Synthesis, Characterization, and Application of Lesquerella Oil and Its Derivative in Water-Reducible Coatings

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Lesquerella oil (LO), a domestically produced vegetable oil of hydroxy fatty acid composition, has been used as a raw material for the synthesis of novel, water-reducible polyester coatings. The properties of these and castor oil derived polymers have been compared. Accordingly, polyesters of acid values approaching 50 were synthesized from LO, dehydrated lesquerella oil (DLO), castor oil (CO), and dehydrated castor oil (DCO). Aqueous solutions of the polyesters were prepared and used as ingredients in the formulation of industrial melamine-polyester baked coatings and air-dry polyester coatings. They were applied, cured, and their properties evaluated. The LO and CO derived coatings were comparable in pencil hardness, adhesion, gloss, and gloss retention properties. However, coatings from LO were superior in flexibility and ultraviolet stability.

INTRODUCTION

Castor oil (CO) and its ricinoleic acid derivatives are widely used for the manufacture of lubricants, plastics, coatings, and pharmaceutical supplies.[1] The annual consumption by U.S. industries is nearly 90 million pounds or nearly one-seventh of the total world export of castor oil. All CO consumed by the U.S. is imported and its price is generally higher than common domestic vegetable oils. Therefore, there is sufficient reason to consider dependable domestic alternatives that can deliver cost and/or performance comparable to those provided by CO.

The relatively high concentration of hydroxy fatty acids in the seed oils of *Lesquerella* makes it an attractive candidate for a castor oil replacement.[2] The seed of *L. fendleri*, the species under breeding and agronomic development in Phoenix, AZ, contains in excess of 25% oil by weight of which approximately 55% is lesquerolic (14-hydroxy-11-eicosenoic) acid, the C_{20} homologue of ricinoleic acid.[2] Thus, this higher carbon content fatty acid is an ideal reactant for polymer synthesis and modification to a value-added, industrial raw material.[3]

Accordingly, our study focuses on the commercialization of lesquerella oil (LO) as a raw material for novel surface coating products. Initial efforts resulted in the synthesis of dehydrated lesquerella oil (DLO) which we have found to be a good drying oil. The polyesters from LO provided attractive coatings demonstrating comparable pencil hardness, gloss, and gloss retention properties, but the flexibility was superior to CO counterparts. In summary, we have prepared and tested novel water-reducible LO derived polyesters as candidate industrial coatings.

EXPERIMENTAL

Materials

Lesquerella oil (refined *Lesquerella fendleri*) was purchased from International Flora Technology, Ltd. Sodium bisulfate, phthalic anhydride (PA), maleic anhydride (MA), trimethyolpropane (TMP), pentaerythritol (PE), diethanolmethylamine (DEMA), 2-butoxyethanol (BE), and xylenes were purchased from Aldrich Chemical Company. Ammonium hydroxide was purchased from Fisher Chemical Company. The esterification catalyst, lithium ricinoleate, was purchased from Pfaltz & Bauer. Dehydrated castor oil was supplied by Welch, Holme & Clark Company. Resimene 747, a melamine crosslinking agent, was supplied by Monsanto Chemical Company. The driers, 5% cobalt Hydro-Cure II, 12% zirconium Hydro-Cure, and 5% calcium Hydro-Cure were supplied by Mooney Chemicals. Nacure 155 (dinonylnaphthalene disulfonic acid) was supplied by King Industries. All chemicals were used as received.

Preparation of Dehydrated Lesquerella Oil

In a 500 mL four-necked, round-bottom flask equipped with a nitrogen inlet, mechanical stirrer, and thermometer

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was charged 300 g (0.31 mol) LO and 3 g (0.025 mol) sodium bisulfate. The flask contents were heated to 240°C and was held at this temperature for 90 min to complete the dehydration process. Filtration was affected to remove residual solids, and the acid value, iodine value, and hydroxyl value were determined to be 3.68 mg KOH/g, 146 g of I_2/100 g, and 6.9 mg KOH/g of oil, respectively.

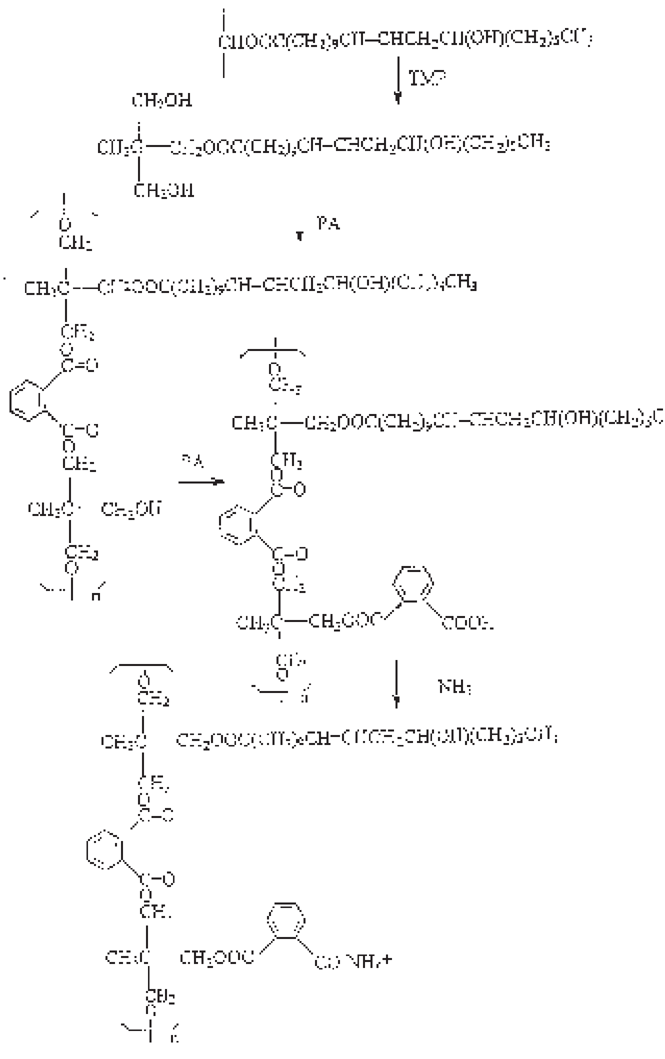
Table 1—Properties of Water-Reducible Polyesters

	WPC36[c]	WPL36[d]	WPDC56[e]	WPDL56[f]
Oil type	CO	LO	DCO	DLO
Oil, g	60.00	60.00	90.00	90.00
Trimethylol propane	51.57	51.57	15.02	15.02
Pentaerythritol, g	—	—	15.25	15.25
Phthalic anhydride, g	62.73	62.73	46.04	46.04
Alkyd constant	1.02	1.02	1.01	1.01
AH type[a]	PA	PA	MA	MA
AH, g	20.06	20.06	12.64	12.64
Non volatiles, %	98.56	98.87	97.52	93.50
Acid value, mg KOH/g	50	52	52	51
Gardner color grade	7	9	9	11
η,[b] cps	1100	450	334	240

(a) Anhydride used to graft extra acid groups to the polyester.
(b) Viscosity of 60% polyester solution in xylenes.
(c) Castor oil based melamine-polyester coating.
(d) Lesquerella oil based melamine-polyester coating.
(e) Dehydrated castor oil based air-drying polyester coating.
(f) Dehydrated lesquerella oil based air-drying polyester coating.

Preparation of Polyester Resins

Two polyester types were synthesized, short-oil polyesters (36% oil length), and long-oil polyesters (56% oil length). In the former case, both LO and CO polyesters were prepared for heat cure melamine-polyester coatings. Similarly, the latter long-oil polyesters utilized DLO and DCO for the chemical reactivity required of polyesters designed for air-dried coatings. The formulations and properties of the polyesters are presented in *Table* 1. The water-reducible polyesters were prepared in two steps (*Scheme* 1). The conventional, solvent-borne polyesters were first synthesized by the monoglyceride process. Subsequently, they were reacted with PA or MA in order to graft hydrophilic carboxylic acid groups into the polymer structure. Neutralization of the acid functionalities was effected with a volatile amine (*Scheme* 1)[4] and gave water-reducible polymers.



Scheme 1—Synthesis of water-reducible polyester.

Polyester Characterization

Acid values were determined according to ASTM D 1639. Viscosities were measured with a Brookfield viscometer, model DV-II at 3 rpm with 60% solids in xylenes at 23°C.

Formulation of Melamine-Polyester Coatings

The LO and CO based short-oil polyesters, WPL36 and WPC36 respectively, and the methylated melamine resin, Resimene 747, were used to formulate melamine-polyester heat cured coatings. The formulations are described in *Table* 2. The polyesters were dissolved in BE to an 80% (w/w) solution. After neutralization with DEMA, dissolution in water was affected (pH=8.3). The remaining reagents were added to the clear solution and agitated with a high-speed mixer. No pigments were employed, and the coatings were evaluated as clear films. Four mil (100 μ) wet films were applied with a drawdown bar onto iron phosphated test panels (type R). The films were heat cured at 170°C for 15 min and equilibrated at ambient for seven days before testing.

Formulation of Air-Dry Polyester Primers

Air-dry polyesters were formulated with DLO and DCO polyester resins, WPDL56 and WPDC56, respectively. The formulation techniques were similar for each ester. For instance, a polyester was dissolved in BE to form a 70% (w/w) solids solution after which 28% ammonium hydroxide solution neutralized the acid groups to pH 8.3. Metal driers were added to accelerate oxidative polymerization. The remaining ingredients were added and agitated with a high-speed mixer (*Table* 2). No pigments were employed, and the coatings were evaluated as clear films. Four mil (100 µ) wet films were applied onto iron phosphated test panels (type R) and were tested after seven days at ambient.

Table 2—Formation of Water Reducible Coatings

	WPC36[f]	WPL36[g]	WPDC56[h]	WPDL56[i]
Polyester, g	53.43	50.05	67.65	67.15
Xylenes, g	0.78	0.57	4.70	4.67
Butoxyethanol, g	12.58	11.94	24.29	24.11
Diethanolmethylamine, g	4.30	4.02	—	—
28% Ammonia, g	—	—	3.81	3.71
Melamine,[a] g	13.64	12.67	—	—
Nacure 155, g	0.75	0.67	—	—
Water, g	48.13	45.06	78.02	71.20
Cobalt drier,[b] g	—	—	1.08	1.07
Zirconium drier,[c] g	—	—	0.84	0.83
Calcium drier,[d] g	—	—	3.38	3.36
pH	8.3	8.3	8.3	8.3
Viscosity,[e] s	68.0	58.0	70.0	68.0
Dry-through time, h	—	—	4.0	3.5
Solids, %	51	51	38	39
VOC, g/L	226	226	326	326

(a) Resimene 747.
(b) 5% Cobalt Hydro-Cure II.
(c) 12% Zirconium Hydro-Cure.
(d) 5% Calcium Hydro-Cure.
(e) Recorded by EZ™ Equivalent "ZAHN" Viscosity Cup #4.
(f) Castor oil-based melamine-polyester coating.
(g) Lesquerella oil-based melamine-polyester coating.
(h) Dehydrated castor oil-based air-dry polyester coating.
(i) Dehydrated lesquerella oil-based air-dry polyester coating.

Coating Characterization

Drying times of air-dry polyester coatings were determined on 3 mil (75 µ) wet films by a Gardner circular drying time recorder. Pencil hardness tests were performed with a Gardco pencil scratch hardness kit according to ASTM D 3363. Adhesion was determined by the cross-hatch tape test, ASTM D 3359. Impact tests were measured with a BYK-Gardner heavy duty impact tester, model #IG-1120, with 1.8 Kg (4 lb) mass and 1.27 cm (0.5 in.) diameter round nose punch. The conical mandrel flexibility was performed according to ASTM D 522. Yellowness indexes were measured by Applied Color System CS-5 chroma-sensor. Ultraviolet (UV) resistance was determined by exposing the coating films in Atlas ultra-violet/condensation screening device equipped with F40 UVB lamps under procedure B specified by ASTM D 4587. Specular gloss was measured by Gardco statistical novoglass. Salt spray testing (ASTM B 117) was performed at 34°C using 5% NaCl in D.I. water solution via a salt spray chamber. Dry film thicknesses were measured by a Gardco mini-test 4000 microprocessor coating thickness gauge.

Glass transition temperature (T_g) measurements were performed with a Mettler DSC 30 differential scanning calorimeter (DSC). An indium metal standard was used to calculate the temperature correction factor. Correction factors were used in the software for all samples. Samples were encapsulated in standard 150 µm aluminum DSC pans and heated from –50° to 300°C under a nitrogen atmosphere at 10°C/min. The T_gs were calculated using the alternate T_g method of Mettler Graphware version 7.1. This method defines the midpoint of the total change in the heat capacity at the T_g.

Infrared (IR) specular reflectance data were collected before and after 500 hr UV exposure test with a Bio-Rad FTS-25 spectrometer resolved to 4 cm^{-1}.

RESULTS AND DISCUSSION

Properties of the polyesters are presented in *Table* 1. The polyesters of LO and CO were designed with similar alkyd constants and acid values. However, the polyesters differed in color grades and viscosities (*Table* 1). For instance, the polyesters of LO and DLO are higher in Gardner color grade, and lower in solution viscosity than their CO counterparts. The darker color is attributed to the higher Gardner color grades of the starting materials, LO and DLO, i.e., 8 and 11, respectively, as contrasted to those for CO and DCO, i.e., 5 and 6, respectively.

Viscosity variations, on the other hand, are likely associated with structural differences of the oils. For instance, LO is composed of approximately 55% lesquerolic acid, while ricinoleic acid makes up 90% of CO. The higher concentration of ricinoleic acid by weight of CO allows extensive hydroxyl hydrogen bonding potential, and consequently higher viscosity.[5] Moreover, LO polyesters may be more effectively "plasticized" by the longer C_{20} fatty acid groups thereby lowering viscosity.

Coating formulations are tendered in *Table* 2. Reagents included BE as co-solvent, DEMA, and ammonium hydroxide for pH adjustments to 8.3.[4]

The curing process of water-reducible, melamine-polyester coatings is complex.[6] For instance, in addition to the traditional crosslinking reactions, e.g., the reaction between hydroxyl (–OH) of polyester resin and methylol ($-NCH_2OH$) of melamine resin, waterborne polymers offer additional crosslinking sites via the carboxyl group (–COOH), i.e., the melamine $-NCH_2OH$ moiety can crosslink with the polyester –COOH groups. Moreover, this latter reaction requires higher curing temperatures than the $-NCH_2OH$ and –OH reaction.[6] In order to determine the appropriate curing profile, the WPL36 melamine-polyester coating was cured at temperatures ranging from 150° to 180°C with variations in cure time of 10 to 20 min. The resulting films were studied via DSC for T_g determinations (*Figure* 1). Films cured at 150°C displayed no major change in T_g when the baking time was increased from 10 to 20 min (167.8° to 168.1°C). When curing was affected at 180°C for 10 min, a final T_g of 175.2°C was

Table 3—Properties of Water-Reducible Coatings

	WPC36[a]	WPL36[b]	WPDC56[c]	WPDL56[d]
Thickness, (µm)	12.77	12.77	12.77	12.77
Crosshatch tape adhesion, D 3359	5B	5B	5B	5B
Pencil hardness, D 3363, scatch/gouge	HB/8H	HB/8H	2B/F	2B/F
Impact resistance, D 2794, direct/reverse, J	18.1/15.8	18.1/18.1	18.1/18.1	18.1/18.1
Conical mandrel, D 522, (0.125 cm)	Pass	Pass	Pass	Pass
MEK double rub resistance	> 400	> 400	10	8
Yellowness index, D 4587	9.00	11.15	6.81	7.91
Gloss (20°), B 523	63	62	85	86
Gloss retention, %	94	97	71	69
Salt fog, B 117	300 hr	300 hr	100hr	100hr
Scribe creep, mm	1	1	< 1	< 1
Scribe blister	No. 2, medium	No. 2, medium	No. 8, medium	No. 8, dense
Surface blister	No. 8, few	No. 8, few	No. 8, medium	No. 8, dense

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(a) Castor oil-based melamine-polyester coating.
(b) Lesquerella oil-based melamine-polyester coating.
(c) Dehydrated castor oil-based air-drying polyester coating.
(d) Dehydrated lesquerella oil-based air-drying polyester coating.

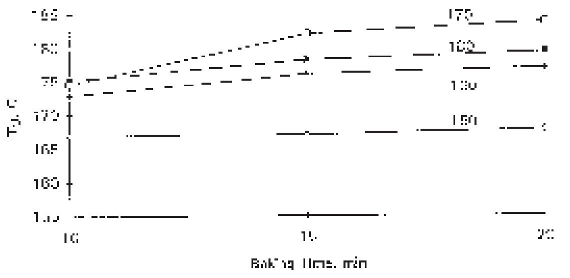

Figure 1—T_g versus baking time for lesquerella oil-based melamine-polyester coatings (WPL36), at different temperatures.

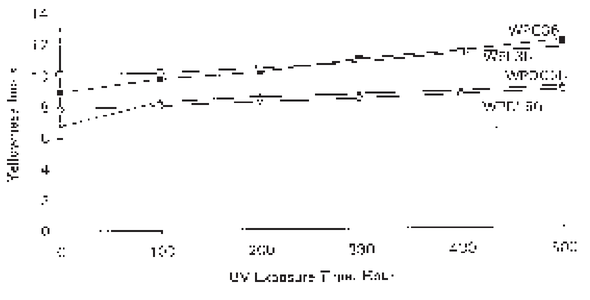

Figure 2—Yellowness index of coating films versus UV exposure time.
WPL36 = Lesquerella oil-based melamine-polyester coating; WPC36 = castor oil-based melamine-polyester coating; WPDL56 = lesquerella oil-based air-drying polyester coating; and WPDC56 = castor oil-based air-drying polyester coating.

recorded. However, at such high temperatures, overbaking can occur resulting in polymer degradation. For instance, *Figure* 1 shows the influence of overbaking at 180°C for greater than 10 min. The resulting films have lower T_g than if they were cured at 170°C for equal time. Accordingly, a cure schedule of 170°C for 15 min was chosen.

Drying properties for the DLO and DCO air-dry polyester coatings are comparable. The dry-through times were recorded as 3.5 and 4 hr for WPDL56 and WPDC56 coatings, respectively.

The physical properties of LO melamine-polyester coatings and DLO air-dry polyester are compared with their CO counterparts in *Table* 3. The LO and CO polyester films exhibited similar pencil hardness and adhesion properties. All coating films possessed excellent adhesion (5B) to the steel substrate. The scratch/gouge cross-cut pencil hardness was HB/8H for heat-cured melamine-polyester coating synthesized from WPL36 and WPC36, respectively, and 2B/F for air-dry polyester coatings made from WPDL56 and WPDC56, respectively. It is not surprising that the long-oil, air-dry polyester coatings were softer than the heat-cured types. The LO short-oil coatings withstood 20 in.-lb (2.3 J) higher impact than the compositionally analogous CO coatings, and all coatings passed the one-eighth inch conical mandrel test.

The heat cured LO and CO polyester-melamine coatings gave excellent MEK double rub data (>400) while the air-dry polyester coatings were less resistant to MEK.

Coatings of LO and CO are comparable in gloss development and gloss retention properties. The thermally cured melamine-polyester coatings retained >95% initial gloss values after 500 hr in the UV condensation cabinet (*Table* 3). The ambient air-cured polyesters retained 70% initial gloss (*Table* 3).

LO polyester coatings were comparable to CO counterparts in the salt spray corrosion evaluations. For instance, the heat-cured LO and CO coatings exhibited 1 mm scribe creep, No. 2 medium scribe blister, and few No. 8 surface blisters after 300 hr salt spray testing. In testing of the air-dry systems, the CO polyester was slightly superior to the LO coating. After 100 hr in salt spray, the CO air-dry coating gave No. 8 medium surface blister while the LO coating exhibited No. 8 dense surface blisters.

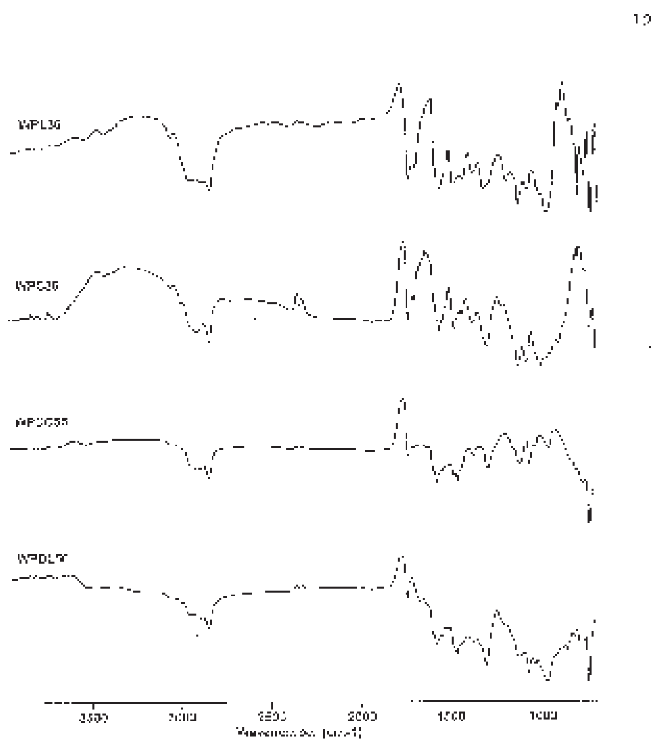

Figure 3—Subtracted IR specular reflectance spectra obtained by subtracting the spectra recorded after 500 hr UV exposure test with their corresponding spectra before UV exposure test.

WPL36 = Lesquerella oil-based melamine-polyester coating; WPC36 = castor oil-based melamine-polyester coating; WPDL56 = lesquerella oil-based air-drying polyester; and WPDC56 = castor oil-based air-drying polyester coating.

The yellowness index (YI), *Figure* 2, of the air-dried polyester coatings was lower than the heat-cured coatings. Both LO and DLO coatings have higher YI values than CO and DCO coatings. Nevertheless, LO seems superior to CO in influencing the YI. For instance, *Figure* 2 confirms a faster increase in YI for CO polyesters than LO coatings tested under identical conditions. Moreover, the CO coatings reached a higher YI than the LO polyesters after 500 hr UV exposure, although the initial YI of the CO polyesters was lower.

Improved UV resistance of LO based coatings was also confirmed via IR specular reflectance analysis (*Figure* 3). IR specular reflectance spectra were recorded for coating films before and after 500 hr UV exposure testing. The former spectrum was subtracted from the latter spectrum in order to determine the absorption differences and highlight changes caused by UV exposure. It is generally known that exposure to UV initiates polymer degradation by oxidation of $-CH_n$ producing various alcohol, carboxyl acid, and aldehyde functionalities.[7] The spectra in *Figure* 3 indicate that compared to WPL36 and WPDL56, WPC36 and WPDC56 possess stronger absorption frequencies at 3000 to 3500 cm^{-1} wavenumber range, which is consistent with –OH and –COOH absorption, and at 1600 and 1780 cm^{-1} corresponding to carbonyl absorption. Further, stronger negative absorbance in the 2800 to 3000 cm^{-1} wavenumber range correspond to decrease in $-CH_n$ absorption. Thus, UV exposure has a greater effect on CO polyesters than the LO analogs.

CONCLUSION

Novel, air-dry, and heat-cure water-reducible polyester polymers were synthesized from LO and DLO. Their physical properties were compared to similar compositions derived from CO and DCO. The comparative study confirmed that LO polyesters were lower in viscosity, but darker in color than their CO counterparts. Waterborne, methylated melamine polyester coatings were studied and a cure schedule of 170°C for 15 min was optimum. The LO and CO polyester coatings were comparable in pencil hardness, adhesion, gloss, and gloss retention properties, however, the LO derived coatings were superior in flexibility and UV stability.

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