500 mL four-necked round-bottom flask equipped with a motorized stirrer, thermometer, nitrogen inlet tube, and a Dean-Stark trap with a condenser. The reaction mixture was stirred constantly, with nitrogen bubbling and a temperature between 220-240 °C. Complete solubility of the reaction mixture in ethanol (resin/ ethanol 1:3 v/v) confirmed the completion of the first stage. In the second stage, acid anhydride was added. Xylene (12.5%, v/w on raw materials) was used as an azeotropic solvent to remove water, formed byproduct. The reaction was monitored by the acid value until reaching a final value between 3-15 mg KOH/g of resin. Similar procedure was adopted for the synthesis of pure flaxseed oil-based resins [17].

C. Characterization of Alkyd Resins

The following physicochemical properties were evaluated: acid value (ASTM D1639), viscosity (ASTM D1545), colour (ASTM D1544), density (ASTM D1475), drying (ASTM D1640), film hardness (ASTM D3363). Gardner bubble time method was used for viscosity measurements; A range from the lower (Z1) to the highest (Z10) viscosity was used. For colour analysis, Gardner scale from lighter yellow (N°1) to dark brown (N°8) was employed.

Alkyd structural verification was carried out by Infrared spectroscopy (FTIR) with a Perkin–Elmer Spectrum Two FTIR Spectrometer, from 4000 to 400 cm^{-1}.

To catalyse the curing process of alkyd resins, cobalt octoate (12% metal content, 0.50 wt. %) and zirconium octoate (24% metal content, 0.75 wt. %) were mixed with uncured alkyd solutions (90% solids). Cured films were obtained by applying the mixture of the resin with the driers on glass plates with a 30 µm Erichsen manual film applicator. They were allowed to dry for a week under laboratory conditions (22–23 °C and 60-70% relative humidity (RH)).

Pencil hardness test was used to determine film hardness (scale from soft (6B) to hard (6H)) of cured films). Besides, their chemical resistance was studied on distilled water, sodium hydroxide (1% (w/v) NaOH), hydrochloric acid (10% (v/v) HCl), sodium chloride (10% (w/v) NaCl) and ethanol for 3 days. The test was performed in duplicate. After immersion tests, hardness of samples were also evaluated.

Results on the characterization of flaxseed oil-based alkyd resins, reported in [17], are presented for comparison purposes.

III. RESULTS AND DISCUSSION

Infrared spectra of medium-oil alkyd resins were recorded on the FTIR spectrometer. Distinctive peaks are identified in Fig. 1. All the samples had strong absorption bands at 1733 cm^{-1}, characteristic of the presence of ester bonds, from both the carbonyl and phthalate groups [18], [19]. Moreover, the presence of peaks between 1582 and 1601 cm^{-1} related to C-C stretching frequencies of C=C alkene and aromatic bands [20], [21] corroborated the presence of the phthalate system in the resins. Meanwhile, the presence of fatty acids chains from the vegetable oil was confirmed by the appearance of a characteristic peak at 3007 cm^{-1}. Results suggested a successful obtainment of alkyd resins.

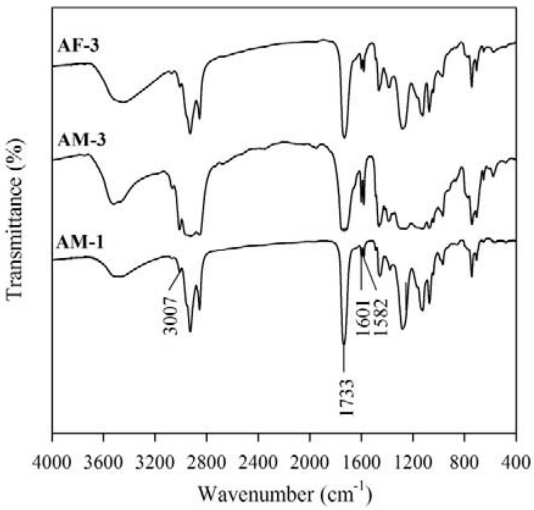

Fig. 1 FTIR spectra of medium-oil alkyd resins

Some properties of the alkyds prepared (90% solids) and their counterparts based on flaxseed oil are shown in Table II. Generally, all resins had a density close to 4 kg/gallon. We decided to keep the acid numbers upper than 10 in the case of resins with the highest amount of PE (e.g. AM-3) to avoid gelation; the high functionality of PE makes the mixture more reactive during the synthesis process [17]. There was no noticeable influence when introducing sacha inchi oil. However, changes in colour and viscosity were observed.

It is clear that the presence of sacha inchi oil decreases the tonality of alkyd resins. From the beginning, sacha inchi oil maintains a lighter colour than flaxseed oil. Besides, it has been reported that this Peruvian oil contains a high content of tocopherols and bioactive compounds [22] that could contribute to decrease the probability of oxidation of the oil during heating. Resins with the highest amount of PE had similar colours, maybe due to the longer times to complete the synthesis reaction (Fig. 2). We also observed that resins containing sacha inchi oil and PE exhibited higher viscosities (Table II). The four hydroxyl reactive groups of PE are responsible of creating branches, possibly influencing the final viscosity [7]. Moreover, it is worth mentioning that sacha inchi oil has a higher amount of linoleic acid (Table 1), increasing the active reaction sites during the cross-linking process [23].

TABLE II
PHYSICAL PROPERTIES OF ALKYD RESINS

Resin	Acid value (mg KOH/g resin)	Density (kg/gallon)	Colour (Gardner)	Viscosity (Gardner)
AM-1	2.9	3.99	14	Z6-Z7
AM-2	4.8	4.00	5	Z6-Z7
AM-3	12.1	3.89	13	Z8-Z9
AF-1	3.0	3.95	16	Z6-Z7
AF-2	3.9	4.00	10-11	Z5-Z6
AF-3	16.8	3.92	13	Z6-Z7

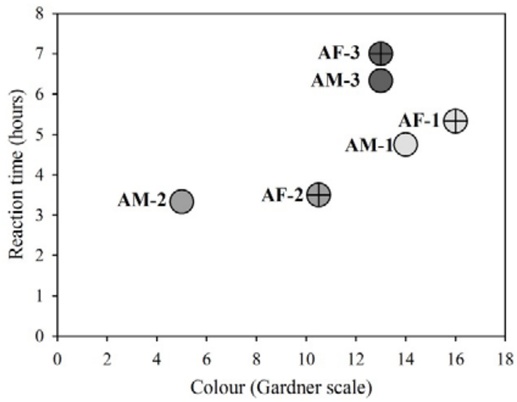

Fig. 2 Influence of the reaction time on the colour of alkyd resins

Table III contains properties, such as drying times and pencil hardness, of alkyd films under study. As it can be appreciated, the addition of *Plukenetia volubilis* L. oil does not alter the properties of the cured resins. Sacha inchi oil slightly decreases the drying time of resins with more PE. Moreover, we observed that the drying time increases as there is more PE in the resin. This tendency may be due to the fact that the cross-linking of branched chains can interfere with the entry of oxygen throughout the film. The pencil hardness of cured films does not change if sacha inchi oil is added. It is confirmed that a higher percentage of PE increases the hardness of the alkyd resin film [7].

The chemical resistance performances of cured alkyds under different aggressive environments are given in Table IV. Weight loss and visual defects, like whitening, blisters, wrinkles and/or total removal of film, were used as criteria for classification. The alkyds films were highly resistant to acid and salt solutions, whereas exhibited a poor performance in ethanol, due to their loss of adhesion. They only had a good resistant to distilled water, because the films become opaque in contact with that medium. Their poor alkali resistance may be related to the presence of hydrolysable ester groups in alkyds' structure [24].

TABLE III
FILM PERFORMANCE PROPERTIES OF ALKYD RESINS

Resin	Dry-to-touch time (h)	Dry-hard time (h)	Pencil hardness
AM-1	2.0	3.5	2H
AM-2	5.8	7.8	2H
AM-3	7.8	8.8	4H
AF-1	2.0	4.0	2H
AF-2	5.8	7.3	2H
AF-3	9.5	11.3	4H

TABLE IV
CHEMICAL RESISTANCE OF CURED ALKYDS

Resin	Alkali	Acid	Salt	Distilled water	Solvent
AM-1	Poor	Excellent	Excellent	Good	Poor
AM-2	Poor	Good	Excellent	Good	Poor
AM-3	Poor	Excellent	Excellent	Good	Poor
AF-1	Poor	Excellent	Excellent	Fair	Poor
AF-2	Poor	Excellent	Excellent	Good	Fair
AF-3	Poor	Excellent	Excellent	Good	Poor

After chemical resistance tests, pencil hardness was also evaluated. Results were compared with the initial hardness values (control), as seen in Table V. We found that samples classified with an excellent chemical resistance (Table IV) do not necessarily maintain their hardness after the immersion tests. In acidic medium, there was no variation as drastic as the one we observed in salt solution.

TABLE V
FILM HARDNESS VARIATION AFTER CHEMICAL RESISTANCE TESTS

Resin	Control	Acid	Salt	Distilled water	Solvent
AM-1	2H	2B	4B	2B	HB
AM-2	2H	HB	2B	HB	HB
AM-3	4H	2B	HB	HB	2H
AF-1	2H	HB	<6B	HB	HB
AF-2	2H	HB	2B	HB	2B
AF-3	4H	HB	HB	2B	2H

In the last case, the presence of sacha inchi oil apparently reinforced the film, whereas the samples prepared with flaxseed and GC were easily peeled off the glass plates with a pencil with the lowest hardness (6B) [17]. Samples in distilled water did not experience extreme hardness changes, as well as in a solvent. It should be noted that alkyd films recovered their adhesion after being immersed in ethanol.

IV. CONCLUSION

From this study, it can be concluded that *Plukenetia volubilis* L. oil possesses the necessary characteristics to be used as a raw material for the production of alkyd resins. FTIR spectroscopy revealed the successful obtaining of medium alkyd resins based on *Plukenetia volubilis* L. oil and *Linum usitatissimum* L. oil. As an advantage over resins purely prepared with flaxseed oil, the presence of sacha inchi oil clarifies the colour of the resins and increases their viscosity. Sacha inchi oil does not adversely affect the hardness, density, drying or chemical resistance of alkyd resins. On the other hand, PE extends the drying time and increases the alkyd films' hardness. The mixture of PE with *Plukenetia volubilis* L. oil improves the performance of cured alkyd resins in saline solutions.

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