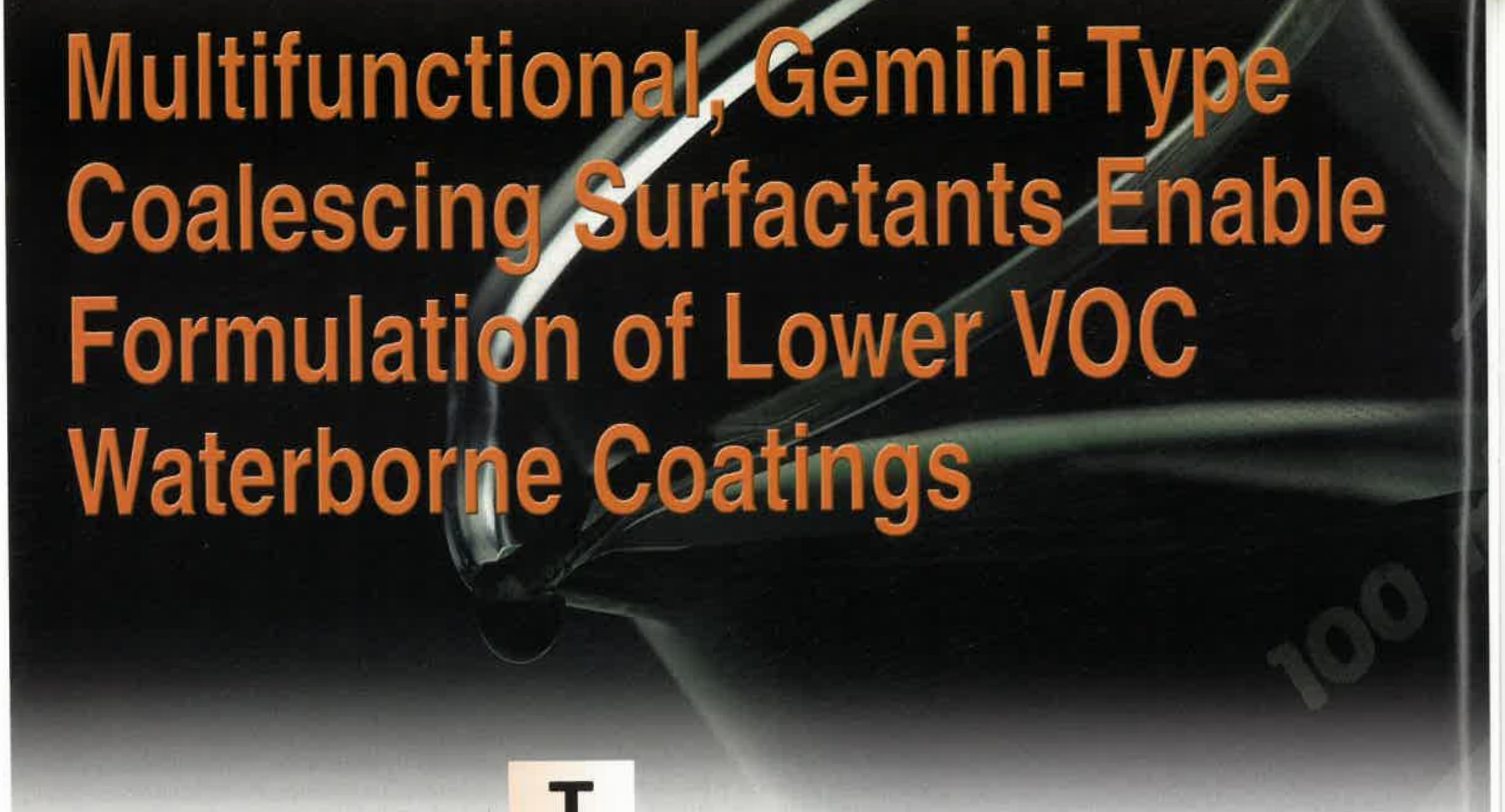

# Multifunctional, Gemini-Type Coalescing Surfactants Enable Formulation of Lower VOC Waterborne Coatings

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Increasingly, surfactants with multifunctional performance benefits are desired to not only lower the surface tension of waterborne formulations, but also to reduce foam. Low HLB, nonionic Gemini-type surfactants are commonly utilized for this reason. As legislation has required coatings with increasingly lower volatile organic compounds (VOCs) and, consequently, lower coalescent levels, the ability of Gemini surfactants to reduce the minimum film formation temperature (MFFT) of emulsion polymers has garnered interest as a means to enable formulation of lower VOC coatings. This article describes the MFFT reduction imparted by Gemini-type surfactants for a wide variety of emulsion polymers. Atomic force microscopy (AFM) showed that films prepared using an alkyl ester (AE) surfactant were generally smoother than films not containing the AE surfactant. While enabling low-VOC formulating, these surfactants were found to have minimal effect on coating performance. Lower HLB surfactants were found to be the most effective coalescents. A simple model whereby these surfactants preferentially adsorb onto the surface of the polymer particles is introduced to explain their efficiency.

## INTRODUCTION AND BACKGROUND

As new and more stringent VOC rules have been adopted or proposed by the South Coast Air Quality Management District (SCAQMD)[1] and Ozone Transport Commission (OTC)[2] for a wide range of coatings including architectural and industrial maintenance (AIM), paint formulators have been evaluating new methods to reduce VOCs and yet maintain the performance of their coatings. For waterborne systems, new developments include emulsion resins[3] with lower MFFTs and low-to-no VOC coalescing agents[4-6] that present the possibility to replace traditional coalescents such as the widely used 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (TMPIB).[7,8]

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Another new class of coalescing agents for low-VOC coatings is that of coalescing surfactants, which also offer the potential of replacing (at least partially) the common coalescents. Not only can the coalescing surfactants lower an emulsion resin's MFFT but, unlike the standard coalescing solvents, they can also provide a waterborne system with the necessary low surface tension for better wetting, flow, and leveling. One group of surfactants that has shown the ability to lower MFFT is that of the so-called Gemini ("twin")-type, nonionic surfactants.[7-11] Unlike conventional monomeric surfactants that have a single, hydrophobic group (often referred to as a hydrocarbon tail) connected to a hydrophilic head (e.g., a hydroxyl group or a polyethylene oxide tail), Gemini surfactants have two hydrophilic heads, which are connected by a molecular segment or "spacer," and two (most commonly) or more hydrophobic tails. The twin surfactant structure has been reported to provide efficiency and multifunctional performance.[12-17] Several Gemini chemistries including acetylenic diols (based on 2,4,7,9-tetramethyl-5-decyne-4,7-diol or TMDD) and alkyl esters have shown effectiveness in a variety of emulsion resins.

In order to further understanding of the Gemini-type coalescing surfactants, the efficacy of a wide range of these surfactants as coalescing aids to reduce MFFTs for emulsion polymers was studied. The purpose of this article is to describe the results of that study and to report on the effect of some of these materials on emulsion properties and coating performance. In addition, a simple model is proposed to describe their coalescing and surface tension behavior.

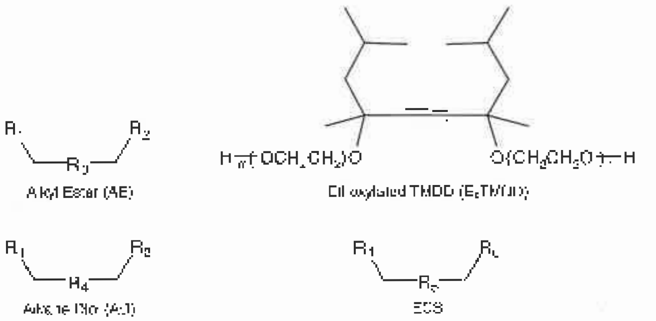
## EXPERIMENTAL

### *Surfactants*

The Gemini-type surfactants evaluated in this study included: 3 alkyl esters (AEs); a non-ethoxylated acetylenic diol (TMDD); a series of ethoxylated acetylenic diols ($E_xTMDDs$); an alkane diol (AD); and an experimental coalescing surfactant (ECS). The generalized chemical structures are provided in *Figure* 1, and the characteristics are provided in *Tables* 1-3. All of these materials are 100% active, low-viscosity liquids (except TMDD which is a solid at 25°C) with no solvents. VOCs as determined by EPA Method 24 were <10% for all surfactants except TMDD (~50%) and $E_{20}$TMDD (28%). Refer to *Appendix* A for material identification and suppliers.

All coating formulations were prepared and applied using standard techniques. MFFT data (ASTM D 2354) were obtained using a Minimum Film Formation Temperature Bar Model MFFT-90 (Rhopoint Instrumentation Ltd.). Films were applied by draw-

Figure 1—Generalized structures of the coalescing surfactants studied. $R_1$ and $R_2$ are alkyl groups that are different for each molecule; $R_3$ is a hydrophilic group which contains ester groups; $R_4$ is a hydrophilic group; $R_5$ is a bridging group; and $R_6$ is a hydrophilic moiety.




down to a wet film thickness of 152 μm (6 mils). Equilibrium surface tension (EST) measurements were performed using the Wilhelmy plate method. Dynamic surface tension (DST) data were obtained by the maximum bubble pressure method using a Bubble Pressure Tensiometer BP2 (Krüss USA).

Glass transition temperatures ($T_g$) of clear films prepared from polymer emulsions were determined by dynamic mechanical analysis (DMA) after drying the films for at least seven days at 20–25°C. The DMA data were obtained using a Rheometrics Solids Analyzer RSA II (Rheometric Scientific) in a tensile dynamic mode with a thin film fixture. The samples were not preconditioned with regard to humidity prior to data acquisition, but dry nitrogen was used as the atmosphere during the measurements. Data was acquired at intervals of 6°C; a one-minute hold time was used at each measurement temperature to ensure isothermal equilibration. The $T_g$ data reported are the temperatures of the tangent delta (δ) peak maximum.

The atomic force microscope (AFM) images were obtained using techniques (tapping mode AFM) as described by Rynders et al.[8]

## Table 1—Properties of the AE Surfactants

| Property | AE01 | AE02 | AE03 |
|---|---|---|---|
| Activity, % weight | 100 | 100 | 100 |
| Viscosity, cP, 25°C | 13 | 71 | 129 |
| HLB[a] | 5 | 4 | 4 |
| Water solubility, % weight, 25°C | 0.2 | 0.05 | 0.05 |
| EST[b], mN/m, 25°C | 42.3 | 34.8 | 35.6 |
| VOC from solvents | None | None | None |

(a) HLB = hydrophile-lipophile balance determined using the Water-Solubility Method, "The HLB System," ICI Americas, Inc., 199[illegible].
(b) Equilibrium surface tension (EST) was measured using the Wilhelmy plate method at 0.1% active weight surfactant concentration in water.

## Table 2—Properties of the $E_x$TMDD Surfactants

| Property | $E_{20}$ | $E_{40}$ | $E_{65}$ | $E_{85}$ |
|---|---|---|---|---|
| Activity, % weight | 100 | 100 | 100 | 100 |
| Viscosity, cP, 20°C | <250 | <200 | <200 | <200[c] |
| HLB[a] | 4 | 8 | 13 | 17 |
| Water solubility, % weight, 25°C | 0.1 | 0.15 | Miscible | Miscible |
| EST[b], mN/m, 25°C | 32.0 | 33.2 | 41.9 | 51.1 |
| VOC from solvents | None | None | None | None |

(a,b) See Table 1 for footnote explanations.
(c) Data for [illegible] active weight solution in water. $E_x$ refers to TMDD with x% by weight of ethoxylation.

## RESULTS AND DISCUSSION

### *AE Surfactants: MFFT Reduction and Effect on Polymer $T_g$*

Since the AE surfactants are esters that have low HLBs and similar structures to TMPIB, it was anticipated that the AEs would be effective coalescing agents. *Figure* 2 shows the MFFT data obtained by adding the AE surfactants to a variety of emulsion polymers, which included urethane-acrylic hybrid (A), vinyl acetate-ethylene copolymer (B), and four acrylics (C-F). As the data show, these products have a significant effect on the MFFT of the emulsion polymers. At a level of only 2% by weight of total emulsion, the AE materials were found to reduce the MFFTs by 10–15°C for the polymer emulsions with the highest MFFTs. The efficiency of the AEs to reduce MFFT generally followed the trend: AE01 > AE02 > AE03.

To illustrate (*Figure* 3) the effect of the AEs on film formation, films were prepared at 10°C (50°F)/95% relative humidity (RH) from neat Polymer Emulsion A and compared with those of Polymer Emulsion A containing AE01 and AE02 at 2% by weight on total emulsion. The film prepared from neat Polymer Emulsion A was severely cracked, while the films containing the AE surfactants were clear and smooth (no surface defects).

## Table 3—Properties of the AD, ECS, and TMDD

| Property | AD | ECS | TMDD |
|---|---|---|---|
| Activity, % weight | 100 | 100 | 100[c] |
| Viscosity, cP, 25°C | 2000 | 92 | Solid[c] |
| HLB[a] | 3–4 | 4 | 3–4 |
| Water solubility, % | 0.06 | 0.01 | 0.1 |
| EST[b], mN/m, 25°C, 0.1 % weight | 35.2 | 27.5 | 33.1 |
| VOC from solvents | None | None | None[c] |

(a,b) See Table 1 for footnote explanations.
(c) TMDD was used as a 50% solution in dipropylene glycol monomethyl ether.

Additionally, the surfaces of films prepared from Polymer Emulsion A were characterized by AFM. Formulations were prepared with and without AE02 and coalescing solvent. For the films containing AE02, a lower amount of coalescing solvent was used such that the total VOC was <100 g/L. Without AE02, a higher level of coalescing solvent was used, and the total VOC was >150g/L. The VOC solvents in these experiments were DPnB (dipropylene glycol mono-n-butyl ether), DMM (dipropylene glycol dimethyl ether), and NMP (N-methylpyrrolidone). The AFM micrographs in *Figure* 4 show that the AE02-containing coating film has a much smoother surface than the films prepared from the higher VOC formulations. To determine whether this effect was the result of the AE02 surfactant forming a surface layer, the AE02-containing film was washed with water for several minutes. No significant changes in surface roughness were found. Therefore, the AFM observations support the notion that the AE02 aided film formation in this system, and these results illustrate the benefits of the AE surfactants for improved coalescence.

Since the AE surfactants significantly lowered the MFFTs of the polymer emulsions, their effect on the $T_g$ of the polymer films was investigated. Ideally, plasticization of the polymer films and a consequent reduction of the $T_g$s would not be desired in order to ensure optimum performance (e.g., block and chemical resistance). Because these materials are essentially non-fugitive, some $T_g$ reduction was expected. The results are shown in *Figure* 5. The addition of the AEs depressed the $T_g$s of the polymers, but the $T_g$ depression (5–10°C) was generally smaller than the observed reduction in the MFFTs (10–15°C). Furthermore, within experimental error, the AE surfactants were observed to have minimal effect on the dry times (*Figure* 6) and to contribute no measurable VOCs (*Figure* 7) to the emulsions.

In a separate experiment, the effectiveness of the AE02 surfactant was tested in Polymer Emulsions A and F. The data are shown in *Figure* 8. As expected, the MFFT showed a linear decline as the AE02 level was increased. Linear regression of the data produced the following equations, where the AE02 weight % is based on polymer solids.

For Polymer Emulsion A:

$$\text{MFFT, °C} = [-2.2 \cdot (\text{AE02 weight \%}) + 31.5]\text{°C} \quad r^2 = 0.99$$

For Polymer Emulsion F:

$$\text{MFFT, °C} = [-2.0 \cdot (\text{AE02 weight \%}) + 25.7]\text{°C} \quad r^2 = 0.99$$

Since the slopes (units of °C/AE02 weight %) of the lines were similar, the effectiveness of AE02 for reducing the MFFT of both polymer emulsions was comparable.

Figure 2—MFFT data for the AE surfactants in various emulsion polymers. For polymer emulsions B and F, the MFFT values at 0°C represent the freezing points of the samples. Refer to Appendix A for material identifications.

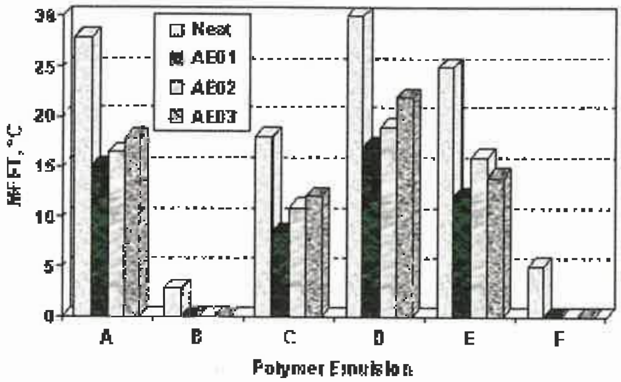
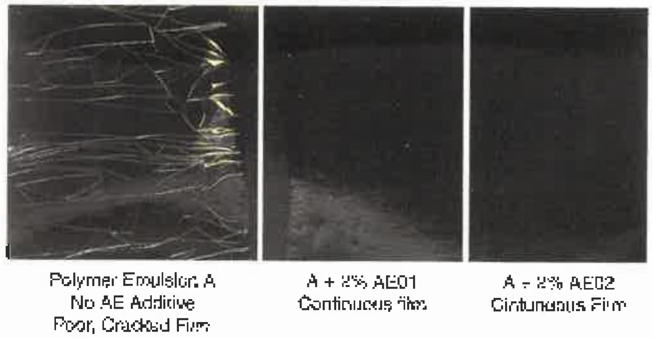



Figure 3—Film formation at 10°C (50°F)/95% RH for Polymer Emulsion A with and without AE surfactants. The films were prepared by drawdown onto black Leneta charts.




In another set of experiments, the efficacy of AE02 was compared to that of TMPIB in a series of emulsions (C, I, J = acrylics; H = styrene-acrylic; K = vinyl-acrylic). As the data in *Figure* 9 show, at a 2% replacement level, AE02 appeared about as effective as TMPIB at reducing the MFFT for these emulsions. The slopes of the regression lines for TMPIB were within the range of - 2.1 to 1.9 (units of °C/TMPIB weight %), which are essentially the same as those obtained for AE02 above. Based on these observations, it can be concluded that AE02 has the same efficiency as that of TMPIB.

## *AE Surfactants: Performance in an Architectural Coating*

Since the AE surfactants were shown to have similar efficiencies as TMPIB, a study was conducted to test AE01 and AE02 surfactants as partial replacements for TMPIB in a semi-gloss architectural coating formulation. The main purpose of this work was to test the AEs for their ability to aid low temperature film formation (LTFF) and to determine whether they imparted any detrimental effects on formulation or film performance. The formulation tested is provided in *Appendix* B. Polymer Emulsion G (acrylic) was the binder resin used in the evaluation. An experimental design was performed to determine optimal levels of TMPIB and AE surfactant. The results are listed in *Table* 4 for the best combinations.

The data in *Table* 4 show that the formulations containing the AE surfactants can reduce VOCs by about 25 g/L. Good LTFF (*Figure* 10) was obtained with AE01 at 1.5% and was comparable or better than the higher VOC TMPIB control. The LTFF was not as good with AE02; the data suggested that 2% AE02 was required for adequate LTFF. Gloss was slightly better than the controls. Due, presumably, to their surfactant character, the AEs significantly improved substrate wetting. Interestingly, the formulation viscosities were higher with the AEs. In separate evaluations on slightly different formulations (150 g/L VOC) containing either Polymer Emulsion G or Polymer Emulsion K, it was found that substitution of 2% AE02 (on binder resin solids) for TMPIB did not detract from performance properties such as LTFF, color float/acceptance, adhesion, stain resistance/removal, scrub resistance, block resistance, or rheology modifier (HEUR type) demand.[13] Thus, the AE surfactants were shown to provide lower VOC coatings with similar performance relative to the higher VOC analogs containing TMPIB as the sole coalescent. Unfortunately, the formulations with the AE surfactants showed a significant rise in vis-

Figure 4—AFM micrographs of films prepared from Polymer Emulsion A. Films containing the AE02 surfactant were smoother than higher VOC analogs.

Figure 5—$T_g$ data for the polymer films containing the AE surfactants. The AE surfactants were tested at 2% by weight on total emulsion.

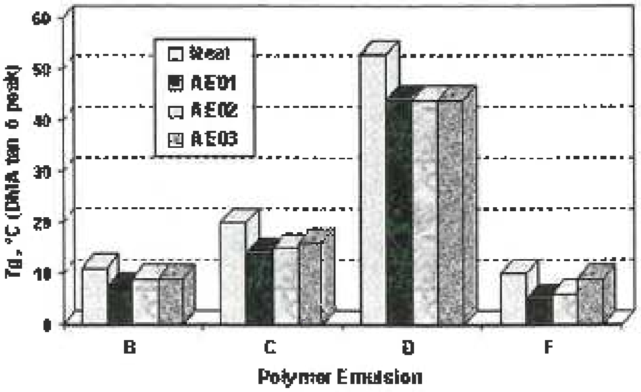



Figure 6—Dry times for polymer emulsions containing the AE surfactants. The AE surfactants were tested at 2% by weight on total emulsion. Dry times were determined according to ASTM D 5895.

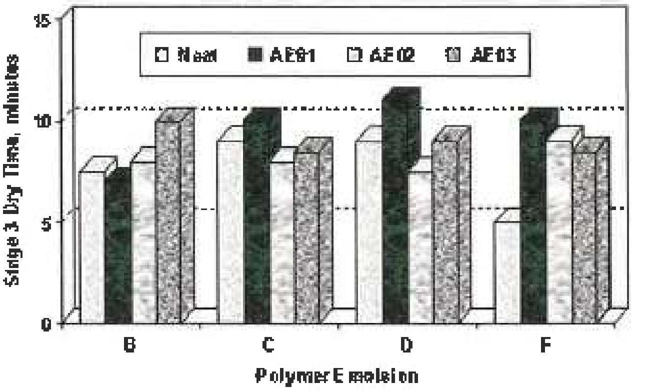
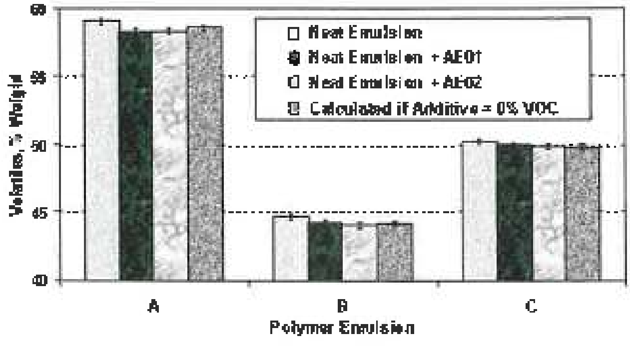



Figure 7—Volatile contents for polymer emulsions containing the AE surfactants. At 2% by weight on total emulsion, the AE surfactants did not contribute to the overall volatile content (including water) of the emulsions. Volatile content was determined by the oven method per EPA Method 24.



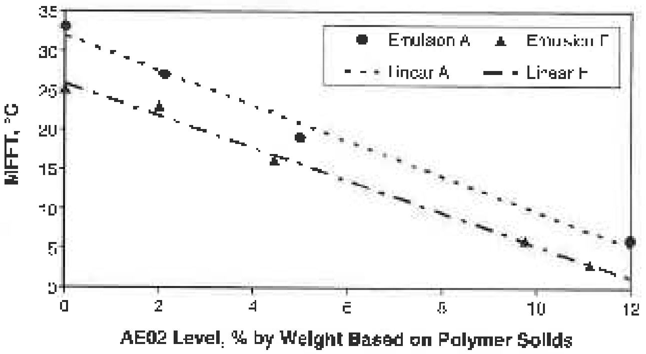

cosity when aged at 60°C for >2 weeks, and this was considered to be unacceptable from a shelf stability perspective. Since the pH was observed to drop during oven aging, it was hypothesized that ester hydrolysis was responsible (at least partially) for the instability. Therefore, the use of the AE surfactants for MFFT reduction in architectural coating formulations is not recommended without performing the proper paint stability testing.

### *Alternative Coalescing Surfactants*

The above work with the AE surfactants demonstrated that the concept of coalescing surfactants was a viable approach for formulating lower VOC coatings with existing resin technology and yet still maintaining adequate performance. However, since the AE surfactants showed instability in the architectural coating formulations studied, other potential coalescing surfactants were evaluated. The MFFTs of polymer emulsions containing 2% by weight of the alternative coalescing surfactants were determined. In the one set of experiments, the AD and $E_{20}$TMDD surfactants were compared with the AE02 surfactant in two architectural acrylic emulsions to determine the relative efficiency of these products. The AD and $E_{20}$TMDD surfactants were tested because of their relatively low HLB values, which were thought to favor better coalescence. The results are provided in *Figure* 11. As can be seen, the AD material provided similar results compared to the AE02. The $E_{20}$TMDD was not quite as efficient, but it still significantly lowered the MFFTs for both emulsions. Therefore, it was concluded that AD and $E_{20}$TMDD could offer similar performance to the AEs and, because these products do not contain ester groups, formulation instability would probably not be an issue. Stability testing confirmed that the AD-containing formulation was stable.

In further experiments, the MFFT reduction efficiency of a new experimental coalescing surfactant (ECS) was evaluated in several emulsions and compared with that of AE02 and $E_{40}$TMDD. The results are shown in *Figure* 12. For all of the emulsions tested, the ECS material lowered the MFFT comparably to AE02. Similar to the AD coalescing surfactant, the ECS should not impart formulation instability, and elevated-temperature stability testing showed the ECS-containing formulation to be stable. In addition to the MFFT, the effect of ECS on the equilibrium surface tension of the Polymer Emulsion A was evaluated. The data in *Figure* 13 show that ECS provides lower surface tensions for all of the emulsions than does AE02 and had comparable surface tensions to $E_{20}$TMDD which, however, does not lower the MFFT as effectively as ECS. So, ECS, like AD and $E_{20}$TMDD, should offer similar MFFT performance to the AEs without the formulation instability is-

Figure 8—Effect of AE02 level on MFFT for two polymer emulsions (A and F). The lines designated "Linear" are regression fits to the data.

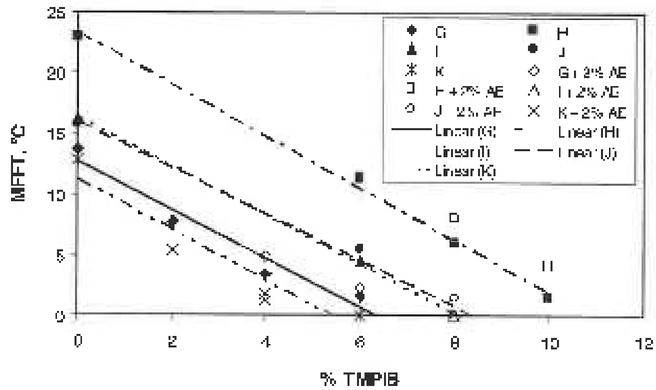



size. Additionally, ECS should offer improved wetting performance due to its lower EST.

### *Effect of Surfactant HLB on MFFT-Reduction Effectiveness*

In order to better understand the parameters that affected the MFFT-reducing effectiveness of coalescing surfactants, a study was conducted to determine what effect the HLB of the surfactant might have on coalescence. To that end, a series of ethoxylated TMDD surfactants ($E_xTMDD$) with calculated HLBs over the range of 3 to 17 were evaluated in Polymer Emulsion A, which was chosen because of its lack of stabilizing surfactants. (Note that for the HLB = 3 case, the data point was obtained using the AD surfactant, since TMDD is a solid at room temperature. The AD surfactant was chosen due to its relative similarity to TMDD. The HLB value of 3 was calculated using the weight % of hydrophilic groups divided by 5.) The results are plotted in *Figure* 14 as the change in MFFT (Delta MFFT = MFFT of Polymer Emulsion A minus MFFT with surfactants) versus the HLB of the surfactant. *Figure* 14 shows that the MFFT reduction depends on the surfactant HLB. The data indicate that the most efficient surfactants have the lowest HLBs. This finding makes sense intuitively based on apparent solubility parameters.

Figure 9—Effect of TMPIB replacement by AE02 surfactant. Addition levels are given in % by weight on polymer solids (Polymer Emulsions G-K). The legend symbols that include "+ 2% AE02" represent MFFT data obtained by replacing 2% TMPIB with AE02 at an equivalent total % of coalescent. The lines designated "Linear" are regression fits to the TMPIB data.




### *Model of MFFT Reduction for the AE Coalescing Surfactants*

In order to understand the MFFT reduction efficiency of the AE surfactants, a study was conducted to understand how these surfactants partitioned between the air-water interface and the polymer particle-water interface. In a manner similar to that described by Mercurio[20] for coalescing solvents, the partitioning of a coalescing surfactant (CS) can be schematically described as in *Figure* 15. In the simplest case without a dispersing surfactant (i.e., a free surfactant added to sta-

**Table 4—Performance Data for Architectural Coatings Containing AE Surfactants**

| Mixtures | A AE01 | B AE01 | C AE02 | D AE02 | Control 1 No TMPIB | Control 2 8% TMPIB |
|---|---|---|---|---|---|---|
| % AE01[a] | 1.5 | 2.0 | 0 | 0 | 0 | 0 |
| % AE02[a] | 0 | 0 | 1.1 | 2.0 | 0 | 0 |
| % TMPIB[a] | 5.6 | 6.1 | 6.1 | 6.1 | 0 | 8 |
| VOC, g/L | 126 | 127.5 | 127.5 | 127.5 | 0 | 148 |
| LTFF[b] | 10 | 10 | 6 | 8 | 1 | 10 |
| Gloss, 20°/60° | 43/81 | 43/81 | 43/82 | 45/82 | 38/79 | 37/78 |
| Wetting[c] | 9 | 10 | 8.5 | 9.5 | 1 | 3.5 |

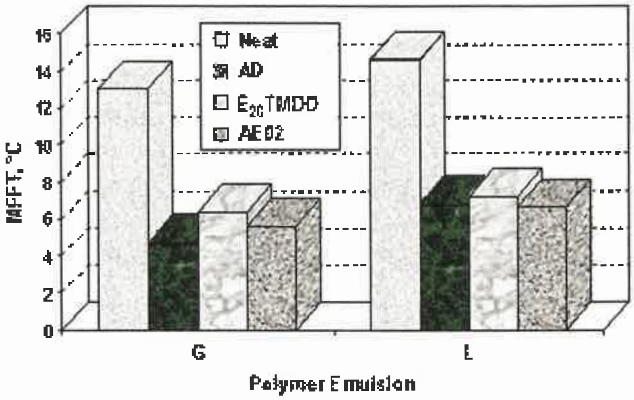
(a) % by weight based on binder resin solids.
(b) Test performed at 1.7°C (35°F)/50% R.H. Rating: 1 = poor; 10 = best.
(c) Onto glossy Leneta chart. Rating: 1 = poor; 10 = best.

Note: VOCs were adjusted by changing the amount of propylene glycol.

Figure 10—Effect of TMPIB replacement by AE01 surfactant on LTFF. Addition levels are given in % by weight on polymer solids for Polymer Emulsion G.

0% TMPIB    6% TMPIB    1.5% AE01 + 5.7% TMPIB

Figure 11 –MFFT-reduction effectiveness of AD and $E_{20}$TMDD surfactants compared to the AE02 surfactant. The coalescing surfactants were added at 2% by weight based on total emulsion.




bilize the emulsion particles), the CS will partition between the polymer particle-water and the air-water interfaces. If the CS does not form micelles and has a low solubility in water, then the bulk of the CS will partition at those two interfaces; this assumption implies that the CS has a low HLB, which we have shown above to provide more efficient MFFT reduction. Notionally, preferential adsorption of the CS at the polymer particle-water interface should afford optimal MFFT reduction, since the CS should soften the surfaces of the particles and, thereby, improve particle-particle coalescence. In the case of preferential adsorption of the CS at polymer particle-water interface, it would be expected that the coalescing surfactant should have less of an effect on the surface tension (air-water interface) of the emulsion than would be anticipated based on measurements in pure water.

In order to test whether the above hypothesis might be true, measurements were made of the DSTs and ESTs of neat Polymer Emulsion A and the emulsion containing either 0.1% or 1% by weight of AE02 or $E_{40}$TMDD, which was chosen because of its lower impact on the MFFT. Polymer Emulsion A was selected because of its lack of stabilizing surfactants, which would complicate the interpretation of the surface tension results. *Figures* 16 and 17 show that the AE02 surfactant did not lower the EST or DST nearly as much as expected from the

Figure 12—MFFT-reduction effectiveness of ECS compared to $E_{40}$TMDD and AE02 surfactants. The coalescing surfactants were added at 2% by weight based on total emulsion.

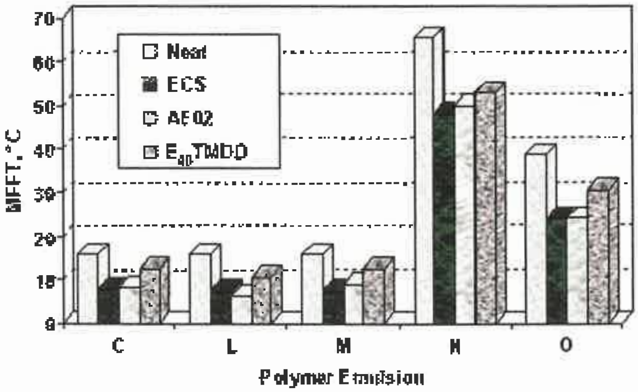



Figure 13—Equilibrium surface tension reducing effectiveness of ECS compared to $E_{40}$TMDD and AE02 surfactants. The coalescing surfactants were added at 2% by weight based on total emulsion. No data were obtained for $E_{40}$TMDD in either Polymer Emulsion L or M.

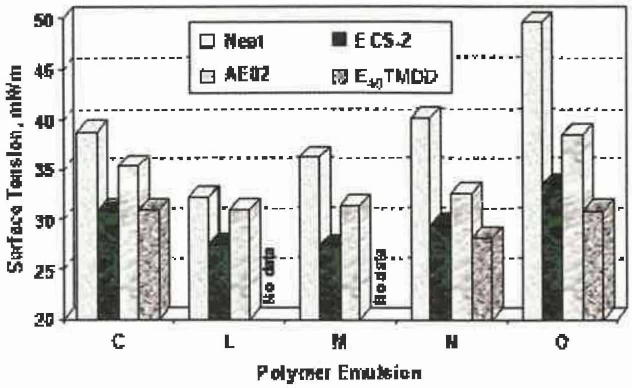


Figure 14—Effect of surfactant HLB on the MFFT-reducing effectiveness. The surfactants were added at 2% by weight based on total emulsion. The regression line has a slope of −0.48 (°C/HLB value), an intercept of 13.1°C, and $r^2$ = 0.92.

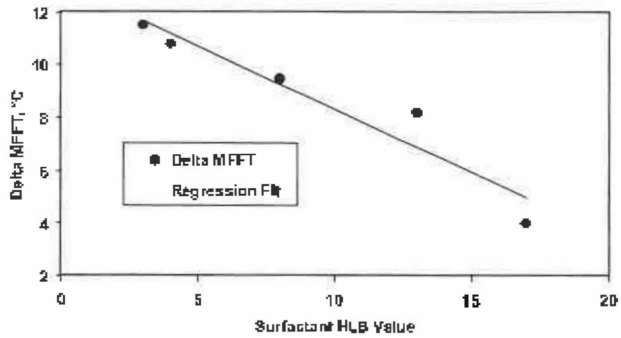



Figure 16—EST data for AE02 and $E_{40}$TMDD surfactants in Polymer Emulsion A and pure water. The legend indicates the weight % of surfactant added.

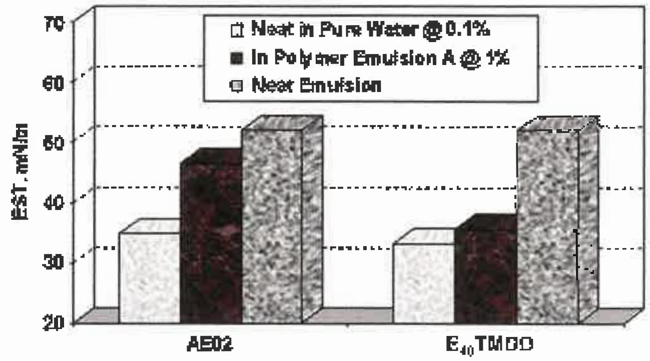



Figure 15—Simple model for partitioning of a CS at low concentration.

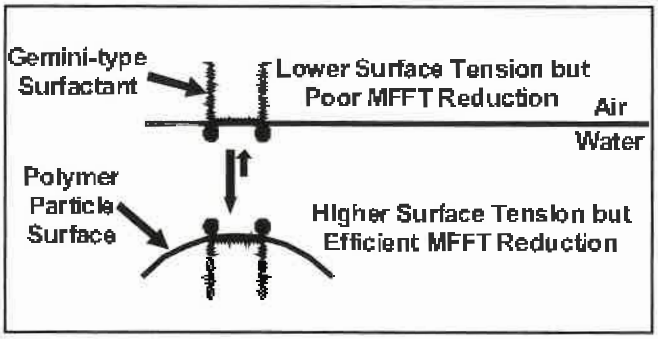
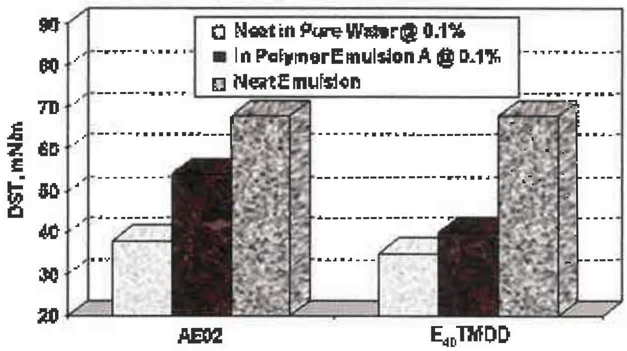



Figure 17—DST data for AE02 and $E_{40}$TMDD surfactants in Polymer Emulsion A and pure water. Data were collected at a rate of six bubbles/per sec.




data in pure water. On the other hand, the $E_{40}$TMDD surfactant significantly lowered the EST and DST to values close to that obtained in water. This data supports the notion that the AE02 surfactant adsorbed preferentially onto the surface of the polymer particles. If this is true, then preferential absorption may partly explain the MFFT reducing efficiency of the AE02 material. Another possible explanation for the surface tension results is that the AE02 dissolved in the polymer particles. This may have occurred to some extent but, since these molecules are surface active, surface adsorption probably predominates up to the point of surface saturation (based on a rough estimate, 2% AE02 should be close to that needed for surface saturation of the polymer particles only).

## SUMMARY AND CONCLUSIONS

A number of Gemini-type surfactants were found to reduce the MFFT for a wide variety of emulsion polymers. The surfactants studied included a series of alkyl esters (AEs), a range of ethoxylated TMDD ($E_x$TMDD) products, an alkane diol (AD), and a new experimental coalescing surfactant (ECS). Atomic force microscopy showed that films prepared using the AE02 surfactant were generally smoother than films not containing the AE surfactant. While enabling low-VOC formulating, the AE01 and AE02 surfactants were found to have minimal effect on coating performance but improved wetting characteristics. The new AD and ECS surfactants performed similarly to AE02 with regard to MFFT reduction. Lower HLB surfactants were found to be the most effective coalescents. Preferential adsorption of the AE02 onto the surface of the polymer particles may explain the effectiveness of this surfactant to lower the MFFT.

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## Appendix A—List of Raw Materials and Suppliers

| Reference Code | Raw Material | Supplier |
|---|---|---|
| TMDD | SURFYNOL® 104 | Air Products and Chemicals, Inc. |
| AD | EnviroGem® AD01 | Air Products and Chemicals, Inc. |
| AE01 | EnviroGem® AE01 | Air Products and Chemicals, Inc. |
| AE02 | EnviroGem® AE02 | Air Products and Chemicals, Inc. |
| AE03 | EnviroGem® AE03 | Air Products and Chemicals, Inc. |
| $E_{20}$TMDD | SURFYNOL® 420 | Air Products and Chemicals, Inc. |
| $E_{40}$TMDD | SURFYNOL® 440 | Air Products and Chemicals, Inc. |
| $E_{65}$TMDD | SURFYNOL® 465 | Air Products and Chemicals, Inc. |
| $E_{85}$TMDD | SURFYNOL® 485 | Air Products and Chemicals, Inc. |
| TMPIB | TEXANOL® Ester Alcohol | Eastman Chemical Company |
| Polymer Emulsion A | HYBRIDUR® 870 | Air Products and Chemicals, Inc. |
| Polymer Emulsion B | AIRFLEX® EF811 | Air Products and Chemicals, Inc. |
| Polymer Emulsion C | Rhoplex® SG-10M | Rohm and Haas |
| Polymer Emulsion D | Maincote® HG-54 | Rohm and Haas |
| Polymer Emulsion E | NeoCryl® XK-12 | NeoResins |
| Polymer Emulsion F | Rhoplex® Multilobe-200 | Rohm and Haas |
| Polymer Emulsion G | Rhoplex® SG-30 | Rohm and Haas |
| Polymer Emulsion H | Rhoplex® 2700 | Rohm and Haas |
| Polymer Emulsion I | Rhoplex® 2500 | Rohm and Haas |
| Polymer Emulsion J | Rhoplex® AC-347 | Rohm and Haas |
| Polymer Emulsion K | Res 3077 | Rohm and Haas |
| Polymer Emulsion L | Rhoplex® SG-20 | Rohm and Haas |
| Polymer Emulsion M | Maincote® PR-71 | Rohm and Haas |
| Polymer Emulsion N | Maincote® HG-86 | Rohm and Haas |
| Polymer Emulsion O | Aquamac® 440 | Resolution Specialty Materials |
| $TiO_2$ slurry | Ti-Pure® R-746 | DuPont |
| Defoamer | BYK®-022 | Byk-Chemie |
| Thickener 1 (1.4%) | Acrysol® RM-2020NPR | Rohm and Haas |
| Thickener 2 (0.2%) | Acrysol® SCT-275 | Rohm and Haas |

## Appendix B—Model Architectural Formulation

| Material | % by Weight |
|---|---|
| Polymer Emulsion G | 51.0 |
| $TiO_2$ slurry | 35.2 |
| Water | 6.9 |
| Propylene glycol | 3.1 |
| Defoamer | 0.1 |
| TMPIB | 2.0 |
| Thickeners 1 and 2 | 1.6 |
| $NH_4OH$ | 0.1 |
| Total | 100.0 |