Surfactant selection is key to many emulsion polymer properties

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Increasingly stringent regulations on emissions of certain solvents are driving coating and adhesive manufacturers toward water-borne products featuring emulsion polymers. Although used at levels that rarely exceed 5% of a batch, based on monomer content, the surfactant component of the emulsion polymerization process has a profound effect on the properties and performance of the resulting polymer latex. The diversity of compositions and applications of emulsion polymers and the myriad surfactants available make careful surfactant selection imperative. “Partnering” of supplier and user can be a valuable selection strategy.

Diversity of product characteristics demanded also dictates having a broad range of surfactant compositions available to match individual process criteria. One manufacturer has built a family of surfactants to meet virtually any emulsion polymerization application. Enhanced by its own technology and broad experience in European markets, this supplier’s diverse product line now includes Igepal and Rhodafac nonionics (GAF Surfactants); Abex, Rhodapex and Rhodapan anionics (Alcolac); and amphoteric (Miranol). In emulsion polymerization, emphasis is on anionics and nonionics.

Vinylics, acrylates, styrenics and combination latices are used in paint, paper, textiles, floor wax and adhesive applications. Particle size plays a key role in the properties of emulsion polymer products. Such properties as viscosity, surface tension and mechanical stability are all related to particle size. In finished products, particle size affects coating rheology, gloss, pigment binding, water resistance and porosity.

Every aspect of the polymerization process can affect particle size. For example, the effect of monomer type is complex and often sensitive to other ingredients and the polymerization procedure. However, the quantity and nature of the surfactants are major factors.

In general, a surfactant molecule contains both polar (hydrophilic) and nonpolar (hydrophobic or lipophilic) groups. These enable it to form stable emulsions of monomers in water. Absorbed surfactant at the water/polymer interface prevents coalescence of the fine polymer particles being formed in the polymerization process.

Anionics have a negative charge. Examples include sodium lauryl sulfate and phosphate esters. Nonionics possess no ionic charge but derive their surfactant properties from extended polar portions within the molecule. Various ethoxylated alcohols and phenols are typical of this class. Within this group, the amount of ethoxylation directly influences such properties as viscosity, surface tension, solubility and foam generation.

Each surfactant has a unique property point at which any increase in the aqueous phase concentration of surfactant results only in the formation of new or larger micellar aggregates. This is known as its critical micelle concentration (CMC). The more efficient the surfactant, represented by a low CMC, the smaller the particle size of the emulsion. In general, the CMC values for anionics are lower than those for nonionics.

All surfactants also have the ability to stabilize latex particles as a result of being absorbed as the particle/water interface. But considerably different mechanisms are involved for ionic and nonionic types. When absorbed on the particle, anionic surfactants surround the particles with a charged double layer. Because of this charge, they exhibit sensitivity to the presence of salts in the system, with loss of stability.

Nonionic surfactants achieve stabilization by surrounding the particles with a hydrated layer of surfactant that acts as a steric barrier to particle coalescence. Because the energy required to overcome a steric barrier is considerably less than that required to overcome the coulombic barrier, nonionics are less efficient in providing latex stability. However, the hydrated layer is considerably less sensitive to electrolytes and freezing.

Combinations of anionics and nonionics take advantage of properties conferred by each. In addition, ethoxylated alcohol surfates (Rhodapex) combine many of the features of both types in one molecule.

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Typical formulations
Virtually every formulation and emulsion polymerization process that produces a latex for a specific end use involves an individual procedure and ingredient determination. Surfactant selection and evaluation can be a bewildering adventure. It can be somewhat demystified by taking advantage of information developed on products that have proven valuable in certain areas.

For a typical large-particle-size vinyl-acrylic emulsion ideal for interior/exterior trade sales coatings, a mixture of nonionic nonylphenol ethoxylation surfactants at about a 5.6% level had provided trouble-free production and extremely low levels of coagulum. This surfactant system is applicable over a broad range of monomer ratios.

Use of a combination of alkylphenol ethoxylates and ether sulfates is a key factor in producing coagulum-free, vinyl-acrylic emulsions at 65% solids. The viscosity of the polymer may be controlled by adjusting the ratio of large to small emulsion polymer particles through variation in the quantity of ether sulfate used. Also important in controlling particle size distribution are control of initiation temperature, sodium persulfate (thermal initiator) concentration and steady-state temperature.

A custom-designed anionic surfactant (Abex-18S) can be used to produce a thermosettable vinyl-acrylic. This latex can be used as solvent-resistant textile binder.

An extremely fine particle size acrylic latex with low coagulum levels can be produced using an ammonium salt of sulfated alkylphenol ethoxylates (Abex EP-120) as the surfactant. This latex, containing 85% butyl acrylate, is ideally suited for pressure-sensitive adhesives. A soft 100% acrylic copolymer suitable for pressure-sensitive applications can also be made using a dodecylphenol hydrophobe, nonionic surfactant (Igepal RC-520).

An acrylic formulation that uses a primary phosphate surfactant (Rhodafac PE-510) demonstrates corrosion resistance. When combined with corrosion-inhibiting pigments, it should produce an excellent water-borne, corrosion-inhibiting coating.

When a high wet adhesion latex paint is desired, a special monomer and anionic/nonionic surfactant system are recommended. The monomer (Sipomer WAM) is incorporated in the polymer backbone through allylic functionality. Adhesion promotion is provided through dual mechanisms: Amine functionality provides a site for interaction with anionic substrate and pigment. A ureido ring promotes interaction via high-polarity and hydrogen bonding.

Surfactants and specialty monomers for emulsion polymerization—Rhone-Poulenc Inc., Cranbury, NJ. Circle 410