Novel Synthesis of Carboxy-Functional Soybean Acrylic-Alkyd Resins for Water-Reducible Coatings

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A new process was developed for synthesis of alkyd resins in which a conventional monoglyceride is reacted with a carboxy-functional acrylic copolymer. The novel products are called acrylic-alkyd resins. The carboxy-functional acrylic copolymers were synthesized by solution-free radical polymerization. Gelation during alkyd resin synthesis was avoided by: (1) limiting the molecular weight of the acrylic copolymers to M_n *3500–5000 and (2) limiting the number average functionality about 6.5-10 carboxyl groups per molecule. Further, the carboxyl groups were derived from a mixture of acrylic and methacrylic acids (1/1.2 mol ratio) in the expectation that this would help control the process. Three series of acrylic copolymers were prepared from various combinations of acrylic monomers and reacted with a monoglyceride prepared from soybean oil and trimethylol propane. The composition of the acrylic resin was adjusted to minimize phase separation [observed visually and by scanning probe microscopy (SPM)] within cast films. The most satisfactory results were obtained with copolymers of 62-71 wt% of methyl methacrylate, 5-21 wt% of lauryl methacrylate, 7.2 wt% of acrylic acid, and 10.3 wt% of methacrylic acid. In preliminary tests, waterborne coatings made from acrylic-alkyd resins based on these acrylics had excellent stability, with acid numbers changing less than 10% after nine months of storage.*

INTRODUCTION

This is a preliminary report of a new method for making alkyd resins in which aromatic di- and tri-acids normally used in making alkyds are replaced by an acrylic copolymer polyacid. This study was undertaken to address one of the key shortcomings of conventional alkyd resins for waterborne coatings: their limited hydrolytic stability.

Waterborne coatings have become widely used in the past several decades.[1-5] Waterborne architectural paints based on synthetic acrylic and vinyl latexes have gained about 75% of the market, supplanting solventborne coatings based partly on vegetable oils. The waterborne latex paints are especially well suited to "flat" (non-glossy) interior wall paints and exterior house paints. They are environmentally friendly, easy to clean, and have generally satisfactory film properties and durability.

Alkyd coatings have certain advantages over latexes. They can be applied in a broader temperature range, generally adhere better, form harder, less permeable films, and it is easier to get glossy appearance. Thus, alkyds have clung to a share of the architectural paint market for uses such as primers, enamels for kitchen cabinets, varnishes, and floor paints. They are usually used in solventborne formulations.

Alkyd resins can be adapted for use in waterborne coatings by making them carboxy-functional and using salts of their carboxyl groups to stabilize them as aqueous dispersions. Such resins are called *water-reducible* or *water-thinnable* resins. They have been available for decades and find substantial uses in certain industrial and maintenance applications. However, their use in architectural paints has been constrained because of the difficulty in making a waterborne alkyd that satisfies the storage stability requirements. An architectural paint may be stored several years before it is used, and it must retain its application and film forming properties. Contemporary waterborne alkyd resins undergo slow hydrolysis at ester linkages that leads to deterioration of

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Table 1—Formulations and Properties of Acrylic Copolymers A1-A3

	A1	A2	A3
Materials	**Weight percentage (wt%)**		
MMA	44.6	44.5	44.5
BA	37.5	/	/
BMA	/	38.0	/
iso-BMA	/	/	38.0
MAA	10.3	10.3	10.3
AA	7.6	7.2	7.2
Resin Properties			
Acid value	113	109	112
T_g (°C)$_{exp.}$	35	43	47
T_g (°C)$_{cal.}$	30	76	92
Conversion (%)	99.3	99.4	99.7

film properties after application and, ultimately, to irreversible physical separation within the paint can.

Looking to the future, the EPA is expected to tighten U.S. environmental regulation of paints, and some localities, notably in California, have or will impose even stricter limits on organic solvent emissions. The coatings industry and its suppliers are working hard to improve latex technology by reducing solvent emissions and improving gloss and film properties. If these efforts are fruitful, they will jeopardize the remaining markets for solventborne alkyd paints. On the other hand, if technology for package stable waterborne alkyds could be developed, it might arrest the slide in alkyd usage and might even make alkyds attractive for some applications already partly lost to latexes, for example, semi-gloss enamels.

This problem has been addressed by many investigators (for examples, see references 6-10). Examples of previous approaches are described in the Discussion Section of this paper. We believe our approach is different. We synthesized a carboxy-functional acrylic copolymer and used it as a polyacid for synthesis of alkyd resins, termed *acrylic-alkyd resins*. It was hoped that this approach would yield alkyds with superior hydrolytic stability. An anticipated obstacle was the need to react some of the carboxyl groups on the acrylic to form the alkyd resin while leaving some carboxyl groups unreacted. The unreacted carboxyl groups can be ionized under basic conditions and enable the resin to form self-stabilizing dispersions in water. Therefore, we used acrylic copolymers that included both acrylic and methacrylic acids. It was theorized that the carboxyl groups in the polymer derived from acrylic acid would esterify more readily than the more sterically hindered carboxyl groups derived from methacrylic acid. We did not prove this theory, but we did demonstrate that it is possible to synthesize acrylic-alkyd resins with unreacted carboxyl groups from such acrylic copolymers. Preliminary studies indicate that the products have exceptional hydrolytic stability.

Table 2—Formulations and Properties of Alkyd Resins R1-R3

	R1	R2	R3
	Weight percentage (wt%)		
Materials			
Acrylic copolymer(A*x)	50.0	50.5	49.2
Monoglyceride	50.0	49.5	50.8
Resin Properties			
Appearance	Clear	Clear	Clear
Oil length (%)	41.5	38.3	38.6
Acid value	40.1	39.2	37.7
%NVM	80.5	83.0	80.2

*Note: x denotes 1, 2, and 3, respectively.

EXPERIMENTAL DETAILS

Materials

Soybean oil was supplied by Cargill Inc. It had an iodine number of 137 and fatty acid content (analyzed by gas chromatography of the methyl esters) of: palmitic, 12.0%; stearic, 4.3%; oleic, 23.1%; linoleic, 53.5%; and linolenic, 7.1%. Methyl methacrylate (MMA), butyl acrylate (BA), butyl methacrylate (BMA), iso-butyl methacrylate (iso-BMA), lauryl methacrylate (LMA), acrylic acid (AA), methacrylic acid (MAA), t-butyl peracetate (50 wt% solution in odorless mineral spirits), 1-dodecanethiol, 2-butoxyethanol, *N,N*-dimethylethanolamine (DMEA), trimethylolpropane (TMP), n-propyl acetate, toluene, 2-propanol, and 0.1 N potassium hydroxide solution in methanol were purchased from Aldrich Chemical Co. and used as received.

Synthesis of Acrylic Copolymers

The acrylic copolymers were prepared by batch-free radical polymerization in solution. Polymerization was conducted in a three-neck round-bottom flask equipped with a thermometer, a reflux condenser, N_2 inlet and outlet tubes, and a mechanical stirrer. The vessel was charged with 9.6 g t-butyl peracetate (50 wt% solution in odorless mineral spirits, a free radical initiator), 5.0 g 1-dodecanethiol (a chain transfer agent), 230 g n-propyl acetate (solvent), and 120 g acrylic monomer (see *Tables* 1, 3, and 5 for quantities) and purged with N_2. The solution was heated with stirring at about 105°C, for about 4.5 hr to yield a colorless, viscous solution of polymer.

PREPARATION OF MONOGLYCERIDE FROM SOYBEAN OIL AND TMP BY ALCOHOLYSIS: Soybean oil (518 g) and trimethylolpropane (158 g) were charged to a three-neck round-bottom flask equipped with a total condenser, an agitator, an inert gas sparge, and a thermometer. The reaction mixture was heated to 204°C under an N_2 atmosphere. Then 0.26 g Fascat® 4100 catalyst was added. Heating was continued until a temperature of 250°C was reached (about 15 min). After the temperature reached 250°C, the reaction was monitored by withdrawing a 1-mL sample from the flask every 10 min, and adding the sample to 3 mL of methanol to check its solubility. After about 1.25 hr at 250°C the 1-mL sample was completely soluble in 3 mL of methanol, indicating that the alcholysis reaction was approaching equilibrium. Heating was discontinued. The product was a light yellow liquid.

SYNTHESIS OF WATER-REDUCIBLE ACRYLIC-ALKYD RESINS—PROCEDURE A: A procedure for synthesis of resin R7

(*Table* 6) is given in the following: acrylic copolymer solution (64.3 g of 50 wt% solution) and monoglyceride (35.7 g) were charged to a three-neck round-bottom flask equipped with a total condenser, a water separator, a mechanical agitator with a teflon blade, an inert gas sparge which leads the N_2 below the level of the liquid, a heating mantle, and a thermometer. Under N_2 flow, the reaction mixture was heated, and the solvent was removed by distillation. When the temperature reached 200°C (after about 20 min), the heating mantle was turned off but left in place. When the polymeric product cooled to about 150°C, sufficient 2-butoxyethanol was added to dilute the polymer to about 80 wt% solids. The acrylic-alkyd resin was a viscous, light yellow solution.

Procedure B: In earlier experiments the procedure differed in several respects, the most important being: (1) the acrylic polymer was made with 3.6 g rather than 5.0 g of dodecanethiol, and (2) temperature during synthesis of the acrylic-alkyd resin was 230°C for a longer time. *Tables* 2, 4, and 6 show the quantities charged, and these products made by Procedure B were used in the stability experiments (*Figure* 2). However, in repeat experiments it was found that Procedure B sometimes results in products with excessive viscosity. Procedure A results in products with similar characteristics and is recommended.

Reduction of Acrylic-Alkyd Resin with Water: N,N-dimethyl ethanolamine (1 mol per equiv. of carboxyl groups in early experiments and 0.75 mol per equiv. of carboxyl groups in later experiments) was dissolved in 100 g of warm (70°C) acrylic-alkyd resin solutions in a wide-mouth glass container equipped with an addition funnel and a high speed air-driven stirrer with a turbine propeller. Under high speed stirring, de-ionized water (about 60 wt% of the final total weight) was metered into the glass container over one hour. The mixture in the glass container became a high viscosity white opaque liquid at first. As more water was added, the viscosity of the mixture decreased. After water addition was complete, the stirring was continued for one hour. The product was a colorless, low viscosity, opaque dispersion of water-reduced acrylic-alkyd with solids of about 30 wt%.

Test and Characterization Methods

Hydrolytic Stability: Samples of water-reduced acrylic-alkyd resins were stored at ambient temperature. After storage, a 3-4 g sample of water-reduced acrylic-alkyd was weighed and dissolved in 100 mL of a solvent mixture (equal parts by volume of isopropyl alcohol and toluene) in a 250-mL Erlenmeyer flask with a magnetic stir bar. After the acrylic-alkyd resin was completely dissolved, it was titrated with a 0.1 N solution of KOH in methanol to measure the acid value.

Glass transition temperature (T_g) measurements were performed with a TA Instruments Model 2100 differential scanning calorimeter (DSC). Samples were encapsulated in standard aluminum DSC pans and heated from –50° to 150°C at 10°C/min under a N_2 atmosphere. Gel permeation chromatography was performed on an HP 1050 series liquid chromatograph with a 1047A diode array detector and a 1047 refractive index detector. Three "Phenogel" columns with three pore sizes (10^5 A, 10^3 A, and 100 A) were used in series. Tetrahydrofuran solvent and polystyrene calibration standards were used. Acid values and non-volatile weight percentages (%NVM) were measured using ASTM D 1639 and ASTM D 2369, respectively.

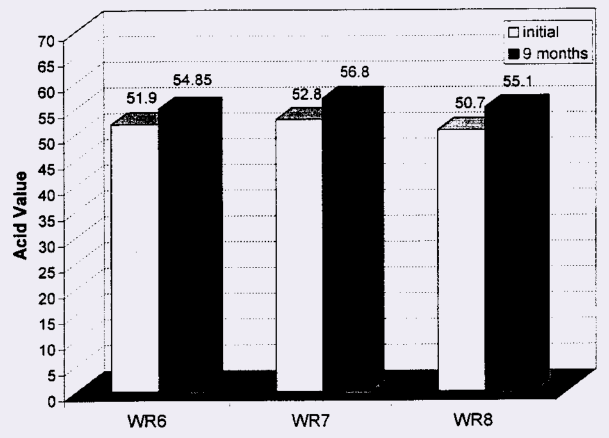

Figure 2—The hydrolytic stability of C6, C7, and C8 during room temperature storage.

SPM images were obtained with a Nanoscope III Scanning Force Microscope manufactured by Digital Instruments of Santa Barbara, CA. The unit was equipped with a J scanner and a V-shaped traditional triangular silicon nitride cantilever with a length of 100 mm, a silicon nitride sharp tip, and a spring constant of 0.58 N/m were used. The scan rate was 2.001 Hz.

RESULTS

Preparation of water-reducible acrylic-alkyd resins was effected in a three-step synthesis procedure:

(1) Synthesis of an acrylic copolymer containing two types of carboxyl groups.

(2) Preparation of a monoglyceride from soybean oil and trimethylolpropane.

(3) Condensation polymerization of the acrylic copolymer and the monoglyceride.

The properties of the products will be influenced by the properties of the acrylic copolymer and of the monoglyceride and by the ratio of acrylic copolymer to monoglyceride. Based on these considerations, three series of acrylic-alkyd resins were prepared to study the influence of key variables on properties. These were range-finding experiments. Further experimentation would be needed to develop products.

Series 1: Preliminary Experiments on Synthesis of Acrylic-Alkyd Resins

A series of acrylic copolymers, which have similar structures but different T_g was prepared; conversion of monomer to polymer was >99%, determined gravimetrically. Their formulations and properties are listed in

Table 3—Formulations and Properties of Acrylic Copolymers A3-A5

	A3	A4	A5
	Weight percentage (wt%)		
Materials			
MMA	44.5	61.9	82.5
iso-BMA	38.0	20.6	/
MAA	10.3	10.3	10.3
AA	7.2	7.2	7.2
Resin Properties			
Acid value	112	102	102
T_g (°C) exp.	47	62	77
Conversion (%)	99.7	98.4	98.6

Table 1. In this series the same hard monomer, MMA, and different soft monomers, i.e., BA, BMA, and iso-BMA were used. An MAA/AA mol ratio of 1.2/1 was used in the hope that this would control the acid values of the acrylic copolymers. Two types of acid monomers were used in an effort to incorporate carboxyl groups with different reactivities into the polymer. The carboxyl group derived from MAA is more sterically hindered than the carboxyl group derived from AA and is expected to be less reactive in the third step. All samples had similar acid values (A.V. ≈ 110 mg KOH/g resin). To limit molecular weight of the acrylics, relatively high levels of initiator (4 wt%) and chain transfer agent (3 wt%) were used. In representative experiments, number average molecular weights (M_n) of the acrylic polymers were about 3500-5000 and polydispersities (M_w/M_n) were about 2.2-2.6. For example, copolymer A1 had $M_n = 4900$ and $M_w = 11{,}900$ as measured by GPC. Conversions were about 99%. At $M_n = 3000$ the acrylic copolymers have number average functionalities (f_n) of about 6.6, with about 3.0 carboxyl groups/mol derived from AA and 3.6 carboxyl groups/mol derived from MAA. When M_n is increased to 4500 the f_n is about 10. Of course, these polymers contain individual molecules with a wide range of molecular weights and functionalities.

Synthesis of the monoglyceride was modeled after standard industrial methods. While such products are conventionally called "monoglycerides," they are made by a reversible transesterification process that yields mixtures of all possible fatty acid mono-, di-, tri-esters derivable from glycerol and trimethylol propane along with small amounts of free triols. During the process the mixtures may or may not approach equilibrium.

Table 4—Formulations and Properties of Alkyd Resins R3-R5

	R3	R4	R5
Materials	Weight percentage (wt%)		
Acrylic copolymer(A*x)	49.2	48.2	49.6
Monoglyceride	50.8	51.8	50.4
Resin Properties			
Appearance	Clear	Clear	Translucent
Oil length (%)	38.3	39.4	41.8
Acid value	37.7	38.3	31.5
%NVM	80.2	81.4	77.8

* Note: x denotes 3, 4, and 5, respectively.

Table 5—Formulations and Properties of Acrylic Copolymers A6-A8

	A6	A7	A8
	Weight percentage (wt%)		
Materials			
MMA	77.5	72.5	61.7
LMA	5.0	10.0	20.7
MAA	10.3	10.3	10.4
AA	7.2	7.2	7.2
Resin Properties			
Acid value	108	108	105
T_g (°C)	72	73	N/A
Conversion (%)	99.4	99.2	99.7

Using the acrylic copolymers and the monoglyceride, three alkyd resins (R1, R2, and R3) were prepared with similar oil lengths and acid values. The results are shown in *Table* 2.

Preliminary experiments showed that coating films that were prepared from water dispersions of resins R1-R3 were very soft and suggested that higher T_g of the acrylic improved hardness. Based on this trend, higher T_g resins were studied.

Series 2: Acrylic-Alkyd Resins Containing Higher T_g Acrylic Copolymers

In this series the T_g of the acrylic copolymers was increased by increasing the MMA content. These copolymers were designated A3, A4, and A5; note that A3 was the same material as A3 in Series 1. The compositions and results are listed in *Table* 3. Other properties, such as acid value and molecular weight, were similar to the copolymers of Series 1. For example, copolymer A5 had $M_n = 4040$ and $M_w/M_n = 2.6$.

With the same procedure, another series of acrylic-alkyd resins (R3, R4 and R5) was prepared from acrylics A3-A5 and the monoglyceride. Again, R3 is the same as R3 in Series 1. The oil lengths of the acrylic-alkyd resins were about 40 as calculated from the following equation:

$$\text{Oil Length} = \frac{\text{(Weight of soybean oil in the monoglyceride)}}{\text{(Weight of acrylic} - \text{alkyd)} - \text{(Weight of water evolved)}} \text{ (100)}$$

The results are shown in *Table* 4. As MMA content increased, the appearance of the resin solutions changed from transparent to translucent suggesting phase separation.

Films cast from water dispersions of resins R4 and R5 had low gloss, further confirming phase separation. Series 3 was prepared to explore ways to correct this problem.

Series 3: Acrylic-Alkyd Resins with Lauryl Methacrylate and Lower Oil Lengths

In this series, two changes were made in an effort to eliminate phase separation while keeping T_g as high as possible. A long side chain monomer, lauryl methacrylate (LMA), was incorporated in the acrylic copolymer at levels of 5, 10, and 20 wt% in the hope that presence of the lauryl group would improve compatibility of polymeric species present in the final product. Also, oil length was reduced from about 40% to about 27.5%.

LMA containing acrylic resins A6–A8 were synthesized by the procedures described previously with similar results (see *Table* 5).

Acrylic-alkyd resins R6, R7, and R8 were synthesized by the procedure described earlier except that oil length was about 27 (see *Table* 6).

Resins R6–R8 were neutralized with *N,N*-dimethylethanolamine, diluted with water, and cast as films designated C6–C8.

A scanning probe microscope (SPM) was used to characterize the surfaces of films C6–C8. The SFM is capable of performing atomic force microscopy (AFM) and a variety of other experiments. It measures the force acting between a very small tip and a solid surface, with the tip mounted on a well-characterized cantilever; high resolution images of surface structure can be obtained. The instrument can be operated in a number of modes; in this study we used the deflection and friction modes.[11,12] Images for the coatings in question are shown in *Figure* 1.

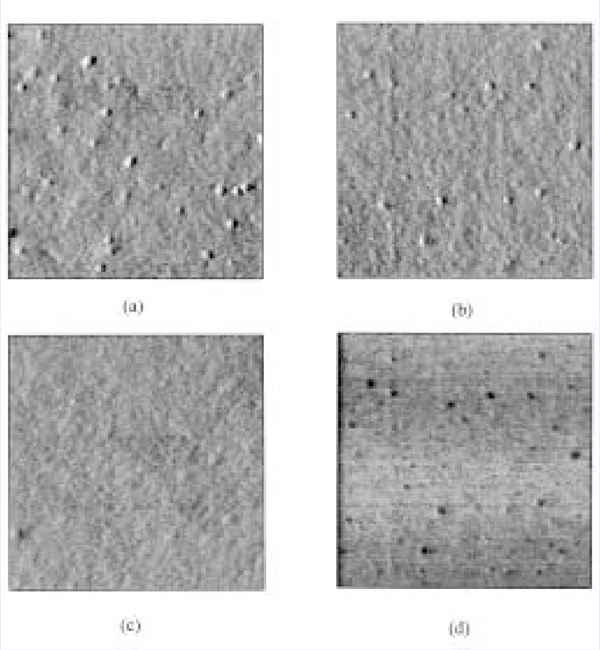

Figure 1—SPM images of films cast from water-reduced acrylic-alkyd resins (a), (b), and (c) are deflection images of C6, C7, and C8, respectively. (d) is a friction image of C7.

Figures 1a-c are deflection images of films of samples C6, C7 and C8, respectively, after air dry for seven days. These images suggest microphase separation of inhomogeneous material on the surface of coatings C6 and C7, but no evidence of phase separation is seen with coating C8. The friction image of coating C7 [*Figure* 1d] confirm this interpretation. The small round hills in the surface exert a different frictional force on the laterally moving probe, indicating that they have different physical properties arising from microphase separation. The appearance of images 1a-c suggest that the surfaces become smoother as LMA content increases. This impression was confirmed by surface roughness analysis using the SPM. As shown in *Table* 7, the root-mean square roughness decreases from 1.20 to 0.47 nm.

After storage for nine months at room temperature, there was no visible change in the appearance of the water dispersions made from R6, R7, and R8. Titration showed that their acid values had increased by less than 10% (see *Figure* 2). This result shows that these coatings have better hydrolytic stability than most water reducible alkyds. For example, an aqueous dispersion of a representative commercial water-reducible short-oil alkyd resin (Kelsol 3906-B2G-75) had a 32% increase in acid number after 10 weeks of storage at ambient temperature.[13] This result suggests that the acrylic-alkyd resin dispersions may be stable enough to last two plus years under normal paint storage conditions.

DISCUSSION

One of the most important elements restricting the use of water-reducible alkyd resins in architectural paints is their limited hydrolytic stability. Many papers[6-8] have addressed this problem, and several methods have been tried to overcome it. The most common method has been to replace phthalic anhydride in alkyd formulations with aromatic or cycloaliphatic acids that form esters with improved hydrolysis resistance.[13] Examples are isophthalic acid and hexahydrophthalic anhydride. This expedient improves outdoor durability of the coatings, and it has a modest positive effect on hydrolytic stability. However, the effect is not great enough to fully solve the problem.

Styrene-modified alkyds and, to a lesser extent, methacrylic-modified alkyds, have been used commercially for decades. These products are prepared by effecting free radical polymerization of styrene or of a mixture of styrene and acrylic monomers in the presence of an alkyd resin. The result is a mixture of graft copolymer, ungrafted alkyd resin, and ungrafted polystyrene (or acrylic copolymer). For example, Shim, Park, and Kim[9] recently described synthesis of an acrylic-modified alkyd by this method and its formulation into a water-reducible paint. The paint was said to have excellent film properties and a shelf life of six months. Six months of shelf life is adequate for many industrial and maintenance paints but is inadequate for architectural paints.

Table 6—Formulations and Properties of Alkyd Resins R6-R8

	R6	R7	R8
	Weight percentage (wt%)		
Materials			
Acrylic copolymer(A*x)	63.9	64.3	64.2
Monoglyceride	36.1	35.7	35.8
Resin Properties			
Appearance	Clear	Clear	Clear
Oil length (%)	27.6	27.3	27.4
Acid value	51.8	52.8	50.7
%NVM	82.9	85.0	81.7

* Note: x denotes 6, 7, and 8, respectively.

Table 7—Influence of LMA on Roughness of AFM Images

Sample	C6	C7	C8
RMS roughness (nm)	1.20	0.88	0.47

Gooch, Wang, Schork, and Poehlein[10] described a novel process in which MMA, BA, and AA were polymerized in the presence of an alkyd resin in a miniemulsion polymerization. The products were emulsions of graft copolymers with particle diameters of about 90–300 nm and shelf lives ranging from a few minutes to three months.

Others have attempted to overcome this problem by using aqueous emulsions of alkyd resins, as reviewed by Bergenstahl, et al.[14]

Here we report a new synthetic approach in which the acrylic copolymer is made first and then used as a polyacid in synthesis of the alkyd. While direct evidence is lacking, the large increase in viscosity and the lack of phase separation by the product suggest that the monoglyceride becomes partially grafted to the acrylic during the process. We call the products *acrylic-alkyd resins* to distinguish them from acrylic modified alkyds, described previously, in which the acrylic is grafted to the alkyd. Potential advantages to this approach include:

- The unreacted carboxyl groups needed to stabilize an aqueous dispersion of the product are attached to an acrylic polymer chain, where they are invulnerable to hydrolysis.
- There is potential for synthesis of acrylic-alkyd copolymers with high crosslinking capacity because the functionality (reactive carboxyl groups per molecule) of the acrylic polyacid can be greater than that of the difunctional acids or anhydrides (isophthalic acid or phthalic anhydride) typically used in alkyd synthesis.
- Properties (T_g, functionality, hydrophobicity) of the acrylic backbone can be varied through a wide range in order to manipulate properties of the final product.

However, synthetic difficulties were anticipated. There was a question of whether the acrylic backbone would have sufficient thermal stability to be used in alkyd processing, which is typically effected at 230-260°C. Second, it was anticipated that the process would be hard to control because of the need to react part, but not all, of the carboxyl groups. Third, there was high potential for gelation during the process, as with any condensation polymerization involving polyfunctional ingredients.

These difficulties were addressed in a number of preliminary experiments, not detailed here. To summarize the results, there was no evidence of depolymerization or decomposition of the acrylics during synthesis of the acrylic-alkyd polymers. The process proved controllable, perhaps because of the use of two types of carboxyl groups in the acrylic, one derived from AA and one derived from MAA. It was theorized that the carboxyl groups derived from AA would react with the monoglyceride at a much faster rate than those derived from MAA, helping control the process. This theory remains unproven, but the relative ease with which the process can be stopped after about half of the carboxyl groups have reacted suggests that it may be valid. Finally, a series of experiments, not detailed here, established that gelation could be avoided by limiting the molecular weight and average functionality of the acrylic copolymers.

The batch process used to make the acrylic copolymers is unconventional, but it yielded products with characteristics (M_n = 3500-5000 and M_w/M_n = 2.1-2.6) very similar to those that would be expected from conventional semi-batch processes. The reaction times and temperatures were such that acrylic polymer presumably contained unreacted initiator; decomposition of initiator would be essentially complete during the subsequent step. Consequences of its presence in the next step are unknown. There were some discrepancies between the T_g measured by DSC and those calculated by the Fox equation) (see *Table* 1). The discrepancies are not surprising. Actual T_g of acrylic copolymers with M_n of 3500-5000 are expected to be lower than those calculated by the Fox equation (which assumes infinite molecular weight),[15] and possible non-uniformity of the copolymers may be a secondary cause of the discrepancies.

The process used to synthesize the monoglyceride was modeled after processes that are widely used in synthesis of alkyd resins.[16] The reaction of the monoglyceride with the acrylic copolymer was accomplished with little difficulty, although prolonged reaction times will cause excessive viscosity build-up and, ultimately, gelation. It is noteworthy that there was no evidence (discoloration, evolution of free monomer) of decomposition or depolymerization of the acrylic copolymers at a reaction temperature (230°C) that permits rapid processing. However, coatings prepared from the initial acrylic-alkyd resins (Series 1) were very soft. In Series 2, higher T_g acrylic-alkyd resins were investigated. Resin R5, which had the highest T_g in this series, showed obvious signs of phase separation in the resin and in the film. While blending can often enhance properties of polymers,[17] blends of polymers used in coatings should be thermodynamically compatible or at least compatible enough that only submicroscopic phase separation occurs during film formation. Resin R5 does not meet this criterion; it apparently contains polymeric species that are mutually incompatible. Resin R5 presumably contains a spectrum of molecules, some totally or predominately acrylic and others predominately alkyd. Apparently, molecules at the ends of this spectrum are mutually incompatible.

It was theorized that incorporation of relatively small quantities of an acrylic monomer with long aliphatic side chains might improve compatibility without excessively reducing T_g. While thermodynamic compatibility might not be attained, this expedient might stabilize the boundary between phases so that any phase separation would occur on a submicroscopic scale. Lauryl methacrylate (LMA), with its n-$C_{12}H_{25}$ side chain, was selected for Series 3. Acrylic copolymers A6–A8 containing 5, 10, and 21 wt% of LMA (see *Table* 5) were synthesized and used to make acrylic-alkyd resins R6–R8 and water-reduced coatings C6–C8. To further improve the situation, the oil lengths of the acrylic-alkyd resins were reduced. These expedients gave transparent resins that showed no visible signs of phase separation. SPM study of the surfaces of cast films revealed clear evidence (see *Figure* 1 and *Table* 7) of submicroscopic phase separation with C6 but not with C8. C7 was intermediate. Thus, it appears that with 5 and 10% of LMA, phase separation occurs, but the phases are too small to be visible. With 21% LMA they are not even detectable with the SPM.

After storage for nine months there was no obvious change in the appearance of water-reduced coatings C6, C7, and C8. Titration showed that their acid values had increased less than 10%. These preliminary data show that acrylic-alkyd resins have substantially better hydrolytic stability than commercial resins.

CONCLUSIONS

A new method of synthesizing acrylic-alkyd resins has been demonstrated. It is especially well suited for synthesis of water-reducible alkyd resins. Hydrolytic stability of the products is superior to that of conventional water-reducible alkyd resins and may be good enough for architectural paints. Acrylic-alkyd resins made from MMA/LMA/AA/MAA copolymers afford glossy, transparent films. With further development, it may prove feasible to develop hydrolytically stable acrylic-alkyd resins that meet all requirements for commercial use.

ACKNOWLEDGEMENTS

We are grateful to P. Beauchamp for GPC measurements and W. Ming for DSC measurement assistance. We thank the United Soybean Board for support of this research.

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