NOVEL 'GREEN' SUCROSE POLYESTER ALKYDS FOR HIGH-PERFORMING Low-VOC Coatings

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INTRODUCTION

Alkyd resins have proven themselves both from a cost and performance point of view over a wide range of coatings applications such as architectural finishes, industrial metal, and agricultural/construction equipment. Since alkyd paints are solventborne, they contribute to our societal VOC emissions. Increasing concerns regarding ground level ozone and indoor air quality have spurred R&D investment to find alternative technologies or approaches directed at lowering VOC emissions without compromising performance. This has proven to be a major challenge for the industry as a whole. The key issue is reformulating solventborne paints to be as low as possible in VOC while still delivering—or surpassing—expected performance benchmarks.

Alkyd resins may be designed to achieve low-VOC coating formulations; however, traditional approaches invariably have compromised coating performance. In one common approach, the molecular weight and viscosity of an alkyd resin must be reduced, thereby decreasing the need for solvent. In doing so, though, the paint made with it takes much longer to dry,[1,2] an undesirable feature for many applications. Another approach is to use VOC-exempt solvents, such as t-butyl acetate, acetone, and Oxsol® 100 (1-chloro-4-(trifluoromethyl) benzene). These solvents tend to be expensive and often have odor and other performance issues. Commercial, low-VOC waterborne acrylic latex paints are available but they have performance tradeoffs that are undesirable for various coating applications, such as short open time, low gloss,[2] and reduced corrosion resistance when compared to solvent alkyd coatings. For all of these reasons, solventborne alkyd coatings continue to be in demand. Sucrose polyester alkyds are a novel class of high-solids resins that offer high organic renewable content with good application and drying characteristics while achieving much lower VOC levels than conventional alkyds.

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BACKGROUND AND THEORY

The functional materials described as sucrose polyesters were originally developed in the 1960s by Procter & Gamble scientists for large-scale commercial use as a fat substitute.[3] Sucrose polyesters essentially consist of a sucrose backbone and natural fatty acid residues linked to sucrose through ester bonds (*Figure* 1). Since one to eight fatty acid chains can be attached onto sucrose, the physical properties and reactivity of sucrose polyesters may be tailored by the degree of esterification and by choosing the appropriate natural oils to achieve the right fatty acid chain length distribution and unsaturation level. Thus, sucrose polyesters offer a unique chemical platform by controlling their molecular architecture and functional density, enabling a compact crosslinking structure to an autooxidizing paint system.

Sucrose polyesters are produced by esterifying sucrose with fatty acid methyl esters (FAME) via a two-stage continuous solventless patented process. In the first stage, sucrose and FAME react with the aid of an emulsifier and base catalyst to yield sucrose partial esters which are soluble in FAME. In the second stage, excess FAME is used to further esterify the sucrose partial esters to highly esterified sucrose polyesters. Excellent control of process variables throughout the two stages and during downstream processing are a must to minimize thermal degradation, i.e., charring, and to prevent saponification and hydrolysis.

Sucrose polyesters can be used in alkyd resins as a nonvolatile low viscosity component that reacts into the polymer film during autooxidative crosslinking processes.[4,5] Alternatively, they can be reacted under the right conditions into the backbone of the polymer to achieve specific characteristics. In an alkyd system, the sugar and fatty acid components of sucrose polyesters displace common alkyd ingredients that are derived from petroleum feedstocks, such as pentaerythritol and isophthalic acids, to result in a high organic renewable content coating system. Although sucrose polyester alkyds lend themselves to high-solids solventborne resin systems, they can also be adapted to emulsion resin systems for formulation of very low-VOC waterborne coatings.

Sucrose polyester alkyds produced from FAMEs of various vegetable oils are expected to have different effects on coating performance depending on the level of unsaturation and conjugation present in the fatty acid chains. For example, Muizebelt et al. conclude that reactive diluents with conjugated double bonds react by a more effective radical chain reaction[5] than diluents containing unconjugated linoleic acids. Understanding the impacts of fatty acid selection and type for construction of sucrose polyesters will enable researchers to unlock the potential of sucrose polyesters as alkyd resin modifiers.

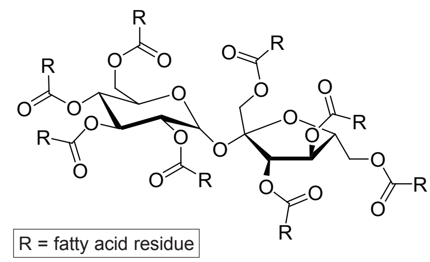

Figure 1—General chemical structure of an example sucrose polyester.

Selecting oils that offer a greater level of unsaturated fatty acid chains is a known method in the art of alkyd design to speed crosslinking processes and improve end properties in a drying alkyd resin.[6] It is hypothesized that the same effects may be seen with oil variations to sucrose polyesters. Van Haveren et al. have explored general characteristics of a sucrose octa-linoleate reactive diluent and conclude that sucrose fatty esters are excellent reactive diluents.[4] However, the impacts of fatty acid compositional variations of fatty acid/carbohydrate reactive diluents on coatings formulations have not been extensively studied. The following research offers a general study of sucrose polyesters synthesized from a variety of vegetable oils and their effect in a high solids alkyd paint system.

EXPERIMENTAL

A variety of highly esterified sucrose polyesters were synthesized containing six to eight fatty acid residues using a laboratory scale process modeled after the sucrose polyester production process previously discussed. The critical variant in the synthesis of the sucrose polyesters was vegetable oil selection. The sucrose esterification reactions were carried out with FAMEs of the following oils: safflower, soybean, dehydrated castor (DCO), linseed, and tung. An additional sample was prepared starting from a 50/50 mixture of FAMEs of soybean and dehydrated castor oils to provide a mid-point of conjugated linoleic acid (C18:2) content.

Resulting fatty acid compositions were characterized by dissolving a small sample of sucrose polyester in acetone and adding a preparatory reagent, trifluoromethylphenyl-trimethyl ammonium hydroxide in methanol, to convert the fatty acids into methyl esters for analysis. The fatty acid methyl ester mixtures were analyzed by gas chromatography using methyltridecanoate as an internal standard.

Table 1—Solventborne Sucrose Polyester Alkyd Paint Formulation

GRIND	lb/100 gal	Gallons
Long oil alkyd—70% NV	112.7	14.3
Organoclay derivative	1.3	0.1
Mineral spirits	12.6	2.0
Pigment dispersant	6.3	0.8
Corrosion inhibiting pigments	10.3	0.4
Titanium dioxide	259.9	7.8
Nepheline syenite extender	152.1	7.0
LETDOWN		
Long oil alkyd—70% NV	331.5	42.0
Sucrose polyester	124.4	15.7
12% Co drier solution	2.2	0.3
12% Zr drier solution	14.5	1.8
2,2-Bipyridyl chelating agent	2.7	0.3
Methyl ethyl ketoxime	2.6	0.3
Mineral spirits	46.4	7.2
TOTAL	1079.5	100.0

Formulation Characteristics	
Pigment/binder ratio	0.94
% Pigment volume concentration	22.6
% Nonvolatile by weight	80.8
% Nonvolatile by volume	67.7
VOC [g/L]	249

The sucrose polyesters were used as a paint ingredient to make a series of 250 g/L long oil alkyd white paints. The paint formulation, shown in *Table* 1, was not optimized for any particular characteristic; it is simply a generic starting point formulation for the purpose of making comparisons between the various resins. A long oil alkyd paint without sucrose polyester modification was also made to be used as an experimental control. The control paint required additional mineral spirits to reach similar application viscosity as the sucrose polyester alkyd paints. The added mineral spirits increases the VOC level of the alkyd paint and further reduces its overall organic renewable content. Because of the added mineral spirits, the control alkyd paint displays the following different end formulation characteristics: VOC of 350 g/L, density of 10.1 lb/gal, %PVC of 23.2, % nonvolatile (NV) by weight 71.1, and % NV by volume of 54.4.

The long oil alkyd used in this experiment is a commercial soya long oil alkyd. The alkyd is 70% NV content by weight in mineral spirits with a typical Gardner-Holdt viscosity range of Z2–Z4 and a Gardner-Holdt viscosity of D-F when reduced in mineral spirits to 50% NV. The paints were made by dispersing pigments and rheological clay additive in a mixture of long oil alkyd resin, dispersant, and mineral spirits. The pigment dispersion was letdown with sucrose polyester, additional alkyd, a standard mixture of drying catalysts (0.06% Co and 0.40% Zr based on sucrose polyester + alkyd resin solids), and mineral spirits. The final ratio of sucrose polyester to solid alkyd resin for the paints is 30:70.

The resulting paints were evaluated for viscosity, drying character, and various film properties; *Table* 2 contains a list of standard test methods that were used to evaluate paints in this study. Films were applied uniformly using standard drawdown bar applicators. For scrub resistance evaluation, the 54.4% NV by volume control alkyd paint was applied using a 5-mil (~125 μm) clearance drawdown bar where the SPE-alkyd paints at 67.7% NV by volume were applied using a 4-mil (~100 μm) clearance drawdown bar to equalize the resulting dry film thickness for side by side evaluations. All other tests were conducted using drawdowns from a 1.5-mil Bird applicator bar. Unless otherwise noted, substrates used for each test are listed in *Table* 2 and films were allowed to cure for a minimum of seven days before testing.

Finally, an emulsified sucrose polyester alkyd (60% sucrose polyester: 40% alkyd) was made into a low VOC, 21 g/L, waterborne white paint formula and evaluated for a variety of performance properties. Formulation for the emulsified sucrose polyester alkyd is shown in *Table* 3.

Table 2—Test Method References and Substrates Used

Test Description	Method Reference	Substrates Used
Adhesion—crosshatch	ASTM D 3359, Method B	Cold rolled steel
Blistering	ASTM D 714	Cold rolled steel
Block resistance	ASTM D 4946	Lacquer-sealed chart
Chemical resistance	ASTM D 1308	Steel and aluminum panels
Dry time	ASTM D 1640	Glass plate
Humidity resistance	ASTM D 4585	Cold rolled steel
Pencil hardness	ASTM D 3363	Cold rolled steel
Scrub resistance	ASTM D 2486, Method B	Black plastic scrub chart
Solvent resistance (MEK 2x rubs)	ASTM D 5402	Cold rolled steel

Table 3—Waterborne Emulsified Sucrose Polyester Alkyd Paint Formulation

GRIND	lb/100 gal	Gallons
Water	74.0	8.9
Organoclay derivative	0.7	0.0
AMP-95	0.7	0.1
Defoamer	0.7	0.1
Dispersant	7.4	0.8
Titanium dioxide	296.1	8.9
Polyurethane rheology modifier	0.7	0.1
LETDOWN		
Sucrose polyester alkyd emulsion	649.0	78.0
Premixed driers:		
Co/Zr/Li drier blend	6.2	0.7
Mineral spirits	4.0	0.6
Flash rust additive	3.2	0.4
Methyl ethyl ketoxime	1.6	0.2
HEUR rheology (high shear)	6.7	0.8
HEUR rheology (low shear)	4.0	0.5
TOTAL	1055.2	100.0

Formulation Characteristics	
Pigment/binder ratio	0.80
% Pigment volume concentration	16.7
% Nonvolatile by weight	63.4
% Nonvolatile by volume	53.5
VOC [g/L]	21

Table 4—Fatty Acid Composition Analysis of Sucrose Polyester Variants

	Oils Used for Sucrose Polyester					
Fatty Acid	Safflower	Soybean	Soya/DCO 50/50	DCO	Linseed	Tung
Saturated	9.2	16.4	10.6	2.3	9.8	6.6
Oleic	15.3	23.7	17.3	4.7	23.1	8.9
Linoleic	75.5	55.2	56.3	56.0	19.3	8.8
Conjugated linoleic	—	—	11.9	32.8	—	—
Linolenic	—	4.7	3.9	4.2	47.8	1.0
Conjugated linolenic	—	—	—	—	—	74.7
# of Double bonds / 100 Fatty acids	166.3	148.2	165.4	194.9	205.1	253.6

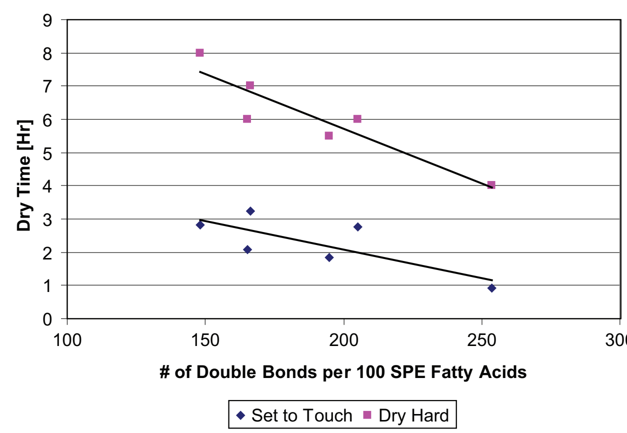

Figure 2—Dry time of sucrose polyester (SPE) alkyd paints relative to concentration of double bonds in the SPE fatty acids.

RESULTS AND DISCUSSION

High Solids Alkyd Systems

Characterization of fatty acids found in the sucrose polyester variants used in this experiment is shown in *Table* 4. The fatty acids content agrees closely with expected fatty acid composition of the various vegetable oils[7] used in this experiment. Viscosity for the sucrose polyesters (SPEs) show similar low viscosity range of 300–600 cP for all SPEs except the tung oil version. The tung oil viscosity was considerably higher at 7800 cP. Although higher in viscosity, the tung oil SPE demonstrated similar viscosity to the other SPEs in a finished paint.

Test results for application and appearance characteristics are shown in *Table* 5. As expected, drying times get shorter for SPE-alkyd systems with a higher concentration of available unsaturation sites for autooxidative crosslinking to occur. This correlation is evident in *Figure* 2, which shows dry times for the various systems versus the level of unsaturation sites based on the oil type(s) used to construct the SPE. The tung oil SPE alkyd system showed slightly faster dry set-to-touch times and faster dry hard times than the control alkyd paint. The second fastest dry time was seen for the DCO SPE-alkyd system. Despite DCO having fewer unsaturation sites relative to linseed oil, it does have a higher level of conjugated unsaturation which may contribute to the faster set to touch dry of the DCO and Soy/DCO SPE-alkyd coatings compared to the linseed oil SPE-alkyd.

Paint films were evaluated for appearance properties of gloss, color, and resistance to yellowing. Gloss levels were mostly comparable for all samples. Yellowing tendency was greatest for the paints consisting of SPEs from linseed and tung oils which contain the highest unsaturation levels among the oils studied herein. Yellowing comparison is shown in *Figure* 3. All the SPE-modified alkyds showed more yellowing than the higher VOC control alkyd formulation with the safflower and soya SPEs showing the closest result to the control alkyd paint.

Film toughness properties for the comparison paints are shown in *Table* 6. The wet scrub resistance test and solvent resistance tests did not correlate with each other across all samples

Table 5—Sucrose Polyester (SPE) Alkyd Paint Application and Appearance Performance

SPE Type	Control Alkyd Paint (no SPE)	Safflower	Soya	Soya/DCO	DCO	Linseed	Tung
Viscosity of SPE [cP]	—	520	330	360	530	190	7800
Paint Properties							
Stormer viscosity [KU]	106.9	101.4	101.2	97.8	99	93.7	94
VOC [g/L]	350	249	249	249	249	249	249
Dry (ASTM D1640) - 1.5-mil Bird drawdown on glass plate							
Set-to-touch dry	50 min	3 hr 15 min	2 hr 50 min	2 hr 5 min	1 hr 50 min	2 hr 45 min	55 min
Dry hard	5 hr	7 hr	8 hr	6 hr	5 hr 30 min	6 hr	4 hr
1.5-mil Bird drawdown on white lacquer-sealed chart							
Gloss @ 20°	81	85	83	85	85	85	78
Gloss @ 60°	91	93	91	93	93	93	92
Initial color							
L*	93.05	93.49	93.25	93.08	93.58	93.23	92.46
a*	-0.97	-0.95	-1	-1.09	-1.06	-1.19	-1.26
b*	2.79	3.12	2.76	3.03	3.16	3.43	4.74
Accelerated yellowing – closed Container ammonia vapor							
Δb*	7.71	8.67	8.62	9.62	9.73	12.21	12.69
ΔE	7.83	8.83	8.76	9.76	9.84	12.46	12.96

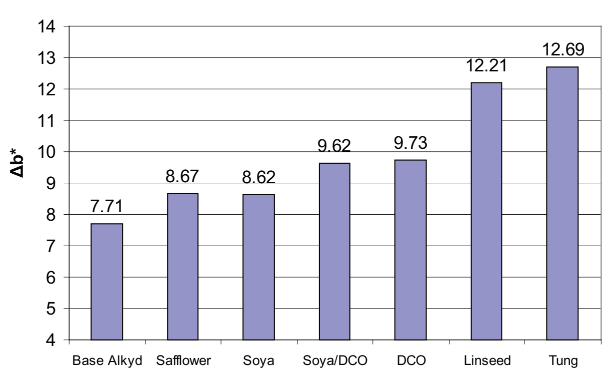

Figure 3—Accelerated yellowing of comparison paints.

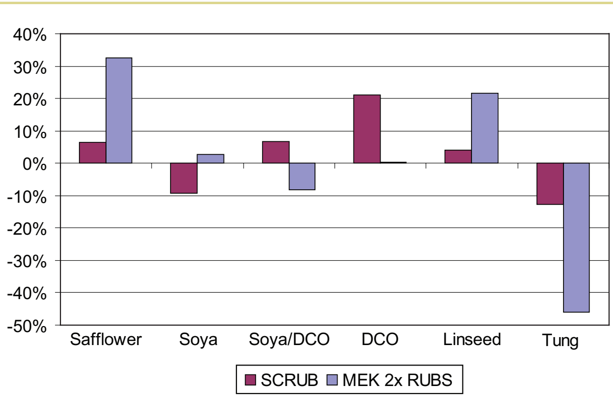

Figure 4—Film toughness of comparison paints

(*Figure* 4). The two test methods assess film toughness differently: the scrub resistance test breaks down the film using mechanical scrubbing with an aqueous abrasive cleaning solution and a bristle brush; the solvent resistance test result comes from speed of chemical dissolution of the film during rubbing with a soft cloth moistened with methyl ethyl ketone. The best scrub resistance result was observed for the DCO SPE-alkyd paint which contains the highest level of conjugated linoleic acid. The best MEK double rub results were from the paints containing SPEs from safflower and linseed oils. Safflower and linseed oils are the two oils with the highest level of nonconjugated C18:2 and C18:3 fatty acids. The paints having SPEs from oils containing conjugated double bonds, DCO and tung, performed lower for MEK double rubs.

Humidity resistance was conducted using a controlled condensation cabinet to expose coated steel panels to continuous condensation in a warm environment. The humidity exposure period was 100 hours. All the test paints showed some blistering, although the blister size for the alkyd paint with no SPE modification was the smallest size. The only sample where the blistering recovered was for the tung oil SPE-alkyd which also had the largest blisters (size 5) after initial removal from the humidity cabinet. Gloss retention after recovery period is shown in *Figure* 5. Gloss retention was best for the SPE-alkyds containing the more highly conjugated oils, tung and DCO. The tung and DCO SPE-alkyds were the only two experimental samples to demonstrate better gloss retention than the control alkyd formulation; the safflower SPE-alkyd rated the same for gloss retention as the control alkyd.

Other film performance properties shown in *Table* 6 did not show significant variation to ascertain trends among the SPE-alkyd paints using SPE derived from the various oils. These characteristics include pencil hardness, adhesion to steel panel, and block resistance tested at both room temperature (RT) and elevated temperature environments.

Waterborne System

It is important to note that surfactant-stabilized alkyd emulsion resin systems are often a challenge to adapt to coatings for light industrial metal coating applications. The surfactants required to emulsify alkyd resins typically result in reduced hardness development and moisture resistance performance. Thus, the solventborne counterpart of the SPE-alkyd emulsion system studied is expected to display even better hardness and humidity resistance characteristics than demonstrated by this example.

Results for the waterborne 21 g/L sucrose polyester alkyd emulsion system are shown in *Table* 7. Adhesion testing shows a favorable adhesion profile of the SPE-alkyd emulsion over various substrates including steel, aluminum, and a TPO plastic substrate that is a challenge for the adhesion of many coatings systems. Set-to-touch dry time was found to be slower for the emulsified system than the high solids solvent-based systems studied previously. MEK double rubs (85), pencil

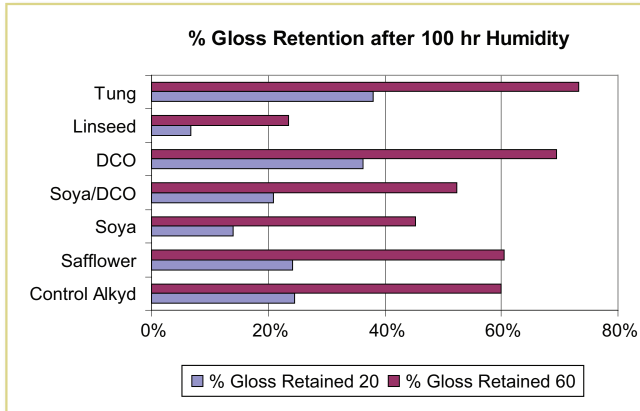

Figure 5—Humidity resistance of comparison paints.

Table 6—Sucrose Polyester (SPE) Alkyd Paint Film Toughness Performance

SPE Type	Control Alkyd Paint (no SPE)	Safflower	Soya	Soya/DCO	DCO	Linseed	Tung
Film Properties							
Scrub resistance (relative to control)	0%	7%	-9%	7%	21%	4%	-13%
MEK 2x rubs	37	49	38	34	37	45	20
Pencil hardness	5B	5B	5B	5B	5B	5B	5B
Adhesion to steel (CRS)	4B	4B	4B	4B	4B	4B	4B
Block Resistance							
Overnight, RT	7	6	8	8	7	8	5
Overnight, 52°C	5	4	5	4	5	5	2
7-Day, RT	8	8	8	8	8	9	7
7-Day, 52°C	6	6	6	6	6	7	5
Humidity Resistance (100 hr Humidity Exposure)							
Initial gloss 20°	61	62	64	62	58	60	58
Initial gloss 60°	85	86	86	86	85	85	86
Blister size	9+	8	9	8	9	8.5	5
Blister density	D	D	D	D	D	D	D
Blistering recovered	no	no	no	no	no	no	yes
After recovery							
Gloss 20°	15	15	9	13	21	4	22
Gloss 60°	51	52	39	45	59	20	63
% Gloss retention 20°	25%	24%	14%	21%	36%	7%	38%
% Gloss retention 60°	60%	60%	45%	52%	69%	24%	73%

Table 7—Waterborne SPE Alkyd Emulsion Paint Performance

Test	Rating/Result
Dry Times - 1.5 mil Bird Drawdown on Glass plate	
Set to touch	5 hr
Dry hard	7 hr 30 min.
Film Performance	
Adhesion	
Bare cold rolled steel	4B
Aluminum	4B
TPO plastic	5B
MEK 2x rubs	85
Pencil hardness	3B
Chemical resistance - 1 hr Open spot	
409 Cleaner	Slight yellowing
Vinegar	No effect
Lemon Juice	No effect
Bleach	Very slight mar
Humidity Resistance, Al panel, 7-day Humidity Exposure	
Initial gloss 20°	64
Initial gloss 60°	81
Blisters	8/Dense
After Recovery	
Blisters	none
Final gloss 20°	55
Final gloss 60°	84

hardness (3B), and chemical spot testing results demonstrate that the SPE-alkyd emulsion film is developing a serviceable degree of toughness. Finally, humidity exposure over aluminum panels shows some blistering initially, but good recovery of blistering and excellent gloss retention. Overall, these results demonstrate that water-based coatings based on SPE-alkyd emulsion systems produce viable film toughness characteristics at very low VOC levels.

CONCLUSIONS

Sucrose polyesters (SPEs) in alkyd coatings enable low VOC levels and increased renewable content compared to conventional alkyd coatings. The use of a variety of natural vegetable oils in forming SPEs yields different properties in a high solids SPE-alkyd coating formulation. Dry times were faster for coatings systems that used SPEs made from oils higher in unsaturation content with even faster dry apparent with the presence of conjugated double bonds. Solvent resistance favored SPEs made from oils such as safflower and linseed, which contain fatty acids having higher nonconjugated unsaturation content. The SPE based on dehydrated castor oil, which is high in conjugated linoleic acid, gave the most favorable scrub resistance result relative to the control; however, scrub resistance results did not demonstrate an overall trend related to fatty acid variations in the SPE. Gloss retention after humidity exposure favored SPEs made from oils that have higher levels of conjugated unsaturation such as DCO and tung oil.

Finally, the performance of the SPE-alkyd emulsion paint system demonstrates the potential of SPE-alkyd technology to be adapted from high solids solventborne systems to very low-VOC waterborne systems. The learning from these studies furthers knowledge in the development of SPE technology and enables optimization of high performance, low-VOC sucrose polyester coating systems.

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