Emulsifiers for Emulsion Polymerization

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The synthetic resins to be used in paints or adhesives have currently been shifted from solvent-based to water-based (emulsion) products in various fields to reduce the impact on the environment, taking into account the issues caused by volatile organic compounds (VOCs), such as health hazards and air pollution. In recent years, measures are required to be taken to solve Sustainable Development Goals (SDGs) and other environmental and social problems and thus the trend toward water-based paints has been accelerated. The global market for emulsion-based products is expected to grow by 2 to 4 percent per year on a price basis.[1] The surfactants called emulsifiers for emulsion polymerization (subsequently referred to as emulsifiers) play an important role in the emulsion polymerization method, one of the manufacturing processes of resin emulsions. This type of emulsifier will be discussed in this article.

Roles of Emulsifiers in Emulsion Polymerization

Emulsion polymerization refers to a technique in which water-insoluble monomers are emulsified and dispersed by stirring in water to induce radical polymerization. This technique is characterized by easily obtainable polymers with a high degree of polymerization, easy-to-control reaction temperature, and rapid reaction due to the micellar reaction field used.

Emulsion polymerization proceeds in the following order[2] **(Figure 1)**. <1> First, the emulsifier dissolved in water forms micelles about 5 nm in diameter. <2> Monomers, when added, are either taken into the micelles and solubilized or else form monomer oil droplets several µm in diameter without being incorporated into the micelles. <3> The initiator forms free radicals which enter the micelles and initiate polymerization. <4> Monomer diffuses from the monomer oil droplets into the micelles, thus allowing these particles to grow. <5> The polymerization process is completed when all monomers provided from the monomer oil droplets to the particles have been polymerized.

The role of emulsifiers changes along the course of this process. The emulsifier used is required to form micelles and solubilize monomers in the early stage; to emulsify monomers and oligomers in the early to middle stages; and to diffuse the emerging and growing polymer particles in a stable manner in the middle to late stages. Thus, emulsifiers perform key functions through the whole process.

Sanyo Chemical's Emulsifiers for Emulsion Polymerization

Table 1 lists the structures and features of our emulsifiers. The products are classified into non-ionic and anionic types. Both types have their own characteristics with respect to emulsifiability, dispersion stability, and particle size, and they are selected depending on the purpose. They are also used in combination on many occasions.

In the past polyoxyethylene alkylphenyl ether (APE) and its sulfate ester salt were commonly used as emulsifiers in terms of performance and cost. APE-based emulsifiers are considered superior in performance because they contain limited numbers of unreacted alkylphenols and APEs with a low number of moles added, which adversely affect their capability.

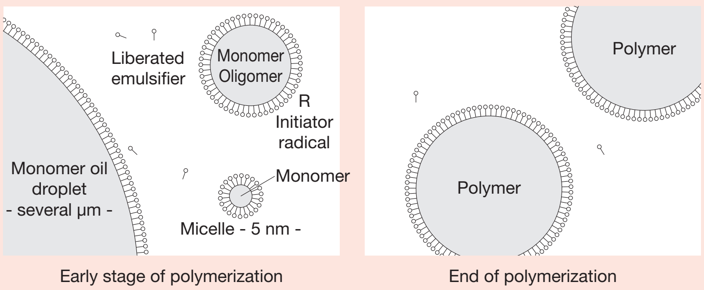

Figure 1 Conceptual diagram of emulsion polymerization

Table 1 Sanyo Chemical's emulsifiers for emulsion polymerization

Reactivity	Ionicity	Product name	Structure	Feature
Non-reactive	Non-ionic	EMULMIN Series	Polyoxyethylene alkyl ether	Has good biodegradability.
		NAROACTY CL Series	Polyoxyalkylene alkyl ether	Has a performance comparable to that of alkylphenyl ether-based products
	Anionic	ELEMINOL CLS-20	Polyoxyalkylene alkyl ether sulfate ester ammonium	Has a performance comparable to that of alkylphenyl ether-based products
		ELEMINOL NS-5S	Polyoxyethylene lauryl ether sulfate ester sodium	Has good stability against polyvalent ions.
		SANDET ONA	2-Ethylhexyl sulfate ester sodium	Suitable for the emulsion polymerization of an emulsion with large particle size.
		SANMORIN OT-70	Sodium dioctyl sulfosuccinate	Offers permeability and leveling property.
Reactive	Anionic	ELEMINOL JS-20	CH_2-COOR / $NaO_3SCHCOOCH_2CH=CH_2$ *R: Alkyl group	Has an excellent copolymerizability with acrylic monomers. Produces an emulsion with good mechanical and chemical stability.
		ELEMINOL RS-3000	CH_3 / $CH_2=C-COO(AO)_nSO_3Na$ *AO: Alkylene oxide	Has an excellent copolymerizability with styrene/acrylic monomers. Produces an emulsion with good mechanical and chemical stability.

When you are interested in using our products, please make an inquiry to our sales offices. Be sure to read beforehand the relevant "Safety Data Sheet" (SDS). It is user's responsibility to evaluate safety and suitability for the purpose of use.

However, since APE-based emulsifiers were suspected of being "endocrine disrupting chemicals," they have been replaced by polyoxyalkylene alkyl ether (AE)-based emulsifiers to reduce risks to the environment. APE and AE are produced by adding alkylene oxides such as ethylene oxide (EO) to phenolic or alcohol groups. The number of moles added and its distribution affect greatly the balance between hydrophilicity and hydrophobicity, a determinant of the performance of an emulsifier. Conventional AE-based emulsifiers contain a significant amount of unreacted alcohols and AEs with a low number of moles added because the EO addition reaction to alcohol groups does not proceed selectively as to phenolic groups. Sanyo Chemical has launched the "NAROACTY CL" product line in which the content of these undesirable components has been reduced by our proprietary alkylene oxide addition polymerization technology, even though these products remain AE-based ones. The distribution of added moles for the "NAROACTY CL" Series is narrower than that of conventional AE-based emulsifiers and is equivalent to that of APE-based products. Accordingly, as shown in **Figures 2** and **3**, the lineup is superior in emulsifiability to conventional AE-based chemicals and is equal to or better than APE-based ones. Likewise, we have also

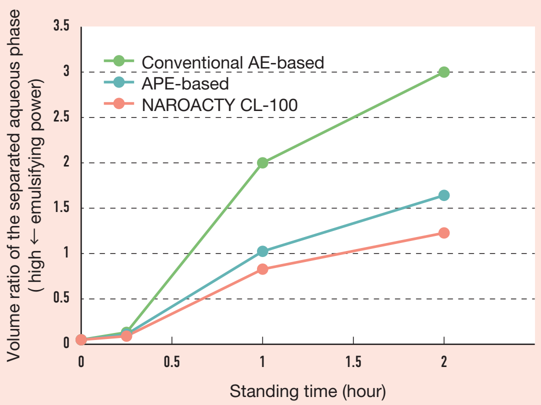

Figure 2 Emulsifying power for butyl acrylate

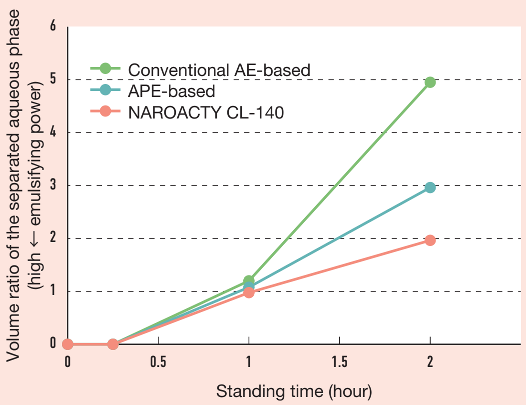

Figure 3 Emulsifying power for styrene

<Test method> Into a 30-mL glass bottle were placed 10 g of a 5% by mass aqueous solution of an emulsifier and 10 g of monomers, and the solution was allowed to stand after being stirred at 600 rpm for 15 minutes with a magnetic stirrer. The height of the separated aqueous phase was measured at specified time intervals, and the measured value was converted to the volume ratio of the separated aqueous phase relative to the height (= 1) for polyoxyethylene alkylphenyl ether after 1 hour.

A smaller volume ratio of the separated aqueous phase indicates better emulsifiability.

- Conventional AE-based: Polyoxyethylene alkyl ether (EO 10 moles)
- APE-based: Polyoxyethylene alkylphenyl ether (EO 10 moles)

developed anion-based emulsifiers, taking advantage of the above-mentioned addition polymerization technique. Sulfate ester salts have been lined up as “ELEMINOL CLS-20” and “ELEMINOL NS-5S,” whose emulsifiability is equal or superior to APE-based sulfate ester salts. As an example, **Table 2** presents the performance of “ELEMINOL CLS-20” in comparison with others. As can be seen from the table, “ELEMINOL CLS-20” is equivalent or better in emulsion polymerizability and emulsion properties when compared with APE- and AE-based sulfate ester salts.

Emulsifier-Induced Side Effects and the Development of Reactive Emulsifiers

Although emulsifiers play a critical role in producing resin emulsions, emulsifier migration can be a significant downside to the shift from solvent- to water-based products. While emulsifiers are generally attracted to the polymer (resin), any free, unbound portion may cause emulsion foaming or faulty coating. In addition, emulsifier molecules may migrate to the surface (interface), thereby increasing water absorption (i.e., whitening) or inhibiting adhesion to the substrate. Reactive emulsifiers have been developed to mitigate these side effects. This type of emulsifier contains radical polymerizable unsaturated double bonds which react with monomers. Reactive emulsifiers have excellent emulsifying properties in an equal or superior level to conventional non-reactive emulsifiers and, after copolymerization with monomers, they chemically bond to the surfaces of resin particles, thus imparting dispersion stability. Since such emulsifiers are incorporated into resin particles, the amount of free emulsifiers is so small that the extent of foaming can be reduced. Furthermore, whitening after drying can be suppressed, as can the inhibition of adhesion to the substrate.

Sanyo Chemical’s Reactive Emulsifiers

Our company has developed “ELEMINOL JS-20” (polymerizable group: allyl group) and “ELEMINOL RS-3000” (methacrylic group) as reactive emulsifiers. Both are superior in copolymerizability with acrylic monomers; “ELEMINOL RS-3000” is also excellent in copolymerizability with styrene-based monomers. **Table 3** provides the results of the comparison with DBS (Sodium dodecylbenzenesulfonate), a non-reactive emulsifier for which foaming is seen less commonly. Both “ELEMINOL JS-20” and “ELEMINOL RS-3000” show an equivalent or better emulsion polymerizability compared with DBS. Their emulsion properties have been improved, as have dry coating properties. “ELEMINOL JS-20” also features less yellowing of the resultant coating even under ignition drying conditions **(Figure 4)**.

Development of New Reactive Emulsifiers

Reactive emulsifiers have been appreciated and thus adopted increasingly not only in Japan but also overseas (especially in China). Resin emulsions are required to deliver higher performance in terms of durability and design although some newer products show the same performance as solvent-based ones. The resin after drying may suffer whitening, like a white fog or

Table 2 Results of the emulsion polymerization test with “ELEMINOL CLS-20”

Monomer used		Methyl methacrylate/butyl acrylate/acrylic acid (49:49:2 by mass)		
Emulsifier		ELEMINOL CLS-20*1	Conventional AE-based sulfate*2	APE-based sulfate*3
Emulsion polymerizability	Emulsion residue on evaporation (% by mass)	50.7	49.3	50.4
	Monomer polymerization conversion rate (% by mass)	99.2	99.0	99.1
	Amount of aggregates (% by mass)	0.1	0.2	0.1
Emulsion properties	Viscosity (mPa·s)	1,380	3,250	1,550
	Particle size (μm)	0.10	0.15	0.11
	Height of bubbles (mm)	72 (○)	90 (×)	77 (△)

○:Low △: Moderate ×: High
*1: Polyoxyethylene alkyl ether sulfate ester salt produced by our proprietary technology
*2: Polyoxyethylene alkyl ether sulfate ester salt
*3: Polyoxyethylene alkylphenyl ether sulfate ester salt

Table 3 Results of the emulsion polymerization test with our reactive emulsifiers and the dry coating performance evaluation

Monomer used		Methyl methacrylate/butyl acrylate (55:45 by mass)		Styrene/butyl acrylate/methacrylic acid (48/48/4 by mass)	
Emulsifier		ELEMINOL JS-20	(Comparison) DBS	ELEMINOL RS-3000	(Comparison) DBS
Emulsion properties	Viscosity (mPa·s)	21	24	14	13
	Particle size (μm)	0.10	0.11	0.12	0.07
	Height of bubbles (mm)	40	66	34	61
	Mechanical stability	○	△	○	△
	Chemical stability	○	△	○	△
Dry coating properties	Water resistance	○	×	○	×
	Adhesion	○	△	○	△

○: Excellent △: Good ×: Poor

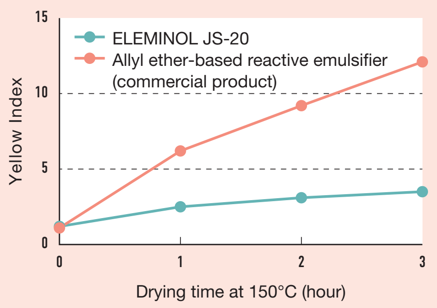

Figure 4 Yellowing behavior of the coating subjected to ignition drying

cast – one of the challenges for resin emulsions. The cause of the whitening phenomenon is said to be the effect of resin's water absorption.[3,4] The market is demanding longer service life as well as improved outdoor weathering resistance. Our company has been committing itself to developing new reactive emulsifiers with a view to further improvement in water whitening resistance. **Table 4** and **Figure 5** show the results of the evaluation of our development product. The development product maintains emulsion polymerization performance and possesses an improved water whitening resistance. To meet these high-level needs, Sanyo Chemical continues to aim for much higher performance.

Conclusion

In this article I have discussed emulsifiers used in resin emulsions. In addition to emulsifiers, the following chemical agents can also contribute to achieving better performance of resin emulsions: those that "can increase adherence to the base material," that "can improve wettability with the base material," or that "can flatten the surfaces of coating." All the needs for these chemicals will be satisfied with the aid of the "surface control technology" for which our company maintains its dominant position. Sanyo Chemical, as a surfactant manufacturer, will work toward development of chemical agents that can enhance the performance of resin emulsions.

Table 4 Results of the emulsion polymerization test of the development product (reactive emulsifier)

Emulsifier		Development product	ELEMINOL JS-20	Non-reactive emulsifier* (conventional AE-based sulfate salt)
Emulsion polymerizability	Emulsion residue on evaporation (% by mass)	40.2	40.2	40.1
	Monomer polymerization conversion rate (% by mass)	99.2	99.2	99.0
	Amount of aggregates (% by mass)	0.04	0.10	0.14
Emulsion properties	Viscosity (mPa·s)	22	23	25
	Particle size (nm)	100	102	102
	Height of bubbles (mm)	35	40	62

* Polyoxyethylene lauryl ether Na sulfate

Development product (reactive emulsifier)

ELEMINOL JS-20

Non-reactive emulsifier

Figure 5 State of coating whitening after the water resistance test

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