Optimizing Low-Foam Grind Step Surfactants for Improved Processing

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With the industry trend to low-VOC latex paints, managing foam is a significant concern for coatings formulators. APEO-free, low-foam, readily biodegradable (by OECD 301) surfactants are now available but some of these actually can be used to help defoam the grind step at elevated processing temperatures. To optimize their use, the low-foam surfactant should be matched to a dispersant system so that the surfactant will become insoluble and act as a defoamer in the grind at temperatures above its cloud point. High throughput screening techniques were used to determine optimal combinations of dispersant and low-foam surfactant. With these leads, a follow-up study of cloud points and foaming of grind step liquids was run to demonstrate the utility of this approach. Through careful selection of grind surfactants matched to a particular dispersant system, a notable reduction in processing foam can be achieved.

INTRODUCTION

Surfactants are used frequently to help wet out pigments by displacing air at the surface of the pigment.[1] Once the air is displaced and the pigment surface is wet out, the dispersant can then surround the pigment particles as the agglomerates are broken down under high shear. The dispersants role is to keep the pigment dispersion from reflocculating during and after the pigment grind. Once the pigment dispersion is complete, the surfactants that were used can have other effects in the finished paint. They can improve heat age stability, color acceptance, or freeze–thaw resistance.

Foam can be formed during the pigment dispersion step as air is displaced from the pigment surface or during the high speed pigment grind. The foam can reduce the efficiency of the Cowles disperser and can also persist into the final stages of paint making where it can cause problems in container fill levels or in quality control of paint properties. Recently, there has been an industry shift toward lower VOC in paints which has contributed to worse foaming. The higher foam may be caused by lower levels of hydrophobic coalescents or plasticizers (which can act as defoamers) and lower levels of glycols which can contribute to film flow after foam break.

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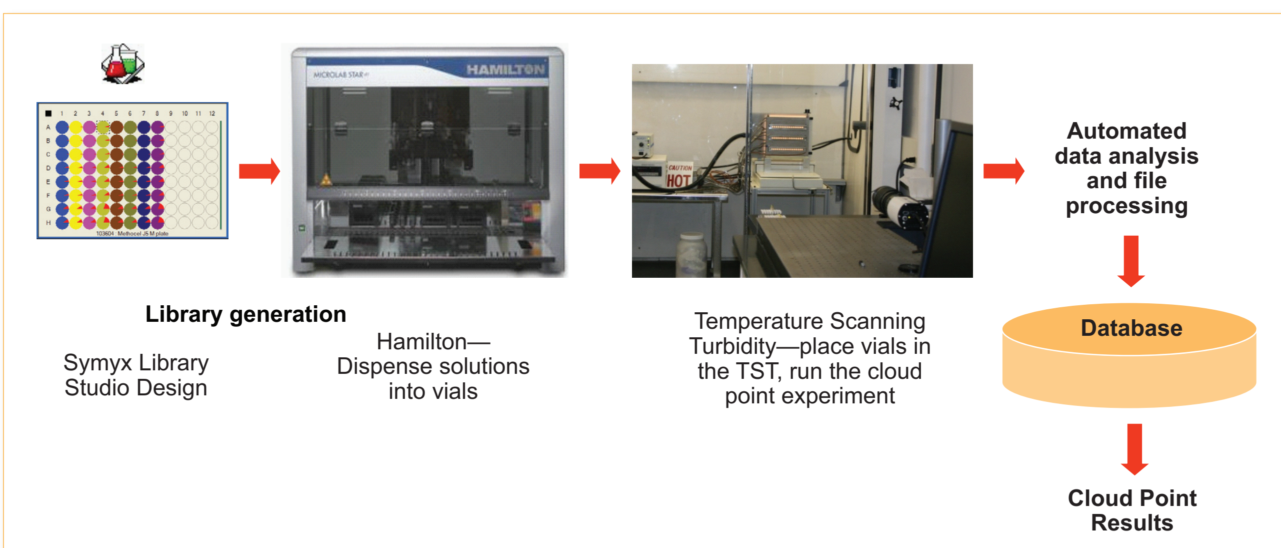

Figure 1—Cloud point analysis workflow.

Table 1—Surfactants

		APEO-Free	Readily Biodegradable (OECD 301)	HLB	Cloud Point 1% Aq Soln	Foam Height (Ross Miles)	CMC	Surface Tension 1% Aq
1	Alcohol Ethoxylate, 3 EO CP<20	Yes	Yes	8	Insol	Insol	Insol	Insol
2	Alcohol Ethoxylate, EO 5 CP<20	Yes	Yes	10.5	Disp	Disp	Disp	Disp
3	ECOSURF™ LF-20 Surfactant	Yes	Yes	10-11	20	25 / 2	24	35
4	Low-Foam Surfactant CP 21	Yes	No	12.1	21	44 / 4	24	31
5	Low-Foam APEO Surfactant CP 30	No	No	12.6	30	—	75	36
6	ECOSURF LF-30 Surfactant	Yes	Yes	12-13	32	100 / 12	25	30
7	Alcohol Ethoxylate, EO 8 CP 36	Yes	No	13.1	36	130 / 22	800	37
8	Low-Foam Surfactant CP 40	Yes	No	12.6	40	106 / 6	24	31

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To reduce the foaming in the pigment dispersion step, defoamers are used. The defoamers used in pigment dispersions are often relatively insoluble and silicone-based. The defoamers can sometimes cause problems like lower gloss or cratering in the film of the finished paint. A lower foaming grind fluid may allow the use of more water-dispersible defoamers with fewer side effects. Low-foam surfactants are frequently used in the grind step to keep the foam to a minimum.

Low-foam surfactants can be made with hydrophobic modification of the hydrophilic ethylene oxide (EO) chain.[2] This hydrophobic modification disrupts the air–water interface and can help to destabilize the foam. Low-foam surfactants can have an alkyl phenyl hydrophobe and would be classified as APEO surfactants or can be made to be APEO-free by using alkyl chain hydrophobes.

Some nonionic surfactants can act as cloud point defoamers.[3,4] The cloud point of a nonionic surfactant is the temperature at which the surfactant becomes insoluble in an aqueous medium. The reduced solubility at higher temperatures is thought to be caused by reduced hydration of the EO chain, leading to a more hydrophobic surfactant. Above the cloud point, the surfactant is present as a separate but dispersed phase, giving a cloudy appearance to the media. This hydrophobic, dispersed phase can in some cases act as an effective antifoam, and cloud point defoamers are frequently used in industries where high temperatures are common, such as boiler fluids. Cloud point of surfactants can be affected by other soluble species in the medium. Some salts can lower the cloud point of nonionic surfactants, and water-soluble solvents or dispersants can raise the cloud point.[5]

In coatings, there would be advantages to using this characteristic of the nonionic surfactants to improve processing. Low-foam surfactants which are soluble at room temperature in the grind fluids should be chosen since these will help wet out dry pigment during the pigment addition. At elevated temperatures common during the pigment dispersion (30–50ºC), the low-foam surfactant should become insoluble as the cloud point is exceeded, and the surfactant would have less foam during that processing step. During this stage the pigment is prevented from reagglomerating by the dispersants in the grind. As the batch of paint is finished, and the temperature is decreased with the addition of lower temperature binders, other surfactants, and water, the nonionic surfactant again becomes soluble. Once the surfactant is soluble again, it can contribute to other properties of the coating, such as color acceptance and freeze–thaw resistance.

Table 2—Dispersants

Name	Description
TAMOL™ 1124	Hydrophilic copolymer polyelectrolite dispersant
TAMOL 731A	Moderately hydrophobic copolymer dispersant
TAMOL 2002	Hydrophobic copolymer dispersant

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Selecting a wetting agent which functions as a cloud point defoamer will depend on the nature of the grind fluids as well as the expected processing temperature. Some of the variables of typical paint dispersions were studied to help the selection of the best cloud point defoamer and to show the utility of these defoamers in practice.

MATERIALS AND METHODS

A number of surfactants were screened for cloud points in different dispersant solutions. The surfactants used were alcohol ethoxylate surfactants with 3, 5, and 8 moles of EO; an APEO low-foam surfactant; two APEO-free low-foam surfactants; and two new readily biodegradable (OECD 301), APEO-free low-foam surfactants—ECOSURF™ LF-20 and ECOSURF LF-30 Surfactants (*Table* 1). The dispersants were TAMOL™ 1124 Dispersant, a hydrophilic dispersant commonly used with HASE thickened paints; TAMOL 731A Dispersant, a moderately hydrophobic copolymer which can be used

Table 3—Surfactant Cloud Points in Dispersant Solutions[a]

		Cloud Point 1% Aq Soln	Cloud Point TAMOL™ 1124 Soln (Std Dev)	Cloud Point TAMOL 731 Soln (Std Dev)	Cloud Point TAMOL 2002 Soln (Std Dev)
1	Alcohol Ethoxylate, 3 EO CP<20	Insol	<20	<20	<20
2	Alcohol Ethoxylate, 5 EO CP<20	Disp	<20	<20	67 (8)
3	ECOSURF™ LF-20 CP20 Surfactant	20	<20	<20	29 (2)
4	Low-Foam Surfactant CP21	21	<20	23.3 (0.1)	37.5 (0.7)
5	Low-Foam APEO Surfactant CP30	30	24.3 (0.1)	33.6 (0.4)	51.6 (1.0)
6	ECOSURF LF-30 CP32 Surfactant	32	25.9 (0.2)	33.0 (0.2)	47.9 (0.6)
7	Alcohol Ethoxylate, EO 8 CP36	36	29 (0.3)	96.2 (4.4)	>100
8	Low-Foam Surfactant CP40	40	34.7(0)	50 (1)	69 (3)

(a) Midpoint concentrations are shown (5.4% dispersant and 2.4% surfactant).

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with HASE and HEUR-thickened paints; and TAMOL 2002 Dispersant, a hydrophobic copolymer commonly used for HEUR thickened paints (*Table* 2).

Dispersants were evaluated at three concentrations (the equivalent of adding 0.5, 1, and 1.5% dispersant solids on pigment solids to a 225 lb TiO_2 grind using five gallons of water), and the surfactants were also evaluated at three concentrations (the equivalent of 0.5, 1, and 1.5 lb of surfactant actives/100 gal of the finished paint). At the midpoint, the dispersant concentration was 5.4% (of actives) and the surfactant concentration was 2.4% on the water used in the grind.

Formulations were designed using Library Studio (Symyx, CA) and prepared using a high throughput robotic liquid handler (Hamilton Microlab Star) (see *Figure* 1) by dispensing the dispersant and surfactant aqueous stock solutions into water. Samples were prepared on a small scale, using 1.2 mL glass vials in a 96-well format. Total weight of each formulation was kept at 1000 mg. For each material to be dispensed, calibrations were performed to correlate the amount of each volume dispensed with the desired mass. Each calibration volume set was repeated in triplicate to estimate the error of calibration. The dispense weights were within 3% of targets.

Cloud points of prepared formulations were determined using a temperature scanning turbidity (TST) instrument, recently developed by The Dow Chemical Company. With this instrument, optical density of 48 samples is measured and recorded in parallel as samples are heated from ambient temperature to 100°C (for aqueous solutions). An automated image analysis system then calculates cloud points (defined as a relatively sharp transition from clear to opaque) from a turbidity vs. temperature plot. This technique was previously shown to correlate well with other commonly used cloud point measurement approaches, such as UV/VIS and Nephelometry, and was also shown to have very good cloud point reproducibility (1–2°C). For this experiment, 1 mL (for surfactant-dispersant mixture) of sample was placed into a 1.5 mL glass vial, then the vials were capped and placed into TST sample holder. Temperature was varied from 20°C to 95°C for the cloud point screening study and imaging was done at two temperatures (20°C and 40°C) for the foam height study.

Foaming at different temperatures was assessed using a high throughput phase identification and characterization robot (PICA II) equipped with wrist-shaking capability. A picture of each formulation was taken before and after shaking at a pre-set temperature, and a high throughput image analysis was then performed on collected images to characterize foaming.

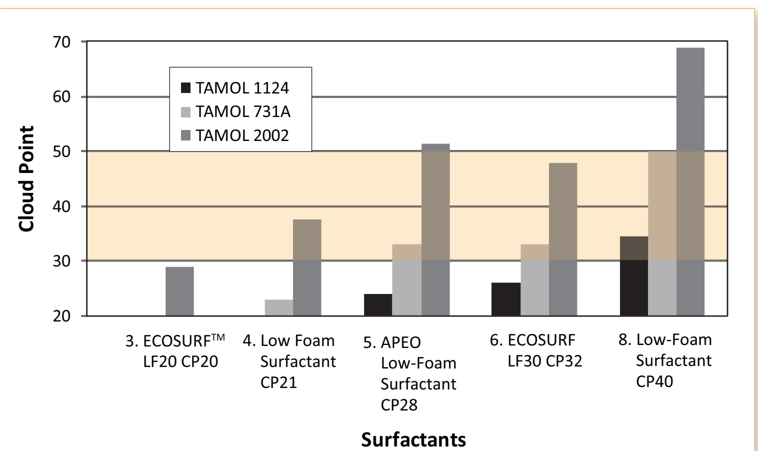

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Figure 2—Cloud points of surfactants in dispersant solutions. Light orange box indicates typical Cowles pigment dispersion temperatures.

RESULTS

The model for the DOE of the high throughput cloud point determination of surfactant and

Table 4—Foaming and Turbidity of Surfactants in TAMOL™ 1124 Dispersant Solution

	Dispersant: TAMOL 1124	20°C Turbidity	40°C Turbidity	20°C Foam Height (Std Dev)	40°C Foam Height (Std Dev)	Change in Foam Height (20–40°C)	%Change in Foam Height (20–40°C)
	No surfactant control	4	5	21 (22)	25 (4)	-5	-24
1	Alcohol Ethoxylate, 3 EO CP<20	136	130	48 (5)	3 (7)	45	97
2	Alcohol Ethoxylate, 5 EO CP<20	142	134	152 (26)	79 (13)	73	48
3	ECOSURF™ LF-20 Surfactant CP20	122	155	60 (11)	65 (25)	-5	-9
4	Low-Foam Surfactant CP21	153	175	96 (26)	52 (24)	44	46
5	Low-Foam APEO Surfactant CP30	7	175	236 (12)	106 (20)	130	55
6	ECOSURF LF-30 Surfactant CP32	6	161	232 (14)	125 (7)	107	46
7	Alcohol Ethoxylate, EO 8 CP36	6	105	414 (80)	203 (22)	212	51
8	Low-Foam Surfactant CP40	5	108	278 (11)	159 (32)	118	43

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dispersant solutions was good (R Squared 0.88), however, there was some design imbalance for the factors "Surfactant Concentration" and "Dispersant Concentration" (Variance Inflation Factors ~30). The error in the cloud point measurements was ± 2°C, an acceptable level. The cloud point was strongly affected by surfactant type, as expected, but also by dispersant type. See *Table* 3 and *Figure* 2 for surfactant cloud points in the dispersant solutions.

The relatively hydrophilic TAMOL 1124 Dispersant lowered the cloud points slightly. TAMOL 731 Dispersant, which is more hydrophobic than TAMOL 1124, either did not change the cloud points or raised the cloud points slightly. The most hydrophobic dispersant, TAMOL 2002, raised the cloud points of the surfactants notably. While the polyelectrolyte TAMOL 1124 Dispersant may have depressed the cloud points because of the salts in solution, the hydrophobic TAMOL 2002 Dispersant was acting as a hydrotrope and helping to solubilize the surfactant. This observation suggests that, depending on the dispersant used in the coating formulation, different low-foam surfactants should be selected to achieve such cloud point defoaming.

In TAMOL 1124 Dispersant solutions, the low-foam surfactants with aqueous cloud points of 30 or higher might be used. For example, in the TAMOL 1124 Dispersant solutions, the Low-Foam Surfactant CP40 is soluble at room temperature and would be expected to help wet out the pigment, but would be expected to cloud out at slightly above room temperature (above 30°C) and give lower foam. However, the APEO low-foam surfactant and ECOSURF LF-30 Surfactant would be clouded at 25°C and might have lower pigment wetting efficiency on hot summer days.

The same three low-foam surfactants might be used in TAMOL 731 Dispersant solutions. In the case of TAMOL 731, the surfactants are soluble at room temperature and cloud out in the range of 30–50°C.

For solutions of the hydrophobic TAMOL 2002 Dispersant, a different set of low-foam surfactants with cloud points of 20°C or less (ECOSURF LF-20 Surfactant and Low-Foam Surfactant CP21) would be used. In TAMOL 2002 Dispersant Solutions, APEO Low-Foam Surfactant CP30 and ECOSURF LF-30 Surfactant would be expected to have cloud points above 50°C and would not be effective cloud point defoamers at typical processing temperatures.

Foaming and clouding behavior of the different surfactants in the three dispersant solutions were also evaluated at both 20 and 40°C (see *Table* 4 and *Figure* 3). The images were analyzed for foam height and turbidity to determine if the cloud point

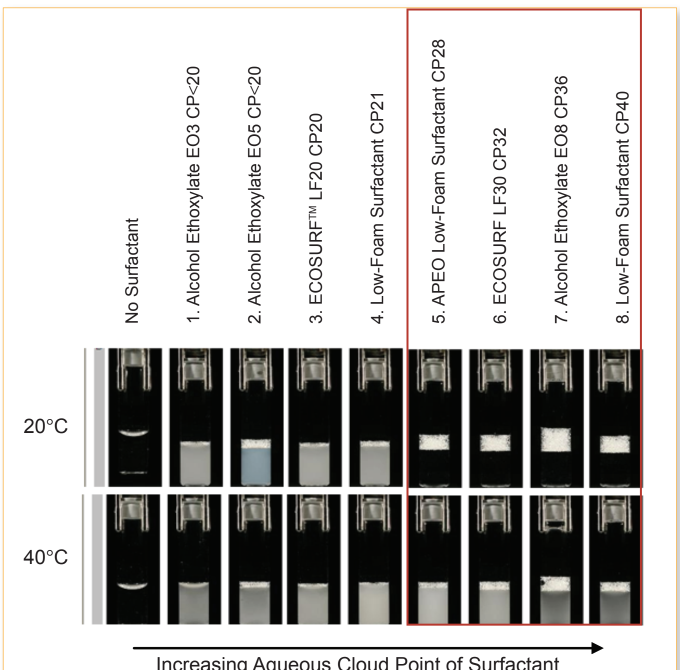

Figure 3—Images of surfactant solutions in TAMOL 1124 Dispersant at 20°C and 40°C. In TAMOL 1124, the higher cloud point surfactants are soluble at 20°C but cloud out at 40°C.

Table 5—Foaming and Turbidity of Surfactants in TAMOL™ 731A Dispersant

	Dispersant: TAMOL 731	20°C Turbidity	40°C Turbidity	20°C Foam Height (Std Dev)	40°C Foam Height (Std Dev)	Change in Foam Height (20–40°C)	%Change in Foam Height (20–40°C)
	No surfactant control	4	4	175 (29)	140 (33)	35	20
1	Alcohol Ethoxylate, 3 EO CP<20	167	181	95 (5)	88 (15)	8	8
2	Alcohol Ethoxylate, 5 EO CP<20	80	29	219 (40)	232 (26)	-13	-6
3	ECOSURF™ LF-20 Surfactant CP20	131	168	52 (8)	17 (13)	35	67
4	Low-Foam Surfactant CP21	5	176	185 (21)	21 (15)	164	89
5	Low-Foam APEO Surfactant CP30	5	77	198 (39)	168 (7)	30	15
6	ECOSURF LF-30 Surfactant CP32	5	71	198 (17)	30 (28)	168	85
7	Alcohol Ethoxylate, EO 8 CP36	6	5	356 (30)	277 (66)	80	22
8	Low-Foam Surfactant CP40	5	5	360 (98)	215 (55)	145	40

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had been reached. Turbidity was assessed using gray scale image analysis, where 0–20 was considered clear, and 20–256 was considered cloudy.

For the hydrophilic TAMOL 1124 Dispersant, surfactants which had cloud points of above 30°C were soluble at room temperature. The foam height of these surfactant/dispersant solutions at room temperature was relatively high. When the temperature was raised to 40°C, and the surfactants clouded out of solution, the foam height was reduced by an average of 50% for the low-foam surfactants. The

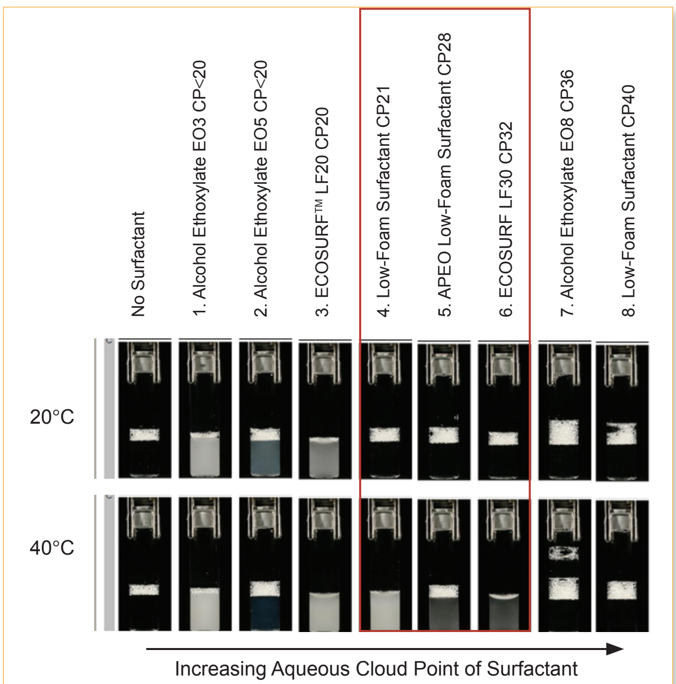

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Figure 4—Images of surfactant solutions in TAMOL 731A Dispersant at 20°C and 40°C. In TAMOL 731A, the intermediate cloud point surfactants are soluble at 20°C but clouded out at 40°C.

advantage of the low-foam surfactants in these dispersant solutions was seen by comparison to the EO8 Alcohol Ethoxylate. Although the foam of the EO8 Alcohol Ethoxylate was lower at 40°F by the same percentage as the low-foam surfactants, the foaming at room temperature was 30–45% higher than the low-foam surfactants.

For the more hydrophobic TAMOL 731A Dispersant, only three surfactants were soluble at room temperature but clouded at 40°C (see *Table* 5 and *Figure* 4).

All three low-foam surfactants had nearly equal levels of foam at 20°C, and two of the three had lower foam heights at 40°C (89% reduction in foam), although all three were more turbid at 40°C than at 20°C. The Low-Foam Surfactant CP21 and ECOSURF LF-30 Surfactant were both more effective at reducing foam than the APEO Low-Foam Surfactant CP30. Both low-foam surfactants also had lower foam at 40°C than the control dispersant solution with no added surfactant, indicating that they were effective cloud point defoamers. The Low-Foam Surfactant CP40 did not cloud out at 40°C in the TAMOL 731 Solution and had a high level of foam at both 20°C and 40°C.

For TAMOL 2002, two of the low cloud point, low-foam surfactants (ECOSURF LF-20 and the Low-Foam Surfactant CP21) were either not clouded or only very slightly at 20°C but clouded at 40°C (see *Table* 6 and *Figure* 5).

Both of these surfactants had approximately 70% reduction of the foam height at 40°F when clouded out. At 40°C, the foam for ECOSURF LF-20 Surfactant and the Low-Foam Surfactant CP21 was 50–65% lower than the foam of the control solution of TAMOL 2002 Dispersant with no added surfactant, so these two surfactants were effective cloud point defoamers. Higher cloud point surfac-

Table 6—Foaming and Turbidity of Surfactants in TAMOL™ 2002 Dispersant Solution

	Dispersant: TAMOL 2002	20°C Turbidity	40°C Turbidity	20°C Foam Height (Std Dev)	40°C Foam Height (Std Dev)	Change in Foam Height (20–40°C)	%Change in Foam Height (20–40°C)
	No surfactant control	7	7	149 (3)	154 (15)	-5	-3
1	Alcohol Ethoxylate, 3 EO CP <20	79	99	176 (32)	120 (11)	56	32
2	Alcohol Ethoxylate, 5 EO CP<20	25	36	266 (47)	243 (9)	22	8
3	ECOSURF™ LF-20 surfactant CP20	19	169	200 (18)	53 (3)	147	74
4	Low-Foam Surfactant CP21	8	98	256 (41)	72 (7)	184	72
5	Low-Foam APEO Surfactant CP30	6	7	261 (49)	208 (23)	53	20
6	ECOSURF LF-30 Surfactant CP32	7	16	210 (18)	178 (3)	32	15
7	Alcohol Ethoxylate, EO 8 CP36	6	6	266 (92)	302 (19)	-36	-13
8	Low-Foam Surfactant CP40	7	7	261 (32)	244 (72)	17	7

tants were soluble in the TAMOL 2002 Dispersant solution at 40°C and had relatively high foam.

The Alcohol Ethoxylate EO5 CP<20 was slightly clouded at 20°C in the TAMOL 2002 Dispersant solution but not notably different at 40°C. This may be because that surfactant is actually an ethylene oxide distribution with the average at EO5. It is likely that there is a small percentage of the 3 mole ethoxylate present in the 5 mole surfactant. The three mole alcohol ethoxylate surfactant was clouded at 20°C in the TAMOL 2002 Dispersant solution.

The new APEO-free, readily biodegradable (OECD 301) low-foam ECOSURF LF-20 and ECOSURF LF-30 Surfactants are good cloud point defoamers for pigment dispersions made with TAMOL 2002 and TAMOL 731A Dispersants, respectively. These have lower foam than Alcohol Ethoxylate Surfactants with similar cloud points or the APEO Low-Foam Surfactant CP30 at 20°C. Above their cloud points in the dispersant solutions, they are effective cloud point defoamers and have much lower foam than the control dispersant solution with no added surfactant. Based on the surface tension in aqueous solutions and their low critical micelle concentration, these surfactants are also capable of being good pigment wetting agents below their cloud points.

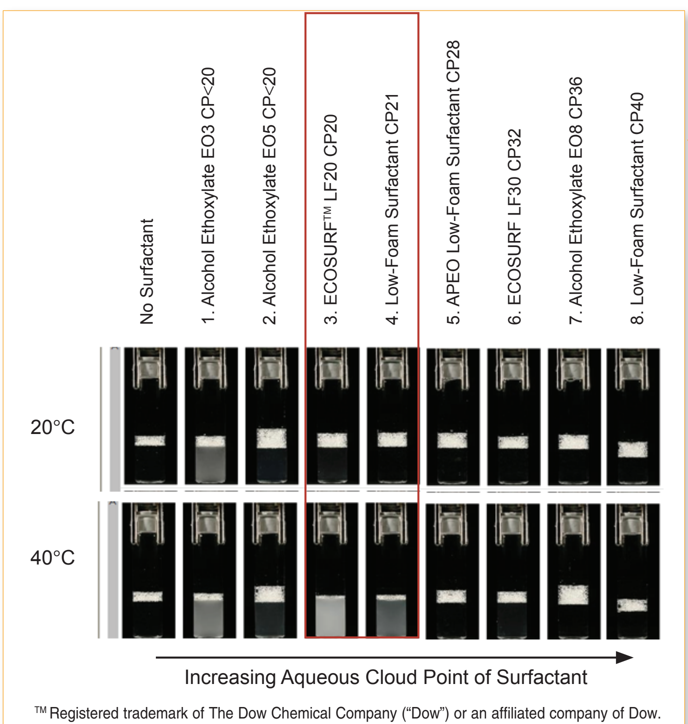

Figure 5—Images of surfactant solutions in TAMOL 2002 Dispersant at 20°C and 40°C. In TAMOL 2002, the low cloud point low-foam surfactants are soluble at 20°C but clouded out at 40°C and have a notable reduction in foam.

CONCLUSION

The hydrophobicity of the dispersants has a large effect on the surfactant cloud point and different surfactants give cloud points in the 30–50°C range typical of processing temperatures during pigment dispersion. Surfactants with lower cloud points are needed in solutions of hydrophobic dispersants.

Low-foam surfactants were found to have much lower foam in grind liquids compared to alcohol ethoxylate surfactants of similar HLB and cloud point. With TAMOL 731A and TAMOL 2002 Dispersants, the foam at 40°C for the matched low-foam surfactants was lower than the control dispersant solution with no added surfactant, indicating that these are good cloud point defoamers.

Selection of low-foam surfactants with cloud points which are matched to the dispersant hydrophobicity can give pigment dispersions which are lower in foam under typical processing conditions. The lower foam in the pigment dispersion can help improve foaming in the paint. CT

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References

1. Ann-Charlotte Hellgren, P.W., "Surfactants in Water-borne Paints," *Prog. Org. Coat.,* 79–87 (1999).
2. Schoff, S.S., "A Survey of Surfactants in Coatings Technology," *Prog. Org. Coat.,* 1–22 (1993).
3. Ratchadaporn Chaisalee, S.S., "Mechanism of Antifoam Behavior of Solutions of Nonionic Surfactants Above the Cloud Point," *J. Surfactants Deterg.,* 345–351 (2003).
4. Zsolt Nemeth, G.R., "Foam Control by Silicone Polyethers—Mechanisms of Cloud Point Antifoaming," *J. Colloid Interface Sci.,* 386–394 (1998).
5. Jing-Liang Li, D.-S. B.-H., "Effects of Additives on the Cloud Points of Selected Nonionic Linear Ethoxylated," *Colloids Surf. A: Physicochemical and Engineering Aspects,* 237–243 (2009).

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