ORGANSOSILANES IN LOW VOC COATINGS

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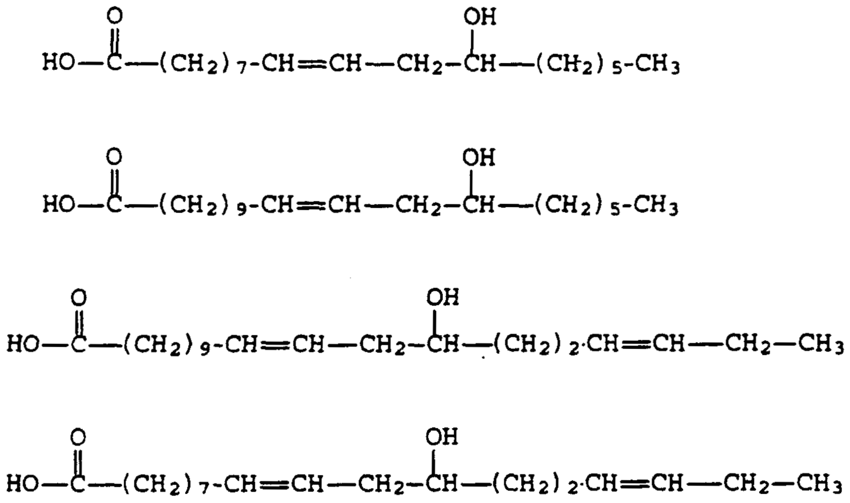
INTRODUCTION

The genus, *Lesquerella*, is a new domestic crop with potential industrial significance, and is native to the Southwest United States. Three hydroxy fatty acids (Figure 1), lesquerolic, densipolic, and auricolic acids, are the primary fatty acids in lesquerella oil (LO) and make up approximately 60% of the oil composition.[1-7] Lesquerella is particularly attractive as a raw material since, unlike other domestic vegetable oils, the three major fatty acids in lesquerella are structurally similar to ricinoleic acid (Figure 1), the principal fatty acid of castor oil (CO). Currently, CO and its derivatives are the sole commercial source of hydroxyl fatty acid.[8-9] However, since the early 1970's, all CO consumed by the United States has been imported. Price instability and inconsistent supply have handicapped end-users, making corporate planning difficult. Consequently, a domestic, economically-attractive, and high performance CO substitute is desirable. However, lesquerella is a semi-drying oil with an iodine value of 102-116, and therefore, must be modified if used in air dry coatings.[10-13]

Silicon-containing polymers have widely been used in industry to improve flow, leveling, exterior durability, electrical resistance, corrosion resistance, and weather resistance. Structurally, most silicon-containing materials have one or more Si-O bonds and are therefore classified as silicones. Organosilane polymers, on the other hand, contain a hydrolytically stable Si-C bond which confers property enhancements normally associated with silicone modification, i.e., increased thermal stability, improved solubility, enhanced processibility, and better weatherability.[14-16] Thames, et al reported the synthesis, characterization, and evaluation of powder coatings containing organosilane diacids and anhydrides as crosslinking agents. These coatings display improved gloss, gloss retention, flow, and leveling.[17-19] Furthermore, Thames, et al have confirmed that silane incorporation lowers glass transition temperatures, enhances thermal stability, and improves solubility in organic solvents.[20-21] Thus, this investigation focused on the combined influence of pendent organosilane dicarboxylic acids in LO based coatings.



$$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_7-CH{=}CH-CH_2-\overset{\overset{OH}{|}}{C}H-(CH_2)_5-CH_3$$

Ricinoleic acid

$$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_9-CH{=}CH-CH_2-\overset{\overset{OH}{|}}{C}H-(CH_2)_5-CH_3$$

Lesquerolic acid

$$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_9-CH{=}CH-CH_2-\overset{\overset{OH}{|}}{C}H-(CH_2)_2\cdot CH{=}CH-CH_2-CH_3$$

Auricolic acid

$$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_7-CH{=}CH-CH_2-\overset{\overset{OH}{|}}{C}H-(CH_2)_2\cdot CH{=}CH-CH_2-CH_3$$

Densipolic acid

Figure 1

EXPERIMENTAL

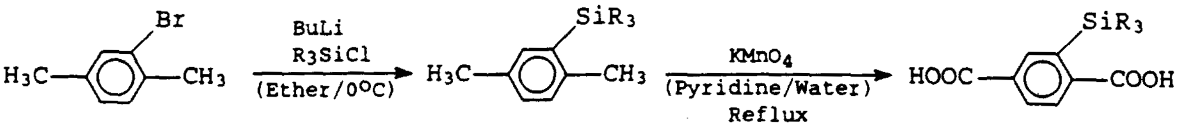
Materials

Lesquerella oil (refined from *Lesquerella fendleri*) was purchased from International Flora Technology Ltd. Phthalic anhydride, terephthalic acid, and trimethylol ethane were obtained from Aldrich Chemical Company, Inc. Lithium ricinoleate was purchased from Pfaltz & Bauer, Inc. Cobalt, zirconium, and manganese driers were provided by Nuodex, Inc. as 6% metal solutions. Exkin No. 2, an antiskinning agent (methyl ethyl ketoxime), was obtained from Huls America, Inc. Activ 8, a drier accelerator, and Nacure 155 (dinonyl naphthalene disulfonic acid) were provided by R. T. Vanderbilt Co., Inc. and King Industries, respectively. Cargill 23-2317, a highly methylated melamine resin, was supplied by Cargill, Inc. All additives, solvents, catalyst, and raw materials with the exception of the organosilane dicarboxylic acids were used as received.

The monosubstituted pendent organosilane dicarboxylic acids, 2-trimethylsilyl terephthalic acid, 2-dimethylphenylsilyl terephthalic acid, 2-diphenylmethylsilyl terephthalic acid, and 2-triphenylsilyl terephthalic acid, were synthesized according to Scheme 1. The disubstituted pendent organosilane dicarboxylic acids, 2,5-di(trimethylsilyl) terephthalic acid and 2,5-di(dimethylphenylsilyl) terephthalic acid, were synthesized according to Scheme 2.

Synthesis of Monosubstituted Organosilane Dicarboxylic Acids - Scheme 1

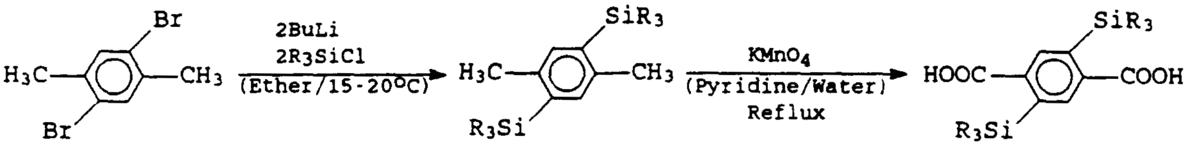
n-Butyl lithium (10 M) in hexanes (10% molar excess) was added to a solution of 2-bromo-*p*-xylene in anhydrous ether at 0°C under nitrogen. After one hour, the desired chlorosilane (10% molar excess) was added dropwise, lithium chloride was subsequently removed by filtration, and the solvents were removed *in vacuo*. The intermediates formed were purified by vacuum distillation or recrystallization followed by oxidation with $KMnO_4$ in a water/pyridine mixture to give the respective monosubstituted organosilane dicarboxylic acids. All monosubstituted organosilane intermediates and dicarboxylic acids were characterized via Fourier transform infra red (FTIR), nuclear magnetic resonance (NMR) spectroscopy, and elemental analysis.



Scheme 1

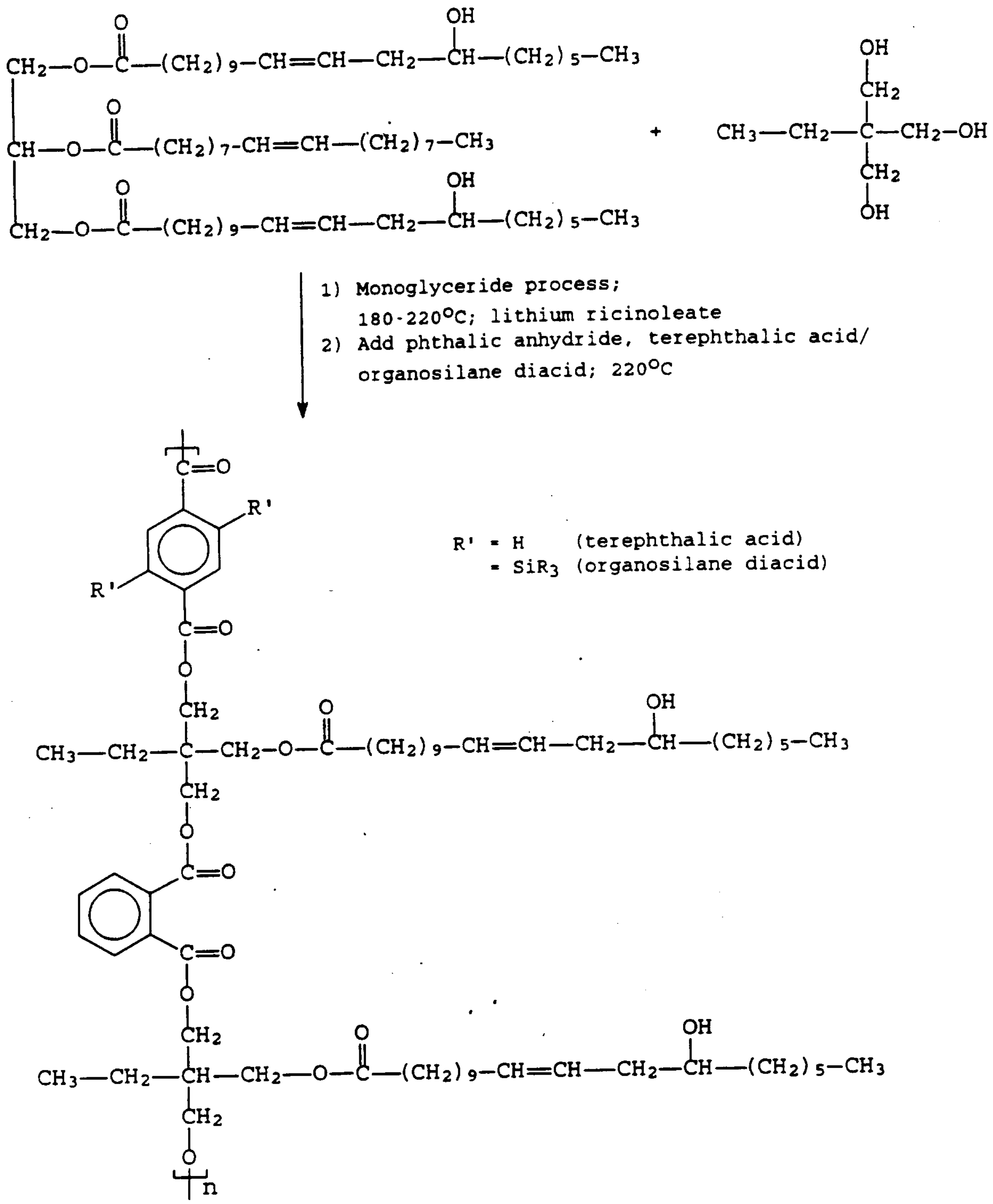
Synthesis of Disubstituted Organosilane Dicarboxylic Acids - Scheme 2

n-Butyl lithium (10 M) in hexanes (10% molar excess) was added to a solution of 2,5-dibromo-*p*-xylene in anhydrous ether at 15-20°C under nitrogen. After one hour, the desired chlorosilane (10% molar excess) was added dropwise. The process of metalation and addition of chlorosilane was completed again in order to obtain the disubstituted product. The intermediates formed were purified by recrystallization and subsequently oxidized with $KMnO_4$ in a water/pyridine mixture to the respective disubstituted organosilane dicarboxylic acids. All disubstituted organosilane intermediates and dicarboxylic acids were characterized via FTIR, NMR spectroscopy, and elemental analysis.



Scheme 2

Alkyd Resin Synthesis - Scheme 3



1) Monoglyceride process; 180-220°C; lithium ricinoleate

2) Add phthalic anhydride, terephthalic acid/ organosilane diacid; 220°C

R' = H (terephthalic acid)

= SiR_3 (organosilane diacid)

Scheme 3

Medium oil length polyester resins (55% oil length), were synthesized via the monoglyceride process.[22] The control formulation was synthesized with LO, trimethylol ethane, phthalic anhydride, and terephthalic acid. In the experimental formulations, terephthalic acid was replaced with organosilane dicarboxylic acid. All alkyd resins were synthesized at an alkyd constant of 1.04 and 10% excess hydroxyl. The polyesterification reaction was monitored by titrating the reaction mixture with alcoholic potassium hydroxide (KOH) and terminated at an acid value of 8±2 mg KOH/g of sample. The percent non-volatiles of each alkyd was determined from the weight loss on heating samples at 150°C until constant weight was attained (ASTM D-1644).

Air Drying Coating Formulation

A control and six experimental air drying coatings were formulated by adding cobalt, manganese, and zirconium driers, Activ 8, and Exkin No. 2, to each of the polyester resins. All formulation components (Table 1) were mixed with a high speed stirrer at 500 rpm for 15 minutes, and allowed to stabilize for 24 hours prior to application. With a draw-down bar, 4 mils thick coatings were applied onto a 3" x 6" x 0.2" low-carbon, mild steel, QD-36 untreated panels previously wiped with methyl ethyl ketone (MEK). The films were air dried for one week before testing.

Table 1 - Air Drying Coating Formulation

Ingredient	% by Weight
Polyester (80% non-volatiles)	92.50
Cobalt drier (6% metal)	1.10
Manganese drier (6% metal)	0.70
Zirconium drier (6% metal)	1.90
Activ 8	1.90
Exkin No. 2	1.90
Total	100.00

Alkyd-Melamine Coating Formulation

The control and six experimental polyester resins were crosslinked with Cargill 23-2317. All coatings were formulated at 70:30 alkyd-melamine ratio by weight. Nacure 155 was added to catayze the crosslinking reaction. All the components in the formulation (Table 2) were mixed with a high speed stirrer at 500 rpm for 15 minutes and then allowed to stabilize for 24 hours prior to coating application. With a draw-down bar, 4 mils thick coatings were applied onto a 3" x 6" x 0.2" low-carbon, mild steel, QD-36 untreated panels previously wiped with MEK. The films were heat cured at 120°C for 30 minutes. The cured films were equilibrated for seven days before testing.

Table 2 - Thermosetting Alkyd-Melamine Coating Formulation

Ingredient	% by Weight
Polyester (80% non volatiles)	68.70
Cargill 23-2317 (84% non volatiles)	28.00
Nacure 155	3.30
Total	100.00
Alkyd:Melamine ratio (by weight)	70:30

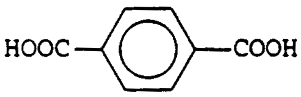
Testing Equipment

Polyester molecular weights were determined with a Perkin Elmer model 250 binary LC pump, equipped with model 13 ultraviolet detector. Three gel permeation chromatography (GPC) columns of pore size 50, 500, and 10^4 angstroms were placed in series and calibrated using polystyrene standards. The GPC results were analyzed with GPC data analysis software from Polymer Labs (PL Caliber version 5.11). Polyester viscosity was measured at 80% solids in xylene, on a Brookfield viscometer model DV-II (ASTM D-2196).

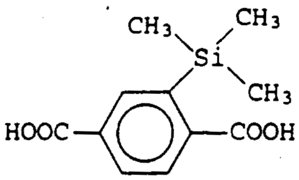
Dry film thicknesses were measured by a Gardco Minitest 4000 Microprocessor coating thickness gauge (ASTM D-1186). Impact resistance was determined with a BYK Gardner impact tester model IG-1120, using a 1.82 Kg., 1.27 cm. diameter steel pin (ASTM D-2794). Pencil hardness was expressed in terms of pencil leads of known hardness (ASTM D-3363). Adhesion was assessed by applying and removing a pressure-sensitive tape over a crosshatch constructed by eleven cutting blades (ASTM D-3359). Flexibility was measured by bending coated panels on a Paul N. Gardner, Model MN-CM conical mandrel (ASTM D-522).

RESULTS AND DISCUSSION

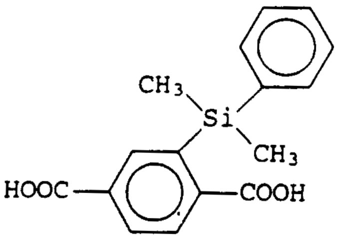
Gel permeation chromatography data (Table 3), indicate that the molecular weight of the polyesters ranged from 3500-4100 g/mol based on polystyrene standards. However, the acid values for all fell in the 8±2 range thus approximating a molecular weight of 5500-6500 g/mol.[23]



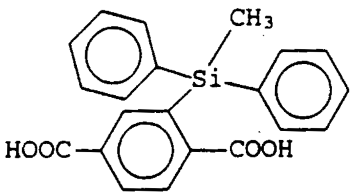
Terephthalic acid
(Control)



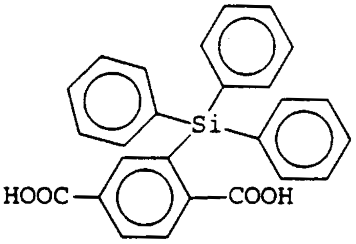
2-Trimethylsilyl
terephthalic acid
(Formulation #2)



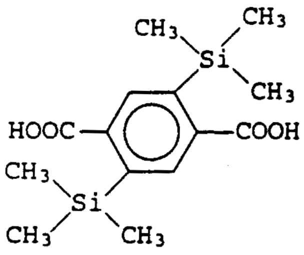
2-Dimethylphenylsilyl
terephthalic acid
(Formulation #3)



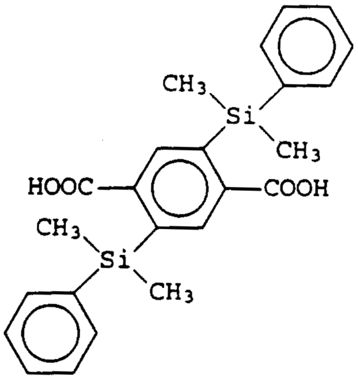
2-Diphenylmethylsilyl
terephthalic acid
(Formulation #4)



2-Triphenylsilyl
terephthalic acid
(Formulation #5)



2,5-Di(trimethylsilyl)
terephthalic acid
(Formulation #6)



2,5-Di(dimethylphenylsilyl)
terephthalic acid
(Formulation #7)

Figure 2

Viscosity and appearance measurements are listed in Table 3. The control, and formulations 2, 3, and 6 were cloudy. On the other hand, formulations 4, 5, and 7 were clear and lower in viscosity. The clarity and reduced viscosity is attributable to the high reactivity and increased acidity of carboxyl in 2-diphenylmethylsilyl terephthalic acid, 2-triphenylsilyl terephthalic acid, and 2,5-di(dimethylphenylsilyl) terephthalic acid as a result of (p-d) π bonding.[19] The increased reactivity reduces synthesis time, therefore limiting viscosity increases due to thermal polymerization. The enhanced acidity of the carboxyl group and the existence of silane moieties bestows improved solubility in organic media and thus a clear polyester. The structure and designation of the dicarboxylic acids used in the polyester syntheses are included in Figure 2.

Table 3 - Polyester Properties

Formulation	Appearance	Viscosity (cps)	Molecular Weight (M_n)	Acid Number mg KOH/g
Control	Cloudy	1750	3589	9.6
Formulation #2	Cloudy	1840	4006	8.5
Formulation #3	Cloudy	2290	3556	9.4
Formulation #4	Clear	1140	4079	9.2
Formulation #5	Clear	830	3812	9.5
Formulation #6	Cloudy	1690	3876	9.4
Formulation #7	Clear	1040	3913	9.2

The physical properties of the air drying coating formulations are included in Table 4. All coating formulations showed excellent impact resistance, flexibility, and adhesion. However, the control formulation was tacky even after one week dry time, indicating incomplete curing via oxidative polymerization. Pencil hardness data corroborated incomplete curing of the control polyester. Dry times for the experimental polymers decreased with increasing aromatic content of organosilane diacids.

Table 4 - Air Drying Coating Properties

Formulation	Drying Time (hr)	Pencil Hardness	Impact Resistance (inch-lbs)	Flexibility (inch)	Adhesion
Control	>168	<6B	160+/160+	0.125	5B
Formulation #2	72	HB	160+/160+	0.125	5B
Formulation #3	24	HB	160+/160+	0.125	5B
Formulation #4	16	HB	160+/160+	0.125	5B
Formulation #5	24	HB	160+/160+	0.125	5B
Formulation #6	48	HB	160+/160+	0.125	5B
Formulation #7	16	HB	160+/160+	0.125	5B

The thermosetting polyester-melamine crosslinked film properties are listed in Table 5. All formulations gave excellent flexibility, impact resistance, and adhesion. Crosslink density (MEK rub resistance) and pencil hardness of the experimental formulations were better than the control, and improved with increasing aromatic content in the silane diacids; a feature of increased (p-d) π bonding.

Table 5 - Polyester-Melamine Coating Properties

Formulation	Pencil Hardness	Impact Resistance (inch-lbs)	Flexibility (inch)	Adhesion	MEK Rubs
Control	2H	160+/160+	0.125	5B	25
Formulation #2	2H	160+/160+	0.125	5B	25
Formulation #3	4H	160+/160+	0.125	5B	40
Formulation #4	4H	160+/160+	0.125	5B	60
Formulation #5	4H	160+/160+	0.125	5B	75
Formulation #6	2H	160+/160+	0.125	5B	35
Formulation #7	4H	160+/160+	0.125	5B	65

CONCLUSIONS

The use of organosilane dicarboxylic acids in LO based polyesters provided a polyester of lower viscosity than a corresponding, non-silane modified control polymer synthesized and formulated to the same molecular weight and non-volatiles, respectively. In air drying formulations, the organosilane modified coatings dried faster to harder films. Furthermore, organosilane, thermosetting polyester-melamine polymers exhibited improved pencil hardness and MEK resistance, properties accruing from high crosslink density. The improvements were obtained without losses in adhesion, flexibility, or impact resistance.

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