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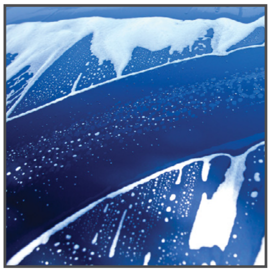

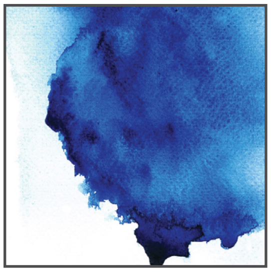

(Patent Pending)

E-SPERSE® 700 SERIES FOR EMULSION POLYMERIZATION

Surfactants have several critical functions in the emulsion polymerization process. They must be able to provide stability during the polymerization in order to prevent loss due to coagulation. Anionic surfactants are generally employed to provide this shear stability to the latex particles. Nonionic surfactants are also generally required at some level in order to provide electrolyte or chemical stability to the latex particles. This becomes critical in pigmented formulations when the emulsion must be stable to the addition of cations and must remain stable for extended periods of time. In general, both types of surfactant are required to achieve optimal emulsion stability.

Ethox Chemicals E-Sperse® 700-series surfactants are listed below:

Product	% Active	Appearance	Performance Benefits
E-Sperse® 700 (POE 40 DSP)	70	Yellow Liquid	• Nonionic • Excellent chemical stability • Smaller particle size emulsions compared to octylphenol ethoxylates
E-Sperse® 701 (POE 40 DSP sulfate)	30	Yellow Liquid	• Anionic, ammonium salt • Excellent mechanical stability and low coagulum • Small particle size
E-Sperse® 702 (POE 20 DSP sulfate)	50	Yellow Liquid	• Anionic, sodium sulfate salt • Excellent mechanical stability and low coagulum in all Acrylic and Styrene/Acrylic formulations • Small particle size
E-Sperse® 703 (POE 20 DSP)	100	Yellow Liquid	• Nonionic • Excellent chemical stability • Smaller particle size emulsions compared to octylphenol ethoxylates
E-Sperse® 704 (POE 20 DSP sulfate)	30	Yellow Liquid	• Anionic, ammonium sulfate salt • Excellent mechanical stability and low coagulum in all Acrylic and Styrene/Acrylic formulations • Small particle size

E-SPERSE®

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In addition, the type and structure of a surfactant can have a dramatic effect on other emulsion properties such as particle size, particle size distribution, and viscosity. Small particle size is highly desirable in both pigmented and clear formulations where a high film gloss is required in the final application.

The hydrophobe of the E-Sperse® 700 series products is distyrenated phenol (DSP). This hydrophobe has excellent affinity for styrene-containing latexes and for many pigments since they contain aromatic groups. This can allow for synergies when E-Sperse® DSP-based surfactants are used both in the pigment grind and in the latex. DSP is not classified as an APE surfactant and can thus deliver APE-type performance without the regulatory restrictions.

The nonionic surfactants, E-Sperse® 700 and 703, vary in their ethoxylation level and thus their hydrophile-lipophile balance or HLB. Matching the HLB of the emulsifier to the monomers and to the polymer is critical for optimal emulsion properties. The choice of the proper one for your emulsion polymer system can best be determined by experimentation. E-Sperse® 700 and 703 nonionic polymerization surfactants may also be used in conjunction with other commonly utilized nonionic or anionic surfactants to produce smaller particle size emulsions. The E-Sperse® series emulsifiers are much lower foaming than traditional alkylphenol ethoxylates so lower levels of defoamers are necessary in the polymerization process.

Ethox E-Sperse® 701 and 702 anionic polymerization surfactants in combination with nonionic emulsifiers produce low particle size dispersions with low coagulum levels and excellent mechanical and electrolyte stability. The use of anionic E-Sperse® 702 along with the nonionic E-Sperse® 700 produced the best combination of properties, better than non-DSP-based emulsifiers in the latex formulations below.

REPRESENTATIVE FORMULATIONS

All-Acrylic Latex Formulations (46% Solids)

Emulsion **A** was synthesized utilizing an anionic/nonionic surfactant composition of E-Sperse® 702 and E-Sperse® 700. Emulsion **B** was synthesized utilizing a standard surfactant composition of sodium dodecylbenzene sulfonate (SDBS) and ethoxylated octylphenol (POE 40). Emulsion **C** was synthesized utilizing SDBS as the anionic surfactant, but with the nonionic octylphenol (POE 40) replaced with E-Sperse® 700. All formulations were adjusted for the differences in solids content of the surfactants and contain the same effective surfactant levels. Substitution of the standard nonionic surfactant in emulsion **B** with E-Sperse® 700 (Emulsion **C**) results in a significantly lower particle size and polydispersity. Replacement of both of the standard surfactants with the E-Sperse® 702/700 combination (emulsion **A**) yields an emulsion with low coagulum, excellent mechanical and chemical stability, and low particle size and polydispersity compared to the standard surfactant formulation

B or the partial replacement emulsion **C**.

Ingredients	**Weight (g)**	**Emulsion**		
		A	**B**	**C**
Deionized water	687.0			
Surfactant Blend				
E-Sperse® 702 (50% Solids)			33.0	–
SDBS (22% Solids)		–	72.0	72.0
E-Sperse® 700 (100% Solids)		15.0	–	15.0
Octylphenol (POE 40)		–	18.7	–
Methyl Methacrylate	333.0			
Butyl Acrylate	333.0			
Methacrylic Acid	6.0			
Potassium Persulfate	5.0			
Deionized Water	100.0			
Ferrous sulfate	trace			
Ammonium Hydroxide	4.0			
Deionized Water	20.0			

Procedure

1. Deionized water (687 g) and the surfactants were charged to a 1500 mL reaction kettle equipped with a four-blade stainless steel stirrer, nitrogen inlet and reflux condenser. The reaction kettle was heated to 65 C and then 10% of the catalyst solution and 10% of the monomer mixture were added to the reaction flask. A trace of ferrous sulfate was then added.

2. After initiation, the remaining monomer and catalyst were added over a 1.5-2 hr period. The rate of addition was such that the temperature of the reaction mixture was maintained at 70-75 C.
3. After the addition was complete, the reaction mixture was held at 70 C for an additional 30 minutes. The emulsion was then cooled to 38-40 C and neutralized with ammonia to a pH of 8-9. The emulsion was then filtered through a 150-micron filter bag and the amount of coagulum determined.

Emulsion Properties

	A	B	C
Solids	46.2	46.0	46.0
pH	8.7	8.5	8.3
Coagulum	< 0.05%	0.1%	< 0.1%
Viscosity*	430	55	240
Mean Particle Size (nm)	112.9	220.0	105.0
Polydispersity Index	0.124	0.309	0.166
Mechanical Stability	Good	Good	Good
Chemical Stability**	Good	Poor	Moderate

* #2 spindle, 30 rpm

** 1M CaCl2

Styrene Acrylic Latex Formulations (39% Solids)

A series of styrene-acrylic emulsions were synthesized utilizing Ethox E-Sperse® 702 and a C12-C14 fatty Alcohol (POE 15) ammonium sulfate as the anionic surfactants; E-Sperse® 700 and octylphenol (POE 40) were utilized as the nonionic surfactants. The Ethox surfactants again demonstrated their utility, yielding small particle size emulsions with low coagulum levels and exhibiting excellent mechanical and chemical stability. The positive effect on particle size and polydispersity was again observed when octylphenol (POE 40) was replaced with the equivalent amount of E-Sperse® 700 (Emulsion C).

Ingredients	Weight(g)	A	B	C
Deionized water	687.0			
Surfactant Blend				
E-Sperse® 702 (50% Solids)		24.0	–	–
C12-14 Alcohol (POE 15) ammonium sulfate (30% Solids)		–	40.0	40.0
E-Sperse® 700 (100% Solids)		7.9	–	7.9
Octylphenol (POE 40) (80% Solids)		–	9.8	–
Styrene	288.0			
Ethyl Acrylate	210.0			
Methacrylic Acid	26.0			
Potassium persulfate	5.0			
Deionized water	100.0			
Ferrous sulfate	trace			
Ammonium hydroxide	8.0			
Deionized Water	20.0			

Procedure

1. 687 g Deionized water and the surfactants were charged to a 1500 mL reaction kettle equipped with a four-blade stainless steel stirrer, nitrogen inlet and reflux condenser. The reaction kettle was heated to 65 C and then 10% of the catalyst solution and 10% of the monomer mixture were added to the reaction flask. A trace of ferrous sulfate was then added.
2. After initiation, the temperature was raised to 80 C and the remainders of the monomer mixture and catalyst solution were added over 4 hours. The temperature was maintained at 80 C during the addition.
3. After addition was complete, the reaction mixture was held at 80 C for an additional 30 min. The emulsion was then cooled to 38 - 40 C and neutralized with ammonia to a pH of 8-9. The emulsion was then filtered through a 150-micron filter bag and the amount of coagulum determined.

Emulsion Properties

	A	B	C
Solids	39.0	39.2	39.4
pH	8.8	8.6	8.7
Coagulum	< 0.2%	< 0.2%	< 0.2%
Viscosity*	26	14	20
Mean Particle Size(nm)	108.8	127.7	79.5
Polydispersity Index	0.205	0.254	0.094
Mechanical Stability	Good	Good	Good
Chemical Stability**	Good	Good	Good

* #2 spindle, 30 rpm

** 1M CaCL2

Soft Acrylic Latex Formulations (46% Solids)

In this formulation Emulsion **A** was synthesized utilizing an anionic/nonionic surfactant composition of Ethox E-Sperse® 702 and 700. Emulsion **B** was synthesized utilizing a standard surfactant composition of nonylphenol (POE 30) ammonium sulfate and octylphenol (POE 40). Emulsion **C** was synthesized utilizing nonylphenol (POE 30) ammonium sulfate as the anionic surfactant but with the octylphenol (POE 40) again replaced with Ethox E-Sperse® 700. All formulations were adjusted for the differences in solids content of the surfactants and contain the same effective surfactant levels. The Ethox E-Sperse® 702/700 combination again yielded an emulsion with a low coagulum level, excellent chemical and mechanical stability, and low particle size. Again, replacement of the octylphenol (POE 40) with Ethox E-Sperse® 700 in this formulation (Emulsion **C**) yielded an emulsion with lower average particle size.

Ingredients	Weight (g)	A	B	C
Deionized Water	687.0			
Surfactant Blend				
E-Sperse® 702 (50% Solids)		50.0	–	–
Nonylphenol (POE 30) Ammonium sulfate (30% Solids)		–	72.0	72.0
E-Sperse® 700 (100% Solids)		15.0	–	15.0
Octylphenol (POE 40) (80% Solids)		–	18.7	–
Methyl Methacrylate	134.4			
Butyl Acrylate	532.0			
Methacrylic Acid	6.0			
Potassium Persulfate	5.0			
Deionized Water	100.0			
Ferrous sulfate	trace			
Ammonium Hydroxide	4.0			
Deionized Water	20.0			

Procedure

1. 687 g deionized water and the surfactants were charged to a 1500 mL reaction kettle equipped with a four-blade stainless steel stirrer, nitrogen inlet and reflux condenser. The reaction kettle was heated to 65 C and then 10% of the catalyst solution and 10% of the monomer mixture were added to the reaction flask. A trace of ferrous sulfate was then added.
2. After initiation, the remaining monomer and catalyst were added over a 1.5 - 2 hr period. The rate of addition was such that the temperature of the reaction mixture was maintained at 70-75 C.
3. After addition was complete, the reaction mixture was held at 70 C for an additional 30 min. The emulsion was then cooled to 38 - 40 C and neutralized with ammonia to a pH of 8-9. The emulsion was then filtered through a 150-micron filter bag and the amount of coagulum determined.

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Emulsion Properties	A	B	C
Solids	46.0	46.0	46.0
pH	8.5	8.8	8.3
Coagulum	< 0.1%	0.1%	< 0.1%
Viscosity*	140	110	280
Mean Particle Size(nm)	125.7	131.2	116.4
Polydispersity Index	0.032	0.040	0.041
Mechanical Stability	Good	Good	Good
Chemical Stability**	Good	Good	Good

* #2 spindle, 30 rpm

** 1M CaCL2

TECHNICAL CONTACT

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