

# Preparation of Glycol Esters of Soybean Oil Fatty Acids and Their Potential as Coalescent Aids in Paint Formulations

N. Jiratumnukul and Michael R. Van De Mark\*

Department of Chemistry, University of Missouri-Rolla, Rolla, Missouri 65401

**ABSTRACT:** Soy oil glycol monoesters have been prepared through the transesterification of soybean oil with ethylene, diethylene, propylene, and dipropylene glycols. The molar ratio of soybean oil to glycol used in these reactions was 1:6. The catalyst used in these reactions was lithium carbonate, 0.5%, based on soybean oil. The transesterifications were carried out at 180–190°C. The composition of soy oil glycol esters and their physical properties were determined. The soy oil glycol esters were incorporated in a water-based paint formulation as the coalescent aid, and the minimum film formation temperature was determined. The minimum film formation temperature results indicated that these esters can be used as coalescent aids in latex paint formulations to help in continuous film formation at or below room temperature.

Paper no. J9233 in *JAACS* 77, 691–697 (July 2000).

**KEY WORDS:** Coalescent aid, fatty acid glycol ester, film formation, glycol ester, latex coatings, minimum film formation temperature, soybean oil.

During the past decade, water-borne coatings have found broad acceptance in architectural as well as industrial applications and are expected to have continued good growth rates in the coating industry. The driving forces behind this trend are based upon both environmental and economic concerns to reduce volatile organic contents (VOC) of most coating materials. Traditionally, latex coatings, based upon small particles of a synthetic resin such as acrylic polymers, have required the use of a coalescent agent in substantial quantities (1). The coalescent aid in latex coatings is added to improve the filming properties of the coatings (2,3). The function of the coalescent aid is to soften the latex particles so they can flow together and form a continuous film with optimal film properties after the water has evaporated. Without the coalescent aid, the latex coatings may crack and not adhere to the substrate surface when dry at ambient temperatures (4–9).

Conventionally, alcohol esters and ether alcohols, such as ethylene glycol monobutyl ether and TEXANOL® (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate; Eastman, Kingsport, TN), are widely used as coalescent aids in the latex coat-

ings industry. These coalescent aids are counted as VOC, which are considered to cause smog and air pollution.

Vegetable oils, such as linseed oil and soybean oil, are used as drying oil in oil-modified alkyd resins (10) or as base fluids for environmentally safe lubricants (11). In Europe, vegetable oils have been used as diesel fuel, either neat or blended with diesel oil (12,13). Soybean oil, because of its abundance, comparatively lower prices, and environmental safety, has been considered in making a new additive for coatings.

Addition of neat soybean oil, without surfactant, to polyacrylic latex will cause a surface problem such as cratering because soybean oil does not dissolve mutually with polyacrylic latex. Soybean oil glycol esters therefore are prepared by transesterification of soybean oil and glycol with an alkaline catalyst at high temperature. Attempts have been made to replace the glycerin part of the oil with glycol to enhance the solubility of the derivatives, making them more miscible with water than neat oil. Soybean oil, when transesterified with excess glycol, yields a mixture of fatty acid alcohol monoesters along with glycerol. The hydroxyl and ester functional groups in the reaction product enhance the hydrophilicity of fatty acid and increase miscibility in water. Moreover, the long-chain fatty acid portion of the reaction product not only is a nonvolatile organic compound but also can be potentially oxidized, resulting in oligomerization or cure, and can help harden the coating after coalescence.

This paper reports on the preparation of several glycol esters, and their specific physiochemical properties, that may be used as coalescent aids, such as ethylene glycol, propylene glycol, diethylene glycol, and dipropylene glycol, in latex paint formulations. The new coalescent aids were evaluated on their ability to lower the minimum film formation temperature (MFFT) of latex polymer so that it would allow a uniform polymer film to be formed at typical ambient temperatures for painting.

## EXPERIMENTAL PROCEDURES

Alkali-refined soybean oil (industrial grade) was supplied by Cargill (Chicago, IL) and used without further purification. The glycols, ethyl ether, and linoleic acid were purchased from Aldrich Chemical Company (Milwaukee, WI). Palmitic

\*To whom correspondence should be addressed at Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65409-0010.  
E-mail: mvandema@umr.edu

acid was purchased from Sigma Chemical Company (St. Louis, MO). Methanol, lithium carbonate, and oleic acid were purchased from Fisher Scientific Company (Pittsburgh, PA). The glycols and methanol were dried by refluxing over and distillation from activated Mg metal.

**Preparation of fatty acid glycol ester.** Ethylene glycol (0.3 mol) was reacted with one of the three different fatty acids (0.1 mol)—palmitic acid, oleic acid, or linoleic acid—in a three-necked flask equipped with magnetic stirrer, thermometer, nitrogen bubbling tube, and a water condenser. Reactions were carried out at 180–190°C for 10 h in the presence of a catalyst, *p*-toluene sulfonic acid at 0.5% by weight, based on the amount of fatty acid. After reaction, glycerol and excess glycol were removed by extraction with five 50-mL portions of distilled water. The fatty acid glycol ester was dissolved in diethyl ether, dried over 2 g of anhydrous magnesium sulfate, and filtered. Diethyl ether was then distilled off, and the fatty acid glycol ester was obtained.

**Preparation of soy oil glycol ester.** Each glycol (0.6 mol) was reacted with soybean oil (0.1 mol) in a three-necked flask equipped with magnetic stirrer, thermometer, nitrogen bubbling tube, and a water condenser. Reactions were carried out in the presence of a lithium carbonate catalyst at 0.5% by weight, based on oil, at 180–190°C for 10 h. The reaction mixture was then neutralized with aqueous 0.1 M acetic acid solution. The excess glycol was removed by extraction with five 50-mL portions of distilled water. The soy oil glycol ester was dissolved in diethyl ether, dried over anhydrous magnesium sulfate, and filtered. Diethyl ether was then distilled off, and the soy oil glycol ester was obtained.

**Preparation of soy oil methyl ester.** Lithium metal (0.24 g) and excess dried methanol (96 g) were added to a three-necked flask equipped with magnetic stirrer, thermometer, nitrogen bubbling tube, and a water condenser. Lithium methoxide, product from a reaction between lithium and methanol, functioned as the catalyst. After the mixture was heated to 60°C, 60 g of soybean oil was added. The reaction was carried out at 60°C for 6 h. The excess methanol was distilled off. The reaction mixture was neutralized with aqueous 0.1 M acetic acid solution and washed five times with 50-mL portions of water. The soy oil methyl ester was dissolved in diethyl ether, dried over anhydrous magnesium sulfate, and filtered. The diethyl ether was then distilled off, and soy oil methyl ester was obtained.

**Thin-layer chromatography (TLC).** The reactions were monitored by TLC, which was carried out on silica gel-G-coated (0.25 mm thickness) plates (Whatman Ltd., Maidstone, England) and developed with hexane/isopropanol/methanol (20:20:60) as the mobile phase. Spots were visualized under short-wavelength ultraviolet radiation. The starting oil had an  $R_f$  of 0.97 while the product was a broad spot of approximately 0.3  $R_f$ .

**Gas chromatography (GC).** The composition of obtained soy oil glycol ester was determined with GC by using a Hewlett-Packard 5890 Series II GC (Palo Alto, CA) equipped with a flame-ionization detector. The GC column was a methyl silicon gum high-performance capillary column, 5 m

in length. Operating conditions for this column were 40 and 20 psi input of nitrogen and hydrogen carrier gas, respectively, with a column temperature gradient between 100 and 275°C at 10°C/min ramping.

**Infrared (IR) spectroscopy.** IR spectra were recorded on a Fourier transform IR (FTIR) Nicolet Magna-IR 750 spectrometer (Madison, WI).

**Nuclear magnetic resonance spectroscopy (NMR).**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a FX-100 Fourier transform NMR spectrometer (Palo Alto, CA) with tetramethylsilane as an internal standard. NMR was used to verify conversion by the ratio of the methylenes of the glycol and the glycerol peaks.

**Surface tension.** Surface tension was determined by the ring method tensiometer according to ASTM D 1331-89 (14).

**Hydrophilic lipophilic balance (HLB) values.** HLB was calculated as follows based on the ethylene oxide moiety in the molecule (15):

$$\text{HLB} = \frac{\% \text{ wt of ethylene oxide in the molecule}}{5} \quad [1]$$

**Solubility parameters.** Values were calculated according to the Hansen method from the *Handbook of Solubility Parameters* (16).

**Density.** Density was determined according to ASTM D-1475 (17).

**Evaporation rate.** Evaporation rate of new glycol derivative soy oil ester was monitored relative to conventional coalescent aids, TEXANOL® (Eastman Kodak, Kingsport, TN) and ethylene glycol *n*-butyl ether (Union Carbide, Danbury, CT). Three replicas of each coalescent aid were weighed into aluminum pans and kept at 25°C. The percentage of weight loss of each coalescent aid was measured as a function of time.

**MFFT measurement.** The method used for measuring MFFT followed ASTM Method D2354-68 (18). Seven different coalescent aids, TEXANOL®, ethylene glycol monobutyl ether (EB), methyl soybean oil ester and ethylene glycol derivatives of palmitic acid, oleic acid, linoleic acid, and soybean oil, were formulated with a high- $T_g$  resin (where  $T_g$  is the glass transition of the polymer), polystyrene methyl methacrylate copolymer (PS-MMA) (UCAR 430; Union Carbide), at levels of 0.5, 0.75, and 1.0% by weight of coating formulation. The master batch formulation is shown in Table 1. The formulations were equilibrated for 2 d before taking MFFT measurements so that the coalescent aid would equilibrate into the formulation. Four replicate measurements were performed for each latex and averaged.

## RESULTS AND DISCUSSION

To get complete transesterification of soybean oil without having side products, i.e., mono- and diglycerides, the reaction time was monitored by TLC. TLC results gave an  $R_f$  value of the starting material of 0.97, while the  $R_f$  values of all derivative products were 0.3 at approximately 10 h of reaction time. A 10-h reaction time, therefore, was chosen to

**TABLE 1**  
The Master Batch Formulation of UCAR 430 for MFFT Study<sup>a</sup>

	Formulation		Solid content	
	lb	gal	lb	gal
Water	288.56	34.64	0.00	0.00
Propylene glycol	43.96	5.08	0.00	0.00
Triton X-102	5.28	0.59	5.28	0.59
Acrysol RM 825	4.00	0.46	1.00	0.10
WET KL245	7.99	0.92	7.99	0.92
UCAR 430	434.03	49.89	195.31	21.23
Drewplus L- 493	2.24	0.30	0.34	0.12
Water	67.62	8.12	0.00	0.00
Total	853.68	100.00	209.92	22.97
wt/gal	8.54			
%solids (wt)	24.59			
%solids (vol)	22.97			

<sup>a</sup>UCAR 430, polystyrene methyl methacrylate copolymer from Union Carbide (Danbury, CT); MFFT, minimum film formation temperature; Triton X-102, surfactant (Union Carbide); Acrysol RM 825, associative thickener (Rohm & Haas, Philadelphia, PA); WET KL 245, wetting agent (Tego Chemical, Hopewell, VA); AMP 95, pH modifier (Angus, Northbrook, IL); Drewplus L-493, defoamer (Drew Chemical, Boonton, NJ).

ensure that all triglycerides were converted to the desired products. In the purification process, the interfacial turbid layer was discarded to expedite a rapid production. The yield of the product after purification therefore was approximately 85–90% based on soybean oil. The typical yield of transesterification, however, is nearly quantitative based upon mass balance. It should be noted that a small amount of diester was seen in ethylene and diethylene glycol systems. The diester was typically less than 6%. GC was used to analyze the composition of the reaction products. The retention times and compositions of reaction products are shown in Table 2. The GC results showed two main broad peaks in each soybean oil

**TABLE 2**  
Retention Time of Standards and Reaction Products by Gas Chromatography

Standards	Retention time (min)	
Palmitic acid	8.3	
Ethylene glycol palmitate	10.4	
Oleic acid	10.0	
Ethylene glycol oleate	12.2	
Linoleic acid	9.6	
Ethylene glycol linoleate	11.9	
Reaction products	Retention time (min)	Composition (%)
Ethylene glycol soyate	10.7	13.8
	12.1	86.2
Diethylene glycol soyate	12.8	11.0
	14.1	89.0
	10.9	12.3
Propylene glycol soyate	12.3	87.7
	13.1	10.1
Dipropylene glycol soyate	14.4	89.9
	7.9	11.7
Methyl soyate	9.4	88.3
	17.7	100.0

derivative. The first peak of each derivative, approximately 10–14%, was the saturated fatty ester, and the second peak, approximately 86–90%, was the unsaturated fatty ester derivative. These results corresponded to the amounts of saturated fatty acid (mainly palmitic acid) and unsaturated fatty acid (mainly linoleic acid and oleic acid) in soybean oil of approximately 14 and 86%, respectively.

The retention times of saturated and unsaturated fatty acid derivatives have been verified by preparation of ethylene glycol derivatives of palmitic acid (saturated fatty acid), oleic acid, and linoleic acid (unsaturated fatty acids) and by investigation of the retention times characteristic of each derivative. The retention times of standards are shown in Table 2. The retention time of ethylene glycol palmitate, 10.4 min, agreed with the retention time of the first separated peak of ethylene glycol soy oil derivative at 10.7 min. The retention times of ethylene glycol oleate and ethylene glycol linoleate, 12.2 and 11.9 min, respectively, also corresponded with the retention time of the second broad peak at 12.1 min. Individual glycol derivative soybean oil esters therefore are composed of two groups of compounds, saturated fatty acid derivative and unsaturated derivative.

*Structural study by NMR and IR.* NMR and IR spectroscopy was used to verify the transformation of functional groups and chemical structures.

<sup>13</sup>C NMR spectra were determined without solvent at room temperature in 5-mm i.d. tubes. Chemical shifts for the fatty acid portion agreed with those given in the literature (19–21). The peak at 25.7 ppm belongs to C<sub>11</sub>, which is allylic to both double bonds of a *cis-cis* diene (linoleic) chain. The peak at 27.3 ppm belongs to the two carbons allylic to *cis* double bonds, i.e., C<sub>8,11</sub> of the monoene (oleic) chain and C<sub>8,14</sub> of the diene chain. The pair of peaks at 129.9 and 129.6 ppm belong to C<sub>10</sub> and C<sub>9</sub> of the oleic chain, while the two smaller pairs at 130.1, 129.9, 128.1, and 127.9 ppm belong to C<sub>13</sub>, C<sub>9</sub>, C<sub>10</sub>, and C<sub>12</sub> of the linoleic chain. The chemical shifts of the glycerol portion at ~60.4 ppm (–CH<sub>2</sub>–) and ~66.0 ppm (–CH–), which appeared in the triglyceride (soy oil) spectra, no longer exist in the fatty ester glycol derivatives. The chemical shift of the carbon next to the oxygen derived from the glycerol was between 60 and 75 ppm. The peak at ~20 ppm belongs to the methyl group of the (di)propylene glycol portion of the (di)propylene glycol derivatives. This evidence indicated that the triglyceride of soy oil had been converted to the ester product.

<sup>1</sup>H NMR spectra were operated with neat liquid reaction products. The peak at 0.96 ppm (*t*, 3H) belonged to –CH<sub>3</sub> in the fatty acid portion. The peak at 1.3 ppm (*s*, 20H) belonged to –CH<sub>2</sub>– in the fatty acid portion. The peak at 1.6 ppm (*t*, 2H) belonged to R–CH<sub>2</sub>–CH<sub>2</sub>–COO–. The peak at 2.0 ppm (*d*, 4H) was assigned to the CH<sub>2</sub> group adjacent to the unsaturated part of the fatty acid. The peak at 2.4 ppm (*t*, 2H) belonged to R–CH<sub>2</sub>–CH<sub>2</sub>–COO–. The peak at 2.8 ppm (*t*, 2H) belonged to –CH=CH–CH<sub>2</sub>–CH=CH– in the linoleic fatty acid part. The peak at 3.8 ppm (*t*, 2H) was identified as the HO–CH<sub>2</sub>–CH<sub>2</sub>–OOC–R. The peak at 4.1 ppm (*t*, 2H) be-

longed to  $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OOC}-\text{R}$ . The peak at 4.3 ppm (*s*, 1H) belonged to the OH group. The peak at 4.8 ppm belonged to  $-\text{CH}-\text{OH}$  in the propylene glycol part of the (di)propylene derivatives. The peak at 5.2 ppm determined the  $-\text{CH}=\text{CH}-$  group. The peak at 3.6 (*s*, 3H) belonged to  $-\text{O}-\text{CH}_3$  of the methyl ester derivative.

IR results showed a peak of OH stretching at  $\nu$  3500  $\text{cm}^{-1}$  in the spectra of the glycol derivative products but it did not appear in the soybean oil spectra. There were peaks of C–O stretching of alcohol at  $\nu$  1350 and 1450  $\text{cm}^{-1}$  in the spectra of the glycol derivative soybean oil esters, but those peaks were not seen in the soybean oil spectra. This result supports that the glycol portion has been introduced into fatty ester products.

**Physical properties.** Physical properties of the coalescent aid are important to provide characteristics of the material. Physical properties, such as solubility parameters, HLB value, density and surface tension, of all five glycol derivative soybean oil esters were studied.

Solubility parameters were calculated based on the Hansen method from the *Handbook of Solubility Parameters* (16). The solubility parameters in Table 3 showed that the total solubility parameter of EB is greater than that of TEXANOL® and glycol soy oil esters. In addition, the polar solubility parameter ( $\delta_p$ ) and hydrogen-bonding solubility parameter ( $\delta_h$ ) decreased in the order of EB > TEXANOL® > glycol soy oil esters. Therefore, EB would be more miscible with water than TEXANOL® and glycol soy oil esters. On porous substrates, coalescents that have high water solubility can transport into the porous surface before they have a chance to be effective. The solubility parameter of PS-MMA is 18.2 ( $\text{J}/\text{cm}^3$ )<sup>1/2</sup> (22). We found that the solubility parameters of glycol soy oil esters and TEXANOL® were closer to that of polystyrene than EB. For hydrophobic coalescent aids, a solubility parameter match will produce a better coalescent aid. As a result,

TEXANOL® and glycol soybean oil esters should coalesce the PS-MMA (UCAR430) better than EB.

HLB values were calculated according to the basic equation based on the hydrophilic moiety in the molecule. The greater the HLB value, the more miscible the material would be with water. Table 3 shows that the HLB value of EB was greater than that of glycol soybean oil esters. This corresponds with the solubility parameter of EB and means that EB is more miscible with water than glycol soybean oil esters.

Interfacial tensions of all reaction products were determined by the ring tensiometer according to ASTM D1331-89. The value of the interfacial tension is a measure of the dissimilarity of the two types of molecules facing each other across the interface. The smaller the interfacial tension, the more similar in nature the two molecules are, and the greater the interaction (23). The interfacial tension of EB was 27.4 dyne/cm (Table 3), which was less than the values for TEXANOL® and glycol soybean oil esters. This means that EB is more miscible with water than TEXANOL® and glycol soybean oil esters.

**Evaporation rate.** The evaporation rate of a coalescent aid is another critical property that needed to be measured because the longer the coalescent aid stays in the coating, the more complete the coalescence of the film. In addition, the weight loss as a function of time will also tell whether the compound is a volatile organic compound.

The weight loss of ethylene glycol, propylene glycol, methyl ester derivatives, TEXANOL®, and ethylene glycol *n*-butyl ether was monitored as a function of time at 25°C. The results are shown in Figure 1.

The evaporation rates of glycol and methyl derivatives of soybean oil ester were less than 0.001 vs. butyl acetate (24), which is much lower than the comparative coalescent aids TEXANOL® and EB, which have evaporation rates of 0.02 and 0.08, respectively, vs. butyl acetate (24). Ethylene glycol monobutyl ether is a water-soluble coalescent aid and may evaporate in part from the film when the water evaporates.

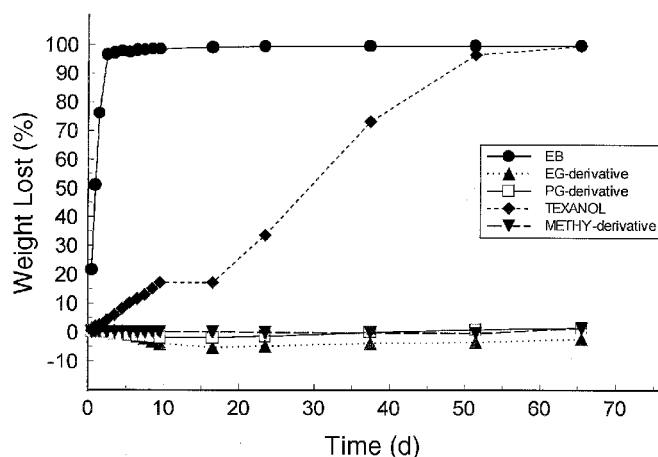
**TABLE 3**  
Physical Properties of Glycol Derivative Soy Oil Esters<sup>a</sup>

Properties	Soy oil derivative esters						
	EG	DEG	PG	DPG	ME	EB	TEXANOL®
Density ( $\text{g}/\text{cm}^3$ )	0.94	0.93	0.91	0.91	0.87	0.9	0.95
HLB <sup>b</sup>	2.7	4.8	3.4	5.9	N/A	14.9	N/A
Interfacial tension (dyne/cm)	36.2	36.1	33.3	35.7	30.1	27.4	28.9
Solubility parameters <sup>c</sup>							
$\delta_{\text{total}}$ ( $\text{J}/\text{cm}^3$ ) <sup>1/2</sup>	18.6	18.2	18.0	17.6	17.9	20.7	19.3
$\delta_d$ ( $\text{J}/\text{cm}^3$ ) <sup>1/2</sup>	16.2	15.8	15.7	15.4	17.2	15.9	15.6
$\delta_p$ ( $\text{J}/\text{cm}^3$ ) <sup>1/2</sup>	2.03	2.04	1.88	1.85	1.50	4.9	3.07
$\delta_h$ ( $\text{J}/\text{cm}^3$ ) <sup>1/2</sup>	8.8	8.7	8.5	8.3	4.6	12.3	10.9

<sup>a</sup>Abbreviations: EG, ethylene glycol soybean oil derivative; DEG, diethylene glycol derivative; PG, propylene glycol derivative; DPG, dipropylene glycol derivative; ME, methyl ester; EB, ethylene glycol monobutyl ether; TEXANOL® (ester alcohol), trademark of Eastman Chemical Company; N/A, not applicable; HLB, hydrophilic lipophilic balance.

<sup>b</sup>See Equation 1.

<sup>c</sup>See Reference 16.



**FIG. 1.** Evaporation rate of ethylene glycol (EG), propylene glycol (PG), methyl ester (METHY) derivatives, TEXANOL® (Eastman Kodak, Kingsport, TN), and ethylene glycol *n*-butyl ether (EB; Union Carbide, Cary, NC).

Therefore, this coalescent aid is a volatile organic compound. TEXANOL® is a water-insoluble coalescent aid that only gradually evaporates from the film while the film ages. On the other hand, the new soybean oil glycol ester derivatives did not show any loss in weight. They actually showed a slight gain in weight because the unsaturated fatty acid glycol soybean oil ester was air-oxidized and became part of the film. Therefore, the new soybean oil glycol esters are not volatile organic compounds.

**MFFT measurement results.** MFFT is an important property of latex coatings. The role of the coalescent aid in latex coatings is to lower the MFFT of the coating and facilitate the formation of a continuous film with good properties at ambient temperature. To investigate the efficiency of new soybean oil coalescent aids in lowering the MFFT of the coating, the high-glass-transition-temperature PS-MMA latex emulsion, UCAR 430, was selected as a model latex system.

In general, soybean oil consists of approximately 15% saturated fatty acids and 85% unsaturated fatty acids. The unsaturated fatty acid ester can be air-oxidized upon drying, which enhances the strength of the film. Therefore, unlike conventional coalescents, the unsaturated fatty acid esters become oligomers and act more as binders than solvents after they are air-oxidized.

The effect of saturated and unsaturated ethylene glycol fatty acid esters in lowering the MFFT of latex emulsions relative to the conventional coalescent aids, TEXANOL® and EB, was studied. TEXANOL®, EB, and ethylene glycol derivatives of palmitic acid, oleic acid, and linoleic acid were added to coating formulations at levels of 0.5, 0.75, and 1.0% by weight. The formulations were equilibrated for 2 d before the MFFT measurements were taken. The MFFT results of coatings formulated with the different ethylene glycol fatty acid esters are shown in Figure 2. Ethylene glycol palmitate ester lowered the MFFT of latex emulsion approximately the same as ethylene glycol linoleate ester and ethylene glycol

oleate ester. Both ethylene glycol unsaturated and saturated fatty acid esters lowered the MFFT more than EB and slightly more than TEXANOL®. Therefore, both saturated and unsaturated fatty acid esters lowered the MFFT in the same manner, but the unsaturated products could possibly be cured, which helped the recovery of the  $T_g$  of the resin after coalescence of the coating.

The effect of ethylene glycol soybean oil esters in lowering the MFFT of latex emulsion relative to the methyl soybean oil ester and the conventional coalescent aids, TEXANOL® and EB, was studied. TEXANOL®, EB, ethylene glycol derivatives of soybean oil, and methyl ester of soybean oil were added to coating formulations at levels of 0.5, 0.75, and 1.0% by weight. The formulations were equilibrated for 2 d before the MFFT measurements were taken. The results are presented in Figure 3. TEXANOL®, methyl soybean oil ester, and ethylene glycol soybean oil ester lowered the minimum film formation temperature better than EB. This might be because EB, a water-miscible coalescent aid with an alcohol functional group, might not be effective in softening this particular resin system (UCAR 430). It would rather dissolve in water than partition to the latex particle surface. Moreover, the solubility parameters of TEXANOL®, methyl soybean oil ester, and ethylene glycol soybean oil ester were closer to the solubility parameter of this particular resin (UCAR 430). As a result, the TEXANOL® and soybean oil ester partition to the latex particle better than EB. EB therefore was less effective in lowering the MFFT of the emulsion than TEXANOL®, ethylene glycol soybean oil esters, and methyl ester. The methyl soybean oil ester had a solubility parameter closest to that of the resin system, relative to TEXANOL® and ethylene glycol soybean oil ester. Methyl soybean oil ester therefore lowered the MFFT better than the formulation with TEXANOL® and ethylene glycol soybean oil ester. As the amount of soybean oil derivative coalescent aids incorporated in the formulation was increased, the MFFT decreased.

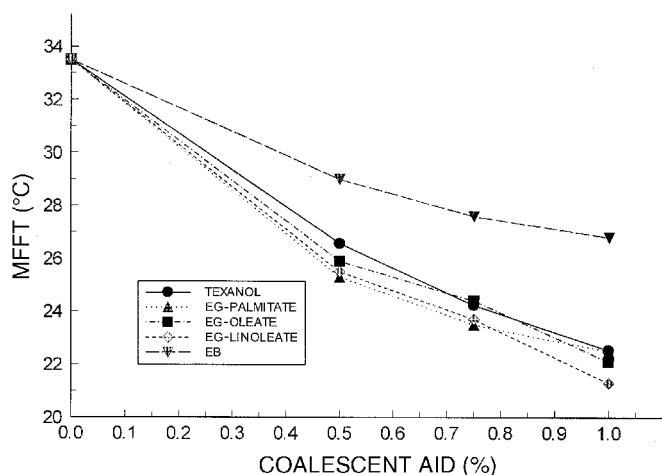


FIG. 2. Minimum film formation temperature (MFFT) of a polystyrene methacrylate copolymer (UCAR 430; Union Carbide, Cary, NC) formulated with different ethylene glycol derivative fatty acid esters. For abbreviations see Figure 1.

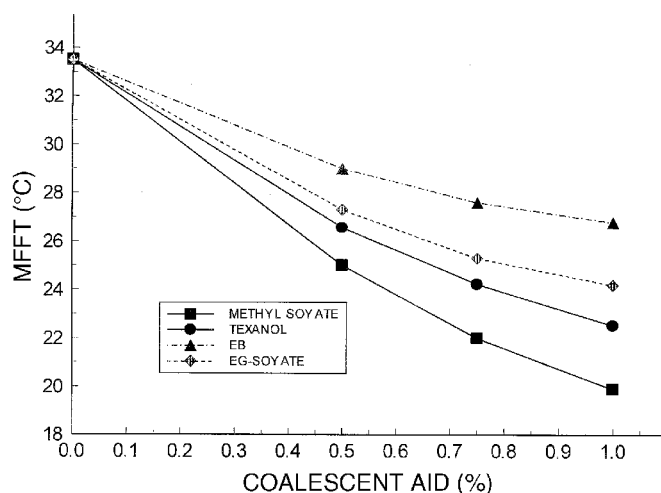


FIG. 3. MFFT of UCAR 430, formulated with different glycol soy oil derivative esters. Methyl soyate, methyl soybean oil ester; EG-soyate, soy oil ester; for other abbreviations see Figures 1 and 2.

In addition, the efficiency in lowering the MFFT of the latex emulsion for the four different glycol esters of soybean oil was studied relative to the conventional coalescent aids. TEXANOL®, EB, ethylene glycol, propylene glycol, diethylene glycol, and dipropylene glycol derivatives of soybean oil were added to coating formulations at levels of 0.5, 0.75, and 1.0% by weight. The formulations were equilibrated for 2 d before the MFFT measurements were taken. The MFFT results of the four different glycol derivative esters are shown in Figure 4. All glycol derivative soy oil esters and TEXANOL® reduced the MFFT of latex emulsion better than the formulation with EB, and all four glycol derivative soy oil esters lowered the MFFT in the same fashion as the commercial coalescent aid, TEXANOL®.

No glycol derivative soybean oil esters were water-miscible; only EB was water-miscible. A mixture of hydrophobic and hydrophilic aids is often employed because of required freeze-thaw and high-temperature stability of the paint in the can. Thus, the MFFT of mixed coalescent aids of glycol soybean oil ester and EB were evaluated relative to the conventional coalescent aids, TEXANOL® and EB. For the blend of glycol soybean oil ester and EB, the MFFT results are presented in Figure 5. All glycol derivative soybean oil esters blended with EB reduced the MFFT slightly better than the formulation with EB, and performed in the same fashion as the commercial coalescent aid, TEXANOL®. The performance was based on the amounts of the two coalescent aids employed and no significant advantage for MFFT reduction was obtained from the blend. However, the blend has advantages in minimizing the loss of water-soluble coalescent aid into porous substrate, and it also benefits freeze-thaw and thermal stability of the paint.

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge funding from the United Soybean Board and the Missouri Soybean Merchandising Council.

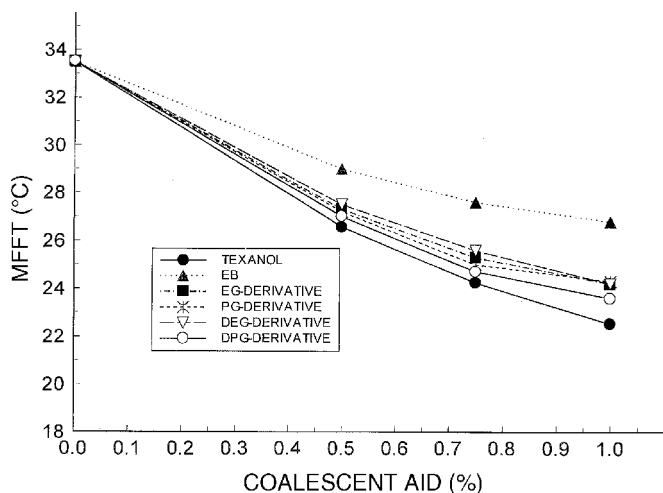


FIG. 4. MFFT of UCAR 430 formulated with different glycol soy oil derivative esters. DEG, diethylene glycol derivative; DPG, dipropylene glycol derivative. For other abbreviations see Figures 1 and 2.

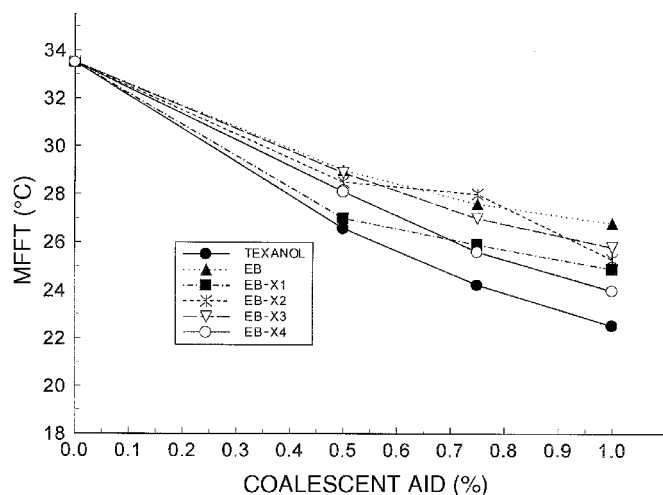


FIG. 5. MFFT of UCAR 430 formulated with different mixtures of EB and glycol soy oil derivative esters. EB-X1, ethylene glycol derivative of EB; EB-X2, propylene glycol derivative of EB; EB-X3, diethylene glycol derivative of EB; EB-X4, dipropylene glycol derivative of EB; EB-X indicates derivatives and EB are mixed 50:50 wt%. For other abbreviations see Figures 1 and 2.

#### REFERENCES

- Wicks, Z.W., Jr., Jones, F.N., and Pappas, S.P., *Organic Coatings Science and Technology*, 2nd edn., John Wiley & Sons, New York, 1999, pp. 33–36.
- Turner, G.P.A., *Introduction to Paint Chemistry*, 3rd edn., Chapman and Hall, London, 1988, pp. 144–149.
- Winnik, M.A., Y. Wang, and F. Haley, Latex Film Formation at the Molecular Level: The Effect of Coalescent Aids on Polymer Diffusion, *J. Coatings Technol.* 64(no. 811):51–61 (1992).
- Hoy, K.L., Effect of Reaction Pathway on Emulsion Polymer Structure, *Ibid.* 51(no. 651):27–41 (1979).
- Vanderhoff, J.W., E.B. Bradford, and W.K. Carrington, Transport of Water Through Latex Films, *J. Polym. Sci. Symp.* 41: 155–174 (1973).
- Protzman, T.F., and G.L. Brown, An Apparatus of the Determination of the Minimum Film Formation Temperature of Polymer Emulsions, *J. Appl. Polym. Sci.* 4:81–85 (1960).
- Eckersky, S.T., and A. Rudin, Mechanism of Film Formation from Polymer Latexes, *J. Coatings Technol.* 62(no. 780) 89–100 (1990).
- Croll, S.G., Drying of Latex Paint, *Ibid.* 58(no. 734):41–49 (1986).
- Eckersky, S.T., A. Rudin and R. O'Daiskey, Surface Energetics of Films of Surfactant Free Poly (methyl methacrylate-co-butyl acrylate) Emulsion Polymers, *J. Colloid Interface Sci.* 152: 455–464 (1992).
- Wicks, Z.W., Jr., Drying Oils, in *Encyclopedia of Polymer Science and Technology*, Wiley-Interscience, New York, 1986, Vol. 5, pp. 203–214.
- Basu, H.N., E.M. Robley, and M.E. Norris, Preparation of Glycol Derivatives of Partially Hydrogenated Soybean Oil Fatty Acids and Their Potential as Lubricants, *J. Am. Oil Chem. Soc.* 71:1227–1230 (1994).
- Clark, S.J., L. Wagner, M.D. Schrock, and P.G. Piennaar, Methyl and Ethyl Soybean Oil Esters as Renewable Fuel, *Ibid.* 61:1632–1638 (1984).
- Hall, D., Put a Sunflower in Your Tank, *New Sci.* (26 Feb): 524–526 (1981).
- ASTM D1331-89, Standard Test Method for Surface Tension

- Determination by the Ring Method Tensiometer, ASTM, Philadelphia, 1997, 15.04, pp. 1–3.
15. Schick, M.J., *Nonionic Surfactants Physical Chemistry*, Marcel Dekker, New York, 1987, p. 438.
  16. Alan Barton, F.M., *Handbook of Solubility Parameters*, CRC Press, Boca Raton, 1991, pp. 182–185.
  17. ASTM D1475-90, Standard Test Method for Density Determination, section 6, vol. 6.01, ASTM, Philadelphia, 1993, pp. 229–231.
  18. ASTM D2354-91, Standard Test Method for Minimum Film Formation Temperature of Emulsion Vehicles, section 6, vol. 6.02, ASTM, Philadelphia, 1993, pp. 104–105.
  19. Wehrli, F.W., A.P. Marchand, and S. Wehsl, *Interpretation of Carbon-13 NMR Spectra*, John Wiley & Sons, New York, 1989, pp. 410–412.
  20. Breitmeier, E., and W. Voelter, *C-13 NMR Spectroscopy: High Resolution Methods and Applications in Organic Chemistry and Biochemistry*, John Wiley & Son, 3rd edn., New York, 1987, p. 119.
  21. Marshall, G.L., and J.A. Lander, Characterization of Alkyd Paint Binder Using C-13 NMR Spectroscopy, *Eur. Polym. J.* 21: 949–958 (1985).
  22. Brandrup, J., and E.H. Immergut, *Polymer Handbook*, 2nd edn., Wiley-Interscience, New York, 1989, p. 519.
  23. Rosen, M.J., *Surfactants and Interfacial Phenomena*, 2nd edn., John Wiley & Sons, New York, 1989, pp. 207–211.
  24. ASTM D 3539-87, Standard Test Method for Evaporation Rates of Volatile Liquids, section 6, vol. 6.01, pp. 459–466, ASTM, Philadelphia, 1993.

[Received May 5, 1999; accepted March 28, 2000]