High-Solids Alkyds Resins with Improved Properties Based on Styrene Allyl Alcohol (SAA) Resinous Polyols

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Stringent VOC content rules on Architectural and Industrial Maintenance (AIM) coatings have recently been enacted by federal, regional, and state regulatory agencies. These new rules effectively ban the use of low-solids solventborne alkyd resins, despite their excellent properties, ease of use, and low cost.

In response to these new regulations, alkyd producers have been developing higher solids and waterborne alkyds, but these new resins do not perform as well and are more costly than the higher VOC versions. High-solids alkyd resins typically have lower molecular weights, which can increase their drying times and reduce their durability. Waterborne alkyds are usually more expensive, despite having lower solids contents. Their dry time is also affected by temperature and humidity and their storage stability is usually lower than solution alkyds. These properties make waterborne alkyds less attractive to contractors who require paints with fast dry times and high coverage and hiding power for maximum productivity.

This paper describes the use of commercial resinous polyols to produce alkyd resins with lower solvent demand, plus improved dry times, humidity and UV resistance compared to conventional medium- and long-oil alkyds. Partial replacement of pentaerythritol with styrene allyl alcohol (SAA) resinous polyols in standard alkyd resin syntheses results in a marked decrease in the resin polydispersities but little change in the number average molecular weights. The SAA polyol can be added to the process as a solid or a liquid, oil-modified polyol. The alkyd resin with the best overall properties was obtained by replacing a portion of the pentaerythritol, soybean oil, and phthalic anhydride with an SAA-modified soy polyol.

INTRODUCTION

Alkyd resin and coating producers have been under increasing pressure to reduce the HAP and VOC content of their products. New national, regional (e.g., Ozone Transport Commission), and state AIM (Architectural and Industrial Maintenance) rules will soon mandate that certain categories of alkyd coatings contain as little as 50 grams of VOCs per liter of paint (*Table* 1).

These regulations are driving resin and coating producers to develop new resins with lower solution viscosities or water-borne alkyds with improved properties.

Current VOC-exempt solvents such as acetone, methyl acetate, and PCBTF are expected to find limited use in alkyd-based coatings because of their odor, cost, or flammability. Traditional alkyd coatings contain mineral spirits or aromatic solvents such as xylene or toluene. HAP regulations are already driving producers away from xylene and toluene, leaving mineral spirits as the main solvent for future alkyd coatings in the U.S.

VOCs are regulated because of their potential to generate ozone when emitted in polluted urban environments. Despite their higher VOC contents, many alkyd coatings based on mineral spirits may generate less tropospheric ozone than the corresponding water-based products. This is because the polar solvents and amines used in water-based formulations generate significantly more ozone than mineral spirits. For example, *Figure* 1 compares the VOC content and ozone-forming potential (based on the MIR values[1] of the contained solvents) of a commercial Direct-to-Metal (DTM) alkyd coating in mineral spirits and a water-based DTM acrylic enamel from the same supplier.

As is usually the case, the VOC content per gallon of paint is higher for the solventborne alkyd. However, due to the higher reactivity of the solvents used in the acrylic latex, the gallon of latex paint would generate more ozone. Furthermore, because the latex has a lower solids content than the alkyd, more latex would have to be applied to achieve the same coverage. When the ozone forming potential per volume of solids is considered, the waterborne acrylic would generate 60% more ozone despite containing half the VOCs per gallon of paint.

Replacing mineral spirits with tert-butyl acetate (TBAc™, a product of Lyondell Chemical Co.) would further reduce the ozone forming potential of the alkyd by a factor of five (*Figure* 1). These facts underscore the need for the U.S. EPA and other regulatory agencies to promptly add TBAc and other negligibly reactive sol-vents to the list of VOC-exempt compounds and to continue developing a more sensible reactivity-based VOC policy.[2]

Without a practical non-VOC alternative to mineral spirits, companies are focusing on the development of new high-solids resins and reactive diluents.[3] Traditional approaches to reducing the solvent demand of alkyd resins (*Table* 2) involve either a reduction in alkyd molecular weight or hardness (T_g). Typically, reducing the resin molecular weight has a detrimental effect on cure speed (hardness development) and reducing the resin T_g affects both cure speed and the final coating hardness. Waterborne alkyds have their own

Table 1—National, Regional, and State VOC Content Rules for Major Architectural and Industrial Maintenance Coating Categories

VOC Content Limit in Grams/liter

Paint Type	EPA Now	CARB Now	SCAQMD Now	SCAQMD June '06	OTC Now	OTC Jan. '05
Flats 250		100	100	50	250	100
Non-flats 380		150	150	50	380	150
Gloss enamels 380		250	n/a	n/a	380	250
Quick-dry enamels 450		n/a	250	50	450	n/a
Industrial maintenance 450		250	400	100	450	250

Figure 1—VOC content and ozone forming potential of a waterborne DTM acrylic and an alkyd enamel in mineral spirits from the same supplier.
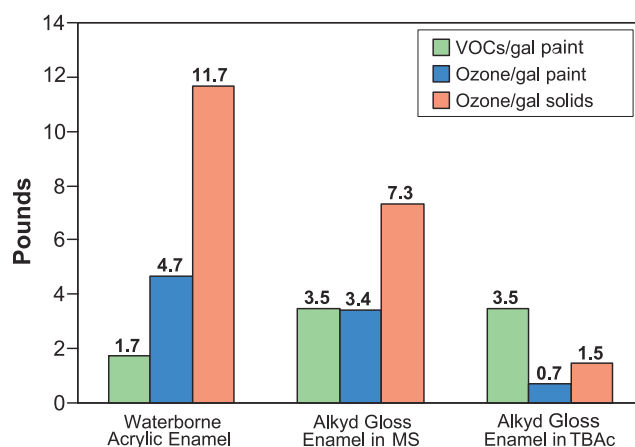
Table 2—Effect of Low-VOC Alkyd Strategies on Coating Performance

Strategies for High-Solids Alkyds	Effect on Coating Properties
Increase oil length	Lowers VOCs, increases dry time, lowers coating hardness
Increase diol content in alkyd	Lowers VOCs, increases dry time, lowers coating hardness and corrosion resistance
Use reactive diluents	Lowers VOCs, increases dry time, lowers coating hardness and corrosion resistance
Chain stop	Lowers VOCs but loses air-drying properties
Use SAA polyols in alkyd	Lowers VOCs, maintains cure speed and coating hardness, improves humidity and corrosion resistance

Table 3—Properties of Commercial Styrene Allyl Alcohol Co-polymers			
Typical Properties	SAA-100	SAA-101	SAA-103
Number average molecular weight (Mn)	1,500	1,200	3,200
Weight average molecular weight (Mw)	3,000	2,500	8,400
Polydispersity (Mw/Mn)	2.0	2.1	2.6
Hydroxyl number (mg KOH/gm)	210	255	125
Hydroxyl content, wt%	6.4	7.7	3.8
Equivalent weight	267	220	448
Average OH functionality per molecule	5.6	5.5	7.1
Glass transition temperature (T_g), °C	62	57	78

limitations, including increased cost, lower solids, limited hydrolytic stability, and variable drying speed and film properties.[4]

In this study, we looked at the effect of styrene allyl alcohol (SAA) polyols as partial replacements for pentaerythritol (PE) and phthalic anhydride (PAN) in long-oil alkyds. Due to the high T_g and aromatic character of SAA polyols, we expected an improvement in hydrolytic stability and hardness development. Surprisingly, we found that SAA polyols also reduced the polydispersity of alkyd resins while maintaining their molecular weight (Mn). This significantly reduced the VOC content of the alkyd coatings while maintaining dry times and greatly improving their hydrolytic stability.

Styrene Allyl Alcohol Copolymers Use in Alkyds

SAA polyols are co-polymers of styrene and allyl alcohol.[5] They were originally developed by Shell Development Company and patented in 1952.[6] They were also sold by Monsanto as RJ-100 and RJ-101 until 1992, now by Lyondell Chemical Company as SAA-100™, SAA-101™, and SAA-103™ (Table 3). SAA-100 and -101 are essentially the same products as RJ-100 and -101. SAA-103 was developed with a lower OH con-

Figure 2—GPC trace of a 60% soy alkyd based on pentaerythritol (PE) and phthalic anhydride showing the broad polydispersity and high molecular weight polymer fraction.

tent for two-component urethane systems where a lower isocyanate demand is desirable to reduce formulated costs and improve coating flexibility.

SAA polyols are hard, low molecular weight, highly functional, hydrophobic resins that are not susceptible to hydrolysis. This makes them particularly well suited for esterification reactions and alkyd resin synthesis. The use of SAA resinous polyols in alkyd coatings dates back to the mid-sixties when PPG developed anionic E-coat technology based on SAA alkyds.[7] Maleinated fatty esters of SAA were also used extensively to improve the film build, hiding, adhesion, leveling, and resistance to flaking, cracking, and mildew in latex paints.[8,9]

Their primary function in the early alkyd resins work was to improve the hydrolysis resistance of water-based alkyds and alkyd-modified acrylics.[10] We were hopeful that they would offer the same benefits and improve the cure speed of high-solids long-oil alkyds. We were surprised to find that they also lower the resin viscosity and VOC content of the resulting coatings.

More recently, Sherwin Williams has developed high solids nonaqueous dispersions (NADs) based on low viscosity alkyds containing SAA-101.[11] The authors noted that the alkyds had narrow polydispersities (2.0 to 6.0) and low Mz values (10,000 to 150,000) but did not attribute this property to the use of SAA. The high-solids alkyds were used as dispersing medium for the co-polymerization of methyl methacrylate (MMA) and hydroxyethyl acrylate. The resulting NADs had lower viscosity and contained fewer insoluble particles (grit) than those prepared with commercial alkyds and could be formulated into fast drying paints with less than 250 grams VOC/liter.
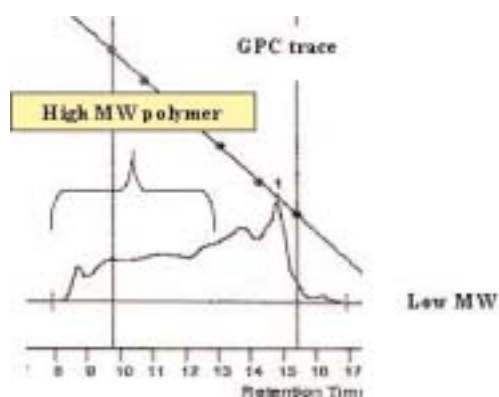
EXPERIMENTAL

Raw Materials

SAA-100, SAA-101, and SAA-103 were obtained from Lyondell Chemical Company. The commercial alkyds were Beckosol™ 10-539 (high-solids alkyd from Reichhold Chemical) and Chempol™ 801-1070 (medium-solids alkyd from Cook Composites and Polymers). Alkali-refined soybean, coconut, and linseed oils were obtained from Cargill and Alnor Oil. All other chemicals were obtained from Aldrich Chemical Company and used as received.

Preparation of SAA Oleates

Soybean or linseed oil was charged to a 1-liter alkyd reactor with stirrer, nitrogen inlet and overhead con-

denser. The oil was heated to 170–180°C under nitrogen with agitation. Solid SAA was added over a 20-min period to prevent agglomeration. Dibutyltin oxide (0.014% on total oil and SAA charge) was then added and the reactor temperature increased to 210°C. The mixture was held at that temperature for 20 minutes to allow water vapor to exit the reactor and minimize foaming. The reactor temperature was raised to 250°C at a rate of 25°C/hr. The reactor contents were kept at that temperature until a clear resin was obtained (~1 hr). Reactor contents were cooled to ~125°C and discharged.

Example Preparation of SAA Alkyds

Soybean oil (420 parts), pentaerythritol (63 parts), SAA-100 (70 parts), and dibutyltin oxide (0.3 parts) were charged to an alkyd reactor similar to the one shown below. The reactor contents were heated to 250°C under nitrogen and stirred at that temperature until an aliquot gave a clear 1:1 solution in methanol (approximately 30 min). The reactor contents were cooled to 160°C, xylene (25–30 parts) and phthalic anhydride (147 parts) added, and the reactor contents heated back to 250°C. Starting at 190°C, a xylene-water azeotrope was collected over-

Figure 3—Effect of SAA polyols on the Mn and polydispersity of a 60% soy alkyd based on pentaerythritol and phthalic anhydride.
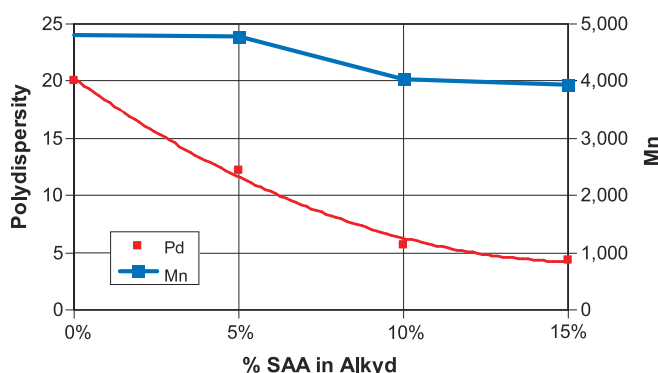
head. After approximately 4–6 hr at 250°C, the clear reactor contents were cooled to 170°C and mineral spirits (300 parts) were added.
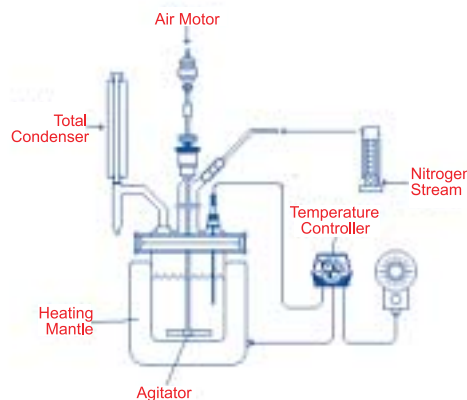

Preparation of Pigmented Alkyds Coatings

The SAA alkyd (100 parts) prepared above was further diluted with 15 parts mineral spirits in a Dispermat™ and titanium dioxide (160 parts) and K-Sperse™ 131 (King Industries, 0.25 parts) were added while stirring. The pigment was dispersed at 5,000 rpm to give a Hegman value of 6+. The grind was then let down with another 100 parts of alkyd resin and mineral spirits (15 parts). To 100 parts of the coating was added a drier package consisting of 0.263 parts of 12% cobalt naphthenate, 1.38 parts of 12% zirconium naphthenate, and 1.75 parts of 6% calcium naphthenate. Exkin™ #2 (0.1 parts; product of Condea Servo LLC.) was also added. The resulting coating had a Zahn #3 viscosity of 35 seconds, a solids content of 80%, and a VOC content of 259 grams/liter.

Table 4—Low-Viscosity Long-Oil Alkyds Based on SAA Polyols

Long-oil alkyds	60% Soy-alkyd	With 5% SAA-100	With 10% SAA-100	With 15% SAA-100
Components	R-216	R-250	R-214	R-254
Soybean oil	60	60	60	60
Pentaerythritol	14.5	11	9	7
SAA-100	0	5	10	15
Phthalic anhydride	25.5	24	21	18
Dibutyltinoxide	0.05	0.05	0.05	0.05
Totals	**100.05**	**100.05**	**100.05**	**100.05**
K value	1.01	0.98	1	1.02
Theo. OHN uncorr	47.5	10	10	10
Acid value (nv)	8	9.3	8.8	10
Appearance	clear	clear	clear	clear
Gardner color @ 70% solids in MS	3	4	4	4

Resin Properties	60% Soy-alkyd	With 5% SAA-100	With 10% SAA-100	With 15% SAA-100
Mn	4,809	4,779	4,028	3,944
Pd	20.0	12.2	5.7	4.4
Gardner-Holt visc. in mineral spirits				
80%	Z10	Z6+	Z2	Y
70%	Z6	Z2	V	R
60%	X-Y	U	I	F
50%	—	F	A	A

Figure 4—Viscosity Profile of Long-oil alkyd Solutions in Mineral Spirits as a Function of SAA content.
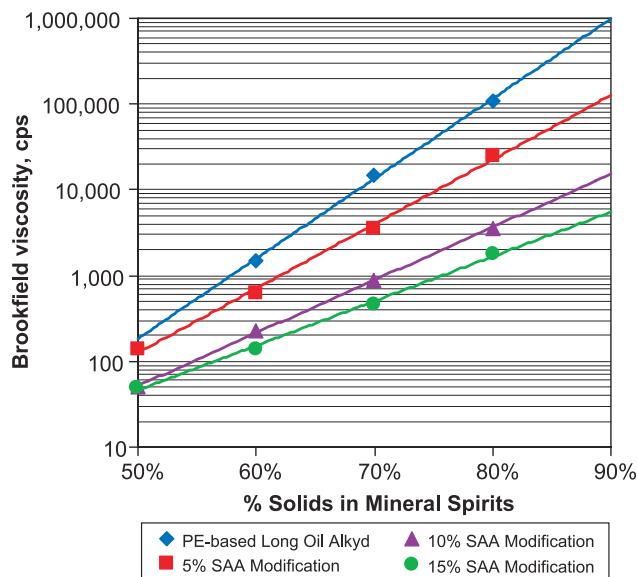

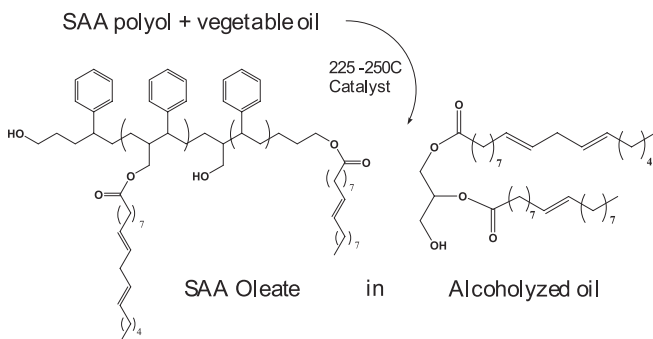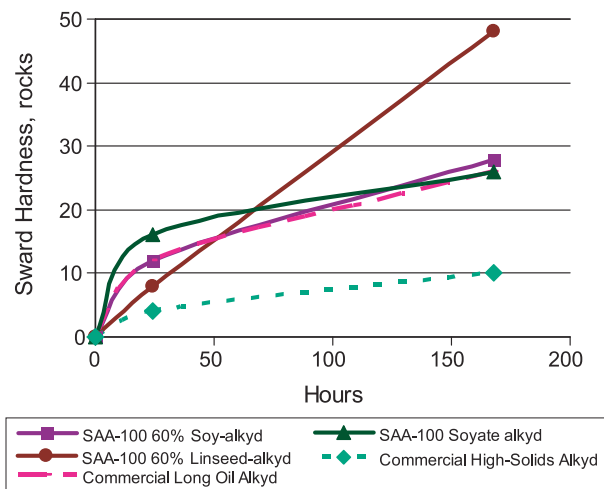Figure 5—Oil alcoholysis reaction with SAA polyols.

Figure 6—Hardness development of SAA-100 modified alkyds vs. commercial long-oil alkyds.

RESULTS AND DISCUSSION

Long-Oil Alkyd Resin Composition, Molecular Weight, and Polydispersity

A 60% soy alkyd was prepared in a two-stage process from the following ingredients:

Components	Parts Wt.
Soybean oil	60
Pentaerythritol	14.5
Phthalic anhydride	25.5
Dibutyltin oxide	0.05

Resin Properties	
K value	1.01
Theo. OHN uncorr	47.5
Acid value (nv)	8
Visc. (nv)	Z10+++
Appearance	clear

GPC analysis revealed that the polymer had a very broad molecular weight distribution (Mw/Mn = 20), and contained substantial amounts of high molecular weight polymer (*Figure* 2). The benefits of narrow poly-dispersity in high-solids alkyds are well known. Elimination of the high-molecular weight fraction significantly reduces the solvent (VOC) required to achieve sprayable or brushable viscosities. This is because high molecular weight impurities have a disproportionate effect on resin viscosity.

Reducing the low molecular weight fraction, on the other hand, improves the drying time and final film properties. Ideally, Mn is maintained while Mw is reduced. Traditional methods to increase solids such as reactive diluents[3] or increasing the oil length decrease Mn, which has a detrimental effect on dry times, final coating hardness, and humidity resistance.

Replacing a portion of the PE with SAA-100 in this standard high-solids alkyd significantly reduced its polydispersity while maintaining Mn above 4,000 (*Figure* 3 and *Table* 4). Solution viscosities were substantially reduced due to a reduction in the high molecular weight polymer fraction (*Figure* 4). Additional reductions in resin viscosities were achieved by increasing the oil length to 65 and 70% but this also resulted in a decrease in Mn to below 3,500.

SAA Oleates

Alcoholysis of vegetable oils with SAA polyols at 250°C for one hour in the presence of a tin catalyst yields low viscosity, air-drying polyols (*Figure* 5). These polyols are useful resins for a variety of coating systems, including baking enamels and two-component urethanes and are useful raw materials for low-VOC resin technologies including UV- and moisture-curable urethanes, high-solids, baked and waterborne alkyds, and nonaqueous dispersions.

Table 5—Composition and Physical Properties of SAA-100 Oleates

Composition	30% SAA Soyate	40% SAA Soyate	45% SAA Soyate	45% SAA Linseed Oleate	45% SAA Coconut Oleate	50% SAA Soyate
Vegetable oil	350	420	385	385	385	350
SAA-100	150	280	315	315	315	350
Dibutyltin oxide	0.1	0.1	0.1	0.1	0.1	0.1
Oleate Properties						
Nonvolatile content	99%	99%	99%	99%	99%	99%
Gardner-Holt viscosity	V-W	Z5	Z5	Z6	Z5	Z9
Hydroxyl value	65	84	94	94	94	105
Pounds per gallon	8.04	8.20	8.13	8.26	8.20	8.15
Mn	1,621	1,660	2,031	2,029	1,527	1,945
Mw	3,274	3,926	4,698	5,035	3,887	5,672
Mz	6,514	8,929	8,846	10,249	7,763	13,084
Polydispersity	2.02	2.36	2.31	2.48	2.54	2.90

Typical SAA oleate properties are listed in *Table* 5. The hydroxyl number and viscosity of the SAA oleate can be varied by changing the ratio of SAA to vegetable oil, by using SAA grades with different hydroxyl contents (e.g., SAA-100 and SAA-103), or by using hydroxy-functional vegetable oils such castor oil.

Oleates with 40–45 wt% SAA resin have low viscosities (<20,000cps) at 100% solids yet give resins and coatings with excellent properties. These oleates can be transferred with pumps and do not require solvents, making transportation and handling safer and giving the formulator a greater choice in solvents.

At 45% SAA modification, the oleates based on soybean, linseed, and coconut oil have ambient viscosities between 10,000 and 20,000 cps except for the SAA-103 coconut oleate with a viscosity of 52,000 cps.

Viscosities decrease rapidly to the 3,000–7,000 cps range as temperature increases to 35°C and further down to the 2,000–4,000 cps range at 45°C. The SAA-103 coconut oil curve is atypical suggesting a tendency to crystallize. Solution viscosities also decrease rapidly with solids content, from Z-Z1 and Y in mineral spirits and xylene at 90% solids to H-I and D at 70% solids.

At 45% SAA modification, OH numbers are 94 for the oleates based on SAA-100 and 54 for the oleates based on SAA-103. Polydispersities range from 2.3–2.9 and Mn from 1500–2200. The oils are generally pale yellow with Gardner colors in the 2 to 6 range. Some of these polyols were used instead of solid SAA polyols in the synthesis of alkyd resins with identical results, as described in the following paragraphs.

Figure 7—Effect of oil length and SAA type on the hardness development of SAA-modified soy alkyds.
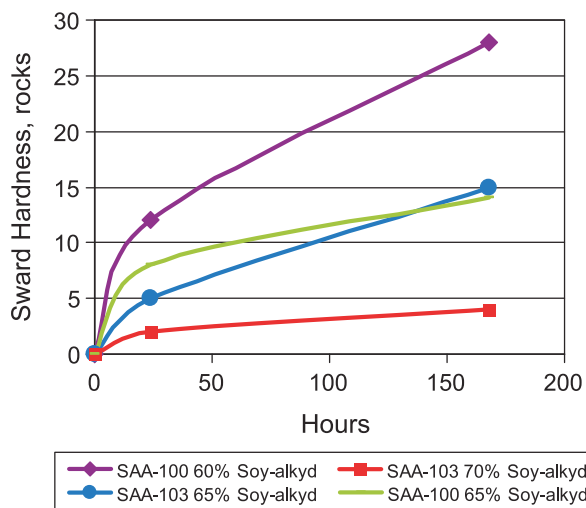

Figure 8—Effect of SAA modification on the humidity resistance of long-oil alkyds.
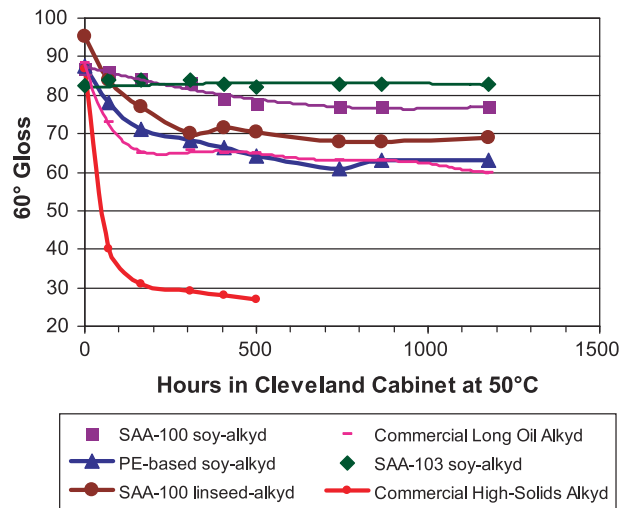
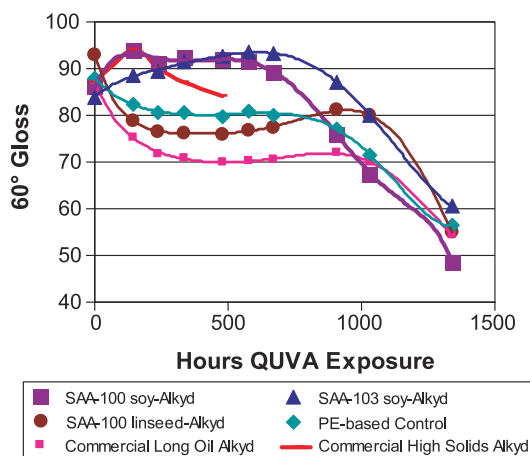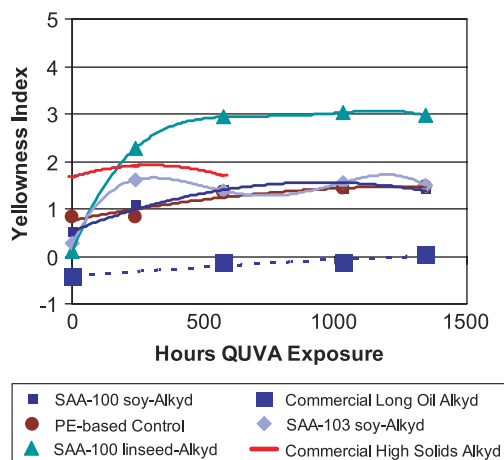Figure 9—Effect of SAA modification on the UVA resistance of long-oil alkyds.

Figure 10—Yellowing of long-oil alkyds under UVA exposure.

Long-Oil Alkyd Coating Properties

SAA-modified, long-oil alkyds were used to formulate clear and pigmented alkyd coatings. The coatings' drying times were measured on clears to eliminate the effect of pigment. The resins were reduced to 60% solids with mineral spirits and a standard drier package added. The clearcoats were then applied 1.5 mil wet on glass, and their Sward hardness measured after one and seven days. *Figure* 6 compares the hardness development of 10% SAA-100 modified alkyds to a commercial high-solids alkyd and a conventional solids alkyd.

The SAA-modified alkyd developed hardness faster than the commercial high-solids alkyd and gave harder, fully cured coatings. The alkyd prepared from pre-reacted SAA soyate hardened faster than the one prepared with solid SAA. Also, the SAA linseed alkyd had slower initial dry but eventually gave a much harder coating than the corresponding soyate.

The effect of oil length and type of SAA used on hardness development was also investigated. *Figure* 7 shows that, at equal oil length, alkyds modified with SAA-100 form faster-drying coatings with slightly lower ultimate hardness than those based on SAA-103. This is consistent with the higher functionality and lower T_g of SAA-100. Increasing the oil length in SAA-modified alkyds has the same effect as in all alkyds: a decrease in VOCs and cure speed and a softening of the final cured coating. A 65% oil soyate/linoleate of SAA-100 may provide the best compromise between low VOCs, cure speed, and ultimate coating hardness.

Pigmented alkyd coatings were also applied to pre-treated metal and subjected to condensing humidity at 40°C (Cleveland Humidity Cabinet). *Figure* 8 compares the 60° gloss of 10% SAA-modified 60% oil alkyd coatings to the same commercial long-oil alkyds and our

control PE-based 60% soy alkyd. Both the conventional PE-based alkyd and the medium solids commercial coating lost 25–30 gloss units after 500 hr of exposure whereas the high-solids alkyd blistered severely and lost 60 gloss units in 500 hr.

In contrast, all the SAA-modified alkyds performed better than the commercial and control systems, especially the SAA-103 soy alkyd, which showed no gloss loss after 1,200 hours of humidity exposure.

The same coatings were also subjected to QUVA exposure without HALS or UV screeners. Initial gloss retention was again better with the SAA-based soy alkyds (*Figure* 9). However, after 1,000 hours of exposure, all the coatings lost significant amounts of gloss (10–20 units) and after 1,300 hours, all the coatings had approximately the same gloss level (50–60 units).

Yellowing due to QUVA exposure was also comparable for all soy alkyds (*Figure* 10). The linseed-based alkyd yellowed more, which is typical. Overall, the SAA-modified alkyds offered superior humidity resistance, slightly better weatherability, and dry time comparable to a medium-solids alkyd resin but in a high-solids system.

CONCLUSIONS

Replacing a portion of the pentaerythritol with SAA resinous polyols in a long-oil alkyd cook yields resins with much lower polydispersities and viscosities. The SAA-modified alkyds were formulated into high-solids alkyd coatings with improved dry times, humidity resistance, and weatherability compared to a commercial high-solids alkyd. Drying and performance properties were comparable or better than a control PE-based alkyd and a commercial medium-solids alkyd.

SAA polyols were also used to alcoholyze soybean and linseed oils. The resulting polyols have narrow polydispersities, low solution viscosities, and are useful resins for a variety of novel low-VOC coating technologies including UV- and moisture-curable urethanes with air-drying properties. These new coating technologies are currently being developed.
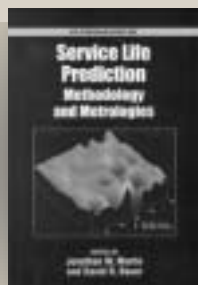
ACKNOWLEDGMENTS

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References

(1) Current MIR values can be found on Dr. William Carter's web page at: ftp://ftp.cert.ucr.edu/pub/carter/SAPRC99/r02tab.xls. The VOC speciation and contents were obtained from the product MSDS.

(2) In September 1999, the U.S. EPA proposed to add TBAc to the list of VOC-exempt compounds. Despite receiving mostly positive comments on their proposal, the EPA has still not published the final rule. For more information on TBAc, see: http://www.lyondell.com/html/products/products/tbac.shtml.

(3) See, for example: U.S. Patent 5,693,715 to Cargill, Incorporated, December 2, 1997.

(4) Tuck, N., "Waterborne and Solvent Based Alkyds and their End User Applications," *Surface Coatings Technology*, *Volume VI*, John Wiley & Sons and SITA Technology Limited, 2000, ISBN 471985910.

(5) Additional information on SAA polyols can be found at: http://www.lyondell.com/html/products/products/saa.shtml.

(6) U.S. Patent 2,588,890 to Shell Development Company, March 11, 1952.

(7) GB Patent 1,149,153 to PPG Industries, December 20, 1966.

(8) Swan, D., "Improved Exterior Latex Paints," *Paint & Varnish Production*, pp 37-42, June 1968.

(9) U.S. Patent 3,293,201 to PPG Industries, April 16, 1969.

(10) U.S. Patent 4,735,995 to Sherwin-Williams Company, April 5, 1988.

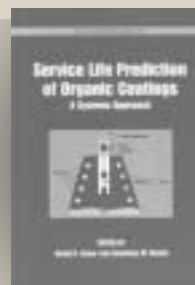(11) U.S. Patent 6,051,633 to Sherwin-Williams Company, April 18, 2000.