Tailored Synthesis of Alkyd Emulsions for Improved Film Performance

By **Jamie Dziczkowski**, Reichhold, Inc.

The molecular weight distribution of alkyd emulsions has been customized to enhance the overall performance of these polymers. Three soya-based resins—a short, medium, and long oil alkyd—were used as controls. A ladder study with three different levels of modification to the molecular weight was performed for each alkyd to determine the effect this had on final film properties. Film properties including dry time, hardness, solvent resistance, mar resistance, and gloss were evaluated in clear coatings. The results show that as the molecular weight is increased, solvent resistance, dry time, and hardness are improved for all oil lengths, while gloss remains rather consistent. This method of modification to the resin provides a novel route to waterborne alkyds that offer coating performance comparable to solventborne alkyds.

INTRODUCTION

As environmental restrictions continue to tighten on the coatings industry, novel routes to low-VOC (volatile organic compound) polymer vehicles that offer comparable performance to solventborne formulas continue to be the focus area. Green chemistries, especially those that incorporate renewable resources, are highly attractive starting points. Alkyd chemistry, although a very mature chemistry in the industry, has resurfaced as the focus of the next generation of waterborne polymers. The concept of alkyd emulsions has been around for decades. Until recently, however, the ability to mimic the performance of solventborne alkyds has been a challenge as a result of incorporation of higher levels of external surfactants.

For many years, alkyd binders have been used in architectural and industrial coatings. Alkyd polymers are a special class of polyesters derived from (semi-)drying oils, dibasic acids, and alcohols or polyols.[1] The reaction mechanism for synthesizing an alkyd resin via the monoglyceride process is given in *Figure* 1. Several naturally occurring oils can be used to synthesize alkyds. These include—but are not limited to—soybean, linseed, sunflower, and safflower oils. The drying characteristic of the resulting polymer is dependant on the oil length

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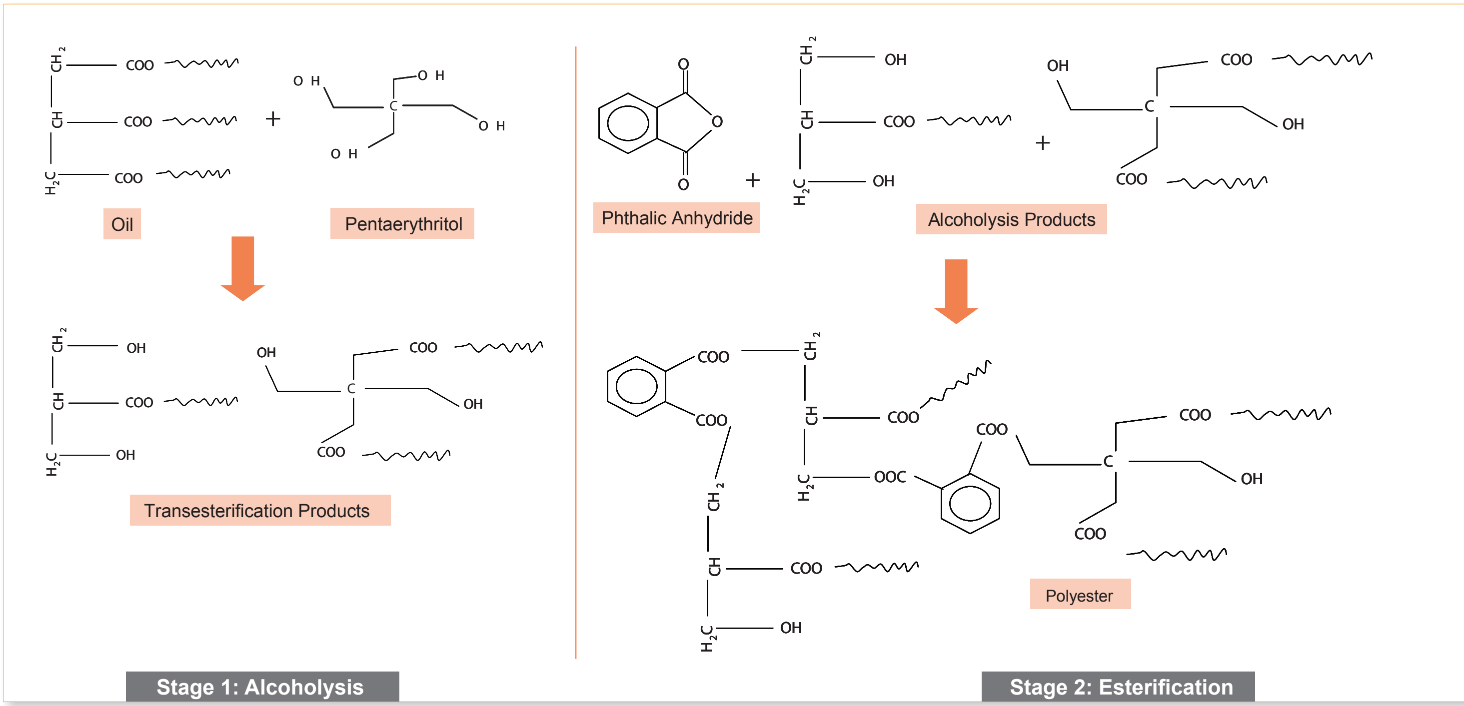

Figure 1—Alkyd (polyester) derived from a drying oil, phthalic anhydride, and pentaerythritol synthesized by the monoglyceride process.

Table 1—Typical Oil Compositions (Average % of Each Fatty Acid)[2]

Name (Double bonds, Carbons)	Coconut	Castor	Soya	TOFA	Linseed	Tung
Lauric (0,12)	48					
Myristic (0,14)	17					
Palmitic (0,16)	9	2	8	7	5	4
Stearic (0,18)	2		4		4	1
Oleic (1,18)	6	7	28	44	22	8
Linoleic (2,18)	2	3	54	37	17	4
Conjugated linoleic (2,18)				11		
Linolenic (3,18)			5		51	3
Eleostearic (3 conjugated, 18)						80
Ricinoleic (1,1 Hydroxyl,18)		87				
Iodine value	9	86	130	167	180	168

of the polymer (more oil, slower drying) and the amount of unsaturation that is present in the corresponding oil.[2] The degree of unsaturation in the oil is determined by the fatty acid composition that makes up the particular oil. Typical oil compositions are given in *Table* 1.

An attractive component of alkyd chemistry is the ability for oxidation that is contributed from the oil component of the polymer. Oxidation occurs through the unsaturated moieties that are found along the pendant fatty acid chains. The reactions that take place during oxidation are rather complex. The free radicals generated from naturally occurring hydroperoxides in combination with hydrogen abstraction from the polymer result in the formation of a combination of ether, peroxy,

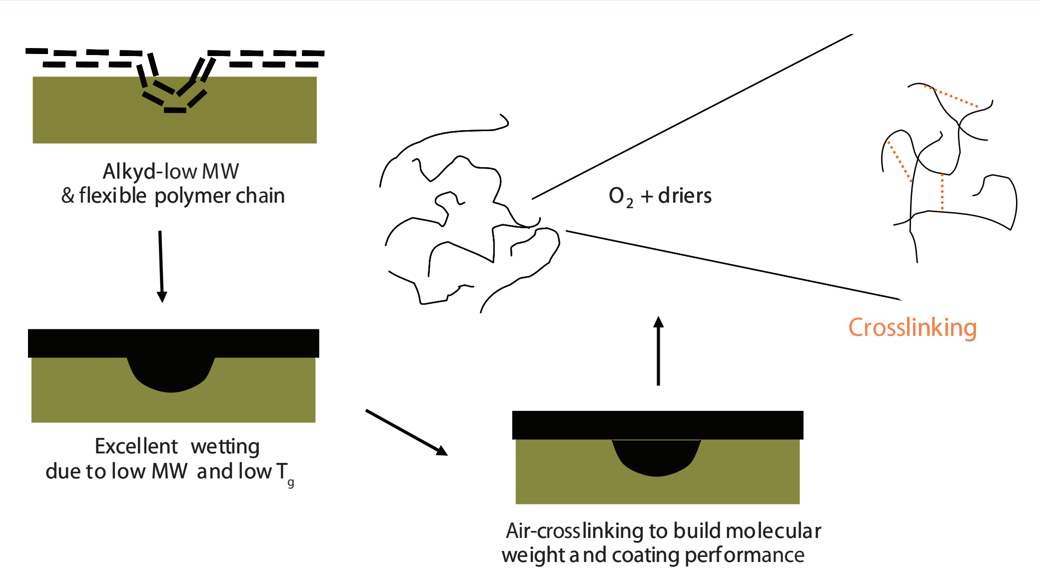

Figure 2—Benefits of oxidation in an alkyd system

and carbon–carbon linkages to achieve a highly crosslinked film.[2] The benefits presented by an oxidizable system are evident. With an alkyd-based coating, the initial film exhibits good flow and leveling characteristics due to the low molecular weight, low glass transition temperature (T_g), and flexibility of the polymer chains. Then, following air crosslinking, the final film exhibits good adhesion, hardness, gloss, and corrosion resistance. The film formation for an alkyd resin is depicted in *Figure* 2. However, conventionally, alkyds have been tailored for solventborne systems.

Alkyd emulsions are formed by the introduction of external surfactants and advanced processing techniques that provide a stable emulsion in a continuous aqueous phase. These stable emulsions are achieved by careful selection of the surfactant system and precise control of the emulsion process. A key factor for stabilization is attaining small emulsion particle diameters. The quality of the emulsion is dependent on the surface tension present in the particles. Alkyd emulsions can be prepared by either direct emulsification or a phase inversion process.[3] During direct emulsification, the alkyd resin is dispersed directly into water using high shear equipment. The inversion process is done by first forming a water-in-oil (W/O) emulsion. Then, by changing the temperature and water concentration, the W/O emulsion inverts to a stable oil-in-water (O/W) emulsion.[4]

Either nonionic and anionic surfactants or combinations thereof can be used to obtain colloidal stability of the alkyd emulsions. When using nonionic surfactants, it is important to consider the hydrophilic/lipophilic balance (HLB) of the materials. The correct HLB should be selected based on the emulsification temperature, the polymer charge density, and the polarity of the resin, which is determined by the acid number, oil length, and hydroxyl value.[5] As the temperature and water concentration of the system changes, the diffusion of the nonionic surfactant from the oil to the water phase favors the emulsification process.[6] Anionic surfactants work through charge stabilization. One advantage to using anionic surfactants is the relative insensitivity to high temperatures, which are frequently needed for emulsification of high viscosity alkyd resins.[3]

First-generation waterborne alkyds, including alkyd emulsions and water-reducible alkyds, were inferior to their solventborne counterparts. According to researchers, this was mainly due to high levels of surfactants, hydrolytic stability, and inexperience of formulators.[7] However, as more research has been done on alkyd emulsions and a better understanding of the systems has been reached, alkyd emulsions are becoming a binder of interest for many formulators.[7,8] By achieving stable emulsions through the introduction of a protective surfactant shell, the core alkyd resin is stabilized and hydrolysis rates are hindered. This type of system addresses the VOC issue and provides the benefits of a traditional alkyd resin. See *Figure* 3 for a pictorial description of an alkyd emulsion.

Some alkyd latexes still present a challenge in the ability to mirror solventborne alkyd performance. Because higher levels of surfactant are needed versus a conventional latex, plasticization of the polymer by the surfactant can occur. This in turn changes the overall interaction of the polymer

Table 2—Alkyd Latex Wet Properties

Alkyd Base	Level of Mod. A	Viscosity (cps) @50 RPM	Solids (%)	Initial pH	AV (On Solids) (mg KOH/ g sample)
Alkyd 1	1	185	55.5	6.96	13.5
Alkyd 1	2	220	55.3	6.90	12.5
Alkyd 1	3	210	55.7	7.00	13.2
Alkyd 2	1	506	55.8	7.07	11.8
Alkyd 2	2	580	55.7	7.07	11.6
Alkyd 2	2	650	55.7	7.22	11.2
Alkyd 2	2	690	55.6	7.10	11.3
Alkyd 2	2	720	55.6	7.18	11.4
Alkyd 2	2	810	56.0	7.16	11.2
Alkyd 2	3	680	55.6	7.09	11.2
Alkyd 3	1	110	55.5	7.08	11.1
Alkyd 3	2	190	55.2	6.85	13.6
Alkyd 3	3	165	55.7	7.02	11.3

chains and decreases the glass transition temperature of the film. This phenomenon creates a false impression of incomplete cure because of a slight after-tack that can be experienced. This minor setback can be addressed by modifying the molecular weight distribution of the polymer phase, thus raising the T_g of the polymer phase to offset the plasticization effect of the surfactant. This article focuses primarily on the modification of the molecular weight distribution of long, medium, and short oil soya-based alkyds by increasing the molecular weight at three different levels. The resulting alkyd emulsions were evaluated in clear formulations to determine the general overall effect the modification affords to final film properties.

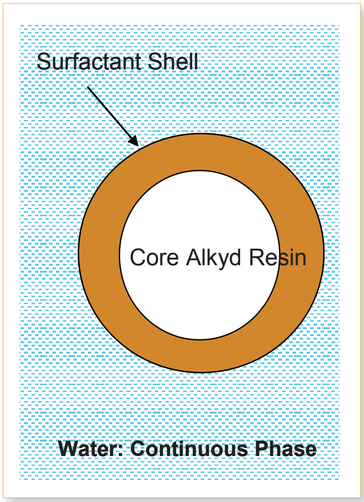

Figure 3—Core alkyd resin stabilized by an external surfactant protective shell.

EXPERIMENTAL

Molecular weight modification was made to long (Alkyd 1), medium (Alkyd 2), and short (Alkyd 3) oil alkyds at increasing levels. The levels were chosen according to a central composite design space that was generated using design of experiment software. The alkyd resins were then emulsified using a proprietary surfactant package. The base resins were used as controls. *Table* 2 presents the different alkyd emulsions and some of their wet properties. Note that all alkyd emulsions shown had particle sizes ≤300 nm.

Following emulsion formation, clear formulations were made with cobalt and zirconium driers

Table 3—Clear Formulation for Alkyd Latexes

General Coating Formula	
Resin, (g)	145
Co drier (5%), (g)	0.79
Zr drier (12%), (g)	0.99
Wetting agent, (g)	0.25
Water, (g)	63.66
Total weight, (g)	211.55
NV, %	38.0
Co drier, ppm (on alkyd solids)	500
Zr drier, ppm (on alkyd solids)	1500
Wetting agent (% on total)	0.15

Table 4—Film Properties of the Modified Long Oil Alkyd Series

	Control Alkyd 1	Alkyd 1/Mod. A Level 1	Alkyd 1/Mod. A Level 2	Alkyd 1/Mod. A Level 3
Film Performance				
Circular dry time, hr:min				
Set	0:30	0:45	0:45	0:30
Through	2:00	2:00	1:45	1:00
Hard	>24:00	19:30	14:00	12:00
Zapon tack free (200 g), hr:min	>24:00	> 24:00	> 24:00	3:10
Sward hardness				
1 day	6	4	6	8
7 days	6	8	10	14
Konig hardness	11	17	20	22
Pencil hardness	5B	5B	4B	4B
Impact resistance, in-lb				
Direct/reverse	80/60	160/160	160/160	160/160
Mar resistance[a]	poor	fair	good	good
Gloss				
60 degree	90.9	92.1	93	92.7
20 degree	81.6	85.9	84	82.5
Chemical resistance, average[b]	3.7	3.9	3.8	4.0
Solvent resistance, dbl rubs				
Methyl ethyl ketone	35	33	47	65

(a) Finger nail scratch (after one day)
(b) ASTM D1307, 4-hr exposure, covered, rating 0-5 no effect

and a wetting agent. The resins were then diluted to ~38% NV to give an application viscosity below 100 cps. An example of the clear formulation is given in *Table* 3. Films were cast on steel panels, Leneta charts, and glass panels for complete coatings evaluation. A #40 WWR was used for the steel panels and a 3-wet mil bird bar was used for casting films on glass and Leneta cards. Films were allowed to air dry for seven days before testing. Dry film thicknesses were 1–1.5 mil. Several tests were conducted to evaluate film performance including dry time, hardness, gloss, and chemical, mar, and solvent resistance. All test procedures used were based upon standard coatings methodology with tests of all clear formulas performed side by side to ensure reliability of comparisons.

RESULTS/DISCUSSION

The film properties for the modified long oil alkyd (LOA) series are presented in *Table* 4. From the table, it is evident that the overall film performance is improving with increasing levels of molecular weight modification. From the dry time data, the circular dry time shows improvement at the lowest level of modification, while the Zapon tack-free time (200 g) does not improve until the highest level of modification is made. An increase in hardness and mar resistance is seen for the LOA series as the level of molecular weight modification is raised. Solvent resistance for this series begins to show advancement at the intermediate level of modification. It is important to note that the gloss remains consistent for all levels of modification to the long oil alkyd control.

The final film properties for the medium long oil alkyd (MOA) series are summarized in *Table* 5. Similar to the LOA series, the overall film performance of the MOA series also improves with increasing levels of molecular weight modification. The circular dry time and the Zapon 200 g tack-free time show improvement at the intermediate level of modification. Once again a general increase in overall hardness is noted based on the results of the various hardness tests. The chemical, solvent, and mar resistance also show improvement, although it appears there is a critical level somewhere between modification level 2 and 3 where the solvent resistance reaches a maximum. It should also be noted that the gloss and impact resistance start to decrease with increasing levels of modification with the MOA series.

Table 5—Film Properties of the Modified Medium Oil Alkyd Series

	Control Alkyd 1	Alkyd 1/Mod. A Level 1	Alkyd 1/Mod. A Level 2	Alkyd 1/Mod. A Level 3
Film Performance				
Dry Time, hr:min				
Set	0:45	0:45	0:45	0:30
Through	3:00	2:00	1:30	1:00
Hard	>24:00	>24:00	12:00	4:00
Zapon tack free (200 g), hr:min	>24:00	23:30	6:00	4:45
Sward hardness				
1 day	8	6	6.4	6
7 days	12	10	14	16
Konig hardness	12	23	34	38
Pencil hardness	4B	2B	2B	2B
Impact resistance, in-lb				
Direct / Reverse	100/100	70/50	76/14	50/20
Mar Resistance[a]	poor	fair	good	good
Gloss				
60 degree	92.6	93.2	92.42	92.8
20 degree	86.3	78.2	73.9	71.8
Chemical resistance, average[b]	3.4	3.9	4.0	4.0
Solvent resistance, dbl rubs				
Methyl ethyl ketone	30	35	54	40

(a) Finger nail scratch (after one day)

(b) ASTM D1307, 4-hr exposure, covered, rating 0-5 no effect

Table 6—Film Properties of the Modified Short Oil Alkyd Series

	Control Alkyd 1	Alkyd 1/Mod. A Level 1	Alkyd 1/Mod. A Level 2	Alkyd 1/Mod. A Level 3
Film Performance				
Dry Time, hr:min				
Set	0:45	0:45	0:30	0:30
Through	4:30	1:15	1:30	1:00
Hard	>24:00	>24:00	8:30	5:30
Zapon tack free (200 g), hr:min	>24:00	23:00	3:30	3:00
Sward hardness				
1 day	18	8	16	20
7 days	22	16	22	28
Konig hardness	21	32	49	57
Pencil hardness	< 5B	2B	2B	2B
Impact resistance, in-lb				
Direct / Reverse	20/failed 10	60/40	30/failed 10	30/failed 10
Mar Resistance[a]	poor	poor	fair	fair
Gloss				
60 degree	96.1	96.2	96.5	95.9
20 degree	91.4	91.1	85.1	80.3
Chemical resistance, average[b]	2.7	3.5	4.0	4.0
Solvent resistance, dbl rubs	15	10	20	15
Methyl ethyl ketone	40	40	80	100

(a) Finger nail scratch (after one day)

(b) ASTM D1307, 4-hr exposure, covered, rating 0-5 no effect

Table 7—Mild Tannin Blocking Primer Formulation

Raw Material	#/100	Gal/100
Water	131.91	15.84
Modified cellulosic thickener	1.34	0.12
28% Ammonia	1.49	0.19
Dispersant	8.44	0.95
Defoamer	0.95	0.09
Surfactant	2.38	0.27
Titanium dioxide	197.05	5.91
Extender	285.90	12.71
Grind Total	*629.46*	*36.09*
High speed disperse to a 4 Hegman		
Alkyd 2/Mod Level 2	425.17	48.43
Premix next three raw materials and add		
Cobalt drier	2.34	0.31
Drier synergist	2.10	0.25
Zirconium drier	4.87	0.60
Propylene glycol	9.73	1.13
Defoamer	0.95	0.09
Water	30.88	3.71
Tannin blocking additive (I)	41.00	4.78
Tannin blocking additive (II)	23.82	2.34
Associative thickener	19.85	2.29
Total	***1190.19***	***100.00***

Table 8—Gloss White Enamel Formulation

Raw Material	#/100	Gal/100
Water	95.24	11.43
Clay thickener	3.49	0.17
Mix high speed until wet out and thickened		
Amine buffer	0.71	0.09
Mix until thickened		
Dispersant	12.32	1.38
Defoamer	1.90	0.23
Titanium dioxide	273.69	8.21
Grind Total	*387.35*	*21.52*
High speed disperse to a 7.5 N.S.		
Alkyd 2/Mod Level 2	523.81	59.66
Defoamer	1.90	0.24
Premix next three raw materials and add		
Cobalt drier	2.88	0.38
Drier synergist	0.72	0.09
Zirconium drier	4.80	0.59
Water	109.52	13.15
Propylene glycol	4.76	0.55
Add grind base		
Water	10.68	1.28
Associative thickener (I)	20.86	2.38
Associative thickener (II)	1.43	0.16
Total	***1068.72***	***100.00***

Finally, the film properties of the short oil alkyd (SOA)-modified series are given in *Table* 6. As with the previous sets of data, the dry time, overall hardness, solvent resistance, and chemical resistance improve with increasing levels of modification to the SOA control. In addition, the gloss of the SOA-modified series is fairly consistent at all levels of modification. The impact resistance starts to show improvement at the lowest level of modification, but falls to its original value as modification levels increase.

Based on the results of the ladder study, one resin was chosen—Alkyd 2 at intermediate level 2—for applications testing. The applications chemists developed several architectural coatings including a primer, gloss enamel, and stain. This particular resin proved to be versatile in all areas and can be used to replace solventborne alkyds, yet still provides the same VOC levels as traditional latex paints. *Tables* 7–9 give examples of the different starting formulas developed based on the modified medium oil alkyd. One important feature of the alkyd latexes is that they formulate like a typical latex paint. Standard latex rheological additives, dispersants, and defoamers are effective in formulating alkyd latex paints. Although the details are outside of the scope of this article, the formulations mentioned are used to illustrate the effectiveness of the concept of modification to the molecular weight distribution of the alkyd latexes to tailor resin properties for certain applications.

The purpose of this study was to determine how molecular weight modification affects the overall performance compared to the control long, medium, and short oil alkyd emulsions. In particular, improving the dry time and overall hardness were of most importance. This specific type of modification has not only been shown to improve the dry time and hardness, but also to improve other key film properties such as chemical and solvent resistance while maintaining good gloss development. These are key features that solventborne alkyds have always provided while most acrylic latex products remain substandard.

Another goal of the study was to determine how versatile this particular modification was for different oil length alkyd systems. Molecular weight modification has demonstrated the ability to work in long, medium, and short oil alkyd systems. This concept is especially important because, as the industry moves forward with alkyd emulsion advancement, product development can be tailored for all applications including architectural and industrial. As alkyd emulsions work their way into existing and emerging application segments, it is important to develop an understanding of performance response to structure variation.

Table 9—Semi-Transparent Stain Formulation

Raw Material	#/100	Gal/100
Water	192.95	23.07
Clay thickener	3.03	0.15
Cellulosic thickener	4.04	0.37
Amine buffer	1.52	0.19
Mix until thickener is activated		
Dispersant	3.03	0.30
Surfactant	3.03	0.39
Defoamer	1.52	0.14
Extender	85.87	3.96
Grind Total	294.98	28.67
High speed disperse to a 5 Hegman		
Alkyd 2/Mod Level 2	262.65	29.91
Premix next three raw materials and add		
Cobalt drier	2.53	0.33
Drier synergist	0.25	0.03
Zirconium drier	3.03	0.37
Biocide	7.07	0.97
Propylene glycol	3.82	0.38
Wax additive	15.15	1.85
UV absorber	1.50	0.21
Free-radical scavenger	3.00	0.35
Water	309.32	37.03
Total	903.82	100.00

Finally, one resin was chosen to demonstrate the effectiveness of alkyd latex binders in different paint applications including primers, gloss enamels, and stains. With regards to formulation, these alkyd latex binders are self coalescing and therefore require no solvent to enhance film formation, wetting, adhesion, film integrity, and gloss development. No added solvent suggests that a formulator need not worry about future VOC regulations or regulations that require computation of minimal incremental reactivity.

SUMMARY

Molecular weight modification proved to be an effective way to improve the dry time and overall hardness of the control alkyd emulsions. With all three series (LOA, MOA, and SOA), the overall performance of the final film increased with increasing levels of modification. This particular modification does not appear to have a pronounced effect on the gloss of the alkyd latexes. Finally, it was shown that the medium oil alkyd with molecular weight modification at the intermediate level provides a resin with balanced properties for various architectural applications. CT

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AUTHOR

Jamie Dziczkowski, Ph.D., Chemist Associate, Reichhold, Inc., P.O. Box 13582, Research Triangle Park, NC 27709 USA; jamie.dziczkowski@reichhold.com.