Calfax® in Emulsion Polymerization

Calfax® products are alkyldiphenyl oxide disulfonic acids and their salts. Calfax® products’ excellent performance as emulsion polymerization surfactants allows for their formulation in latex applications such as synthetic rubbers, paints, coatings, and adhesives. In general, Calfax® products exhibit excellent temperature stability, with half-lives exceeding 400 days at 260°C. Because of this attribute, in recent years the Calfax® line has come to the forefront as surfactants of choice in latexes used in high temperature applications such as ink-jet inks and printer toners.

![Chemical structure of Calfax®](image)

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<thead>
<tr>
<th>NAME</th>
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<tbody>
<tr>
<td>Calfax® 6LA-70</td>
<td>Linear C6</td>
<td>H</td>
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<tr>
<td>Calfax® 10L-45</td>
<td>Linear C10</td>
<td>Na</td>
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<tr>
<td>Calfax® DB-45</td>
<td>Branched C12</td>
<td>Na</td>
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<tr>
<td>Calfax® DBA-70</td>
<td>Branched C12</td>
<td>H</td>
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<tr>
<td>Calfax® 16L-35</td>
<td>Linear C16</td>
<td>Na</td>
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As is the case with their alkylbenzene sulfonate analogs, the linear alkyl materials are considered to be biodegradable by the test criteria of the Soap and Detergent Association semi-continuous activated sludge process, while the branched alkyl compounds are not. Preliminary results suggest that none of the Calfaxes® will pass the new EC 648/2004 biodegradation standard.

**EMULSION POLYMERIZATION APPLICATIONS**

Emulsion polymerization (EP) is used in the preparation of a wide variety of polymers used in an ever-growing number of domestic and industrial applications. The technology represents one of the main industrial uses of Calfaxes® (and surfactants in general) in the world today. EP offers a number of advantages over other radical initiated polymerization processes including:

- Better heat transfer capabilities
- Lower reaction mixture viscosities
- Better particle size control
- Easier copolymer composition control

EP also offers the ability to achieve high polymerization rates and high polymer molecular weights - two factors which have an inverse relationship in “normal” polymerizations. EP reactions are run in one of three ways:

- Batch processes, where all the constituents are present at the beginning of the reaction
- Semi-batch processes, where one constituent (usually a monomer) is metered in over time
- Continuous processes where all the constituents are metered in

All three offer advantages and disadvantages, however, the last two are the most commonly used. There are four main chemical components in most EP processes. These are:

- Water
- An oil soluble monomer or monomers (vinyl monomers such as styrene, vinyl acetate and acrylic acid derivatives are the main components)
- An emulsifier (Calfax® or, more usually at present, sodium lauryl sulfate)
- A water-soluble radical initiator (persulfate or peroxide).

The product is a latex which can be used as is or dried. A solids content of 50 - 60% is the norm.
Technical Bulletin: Calfax® in EP

Given the importance of the surfactant to EP in the areas of monomer solubilization, particle nucleation and size distribution, polymerization rate and colloid or latex stability, detailed studies are somewhat lacking. Most work in the EP area requiring anionic surfactants has been undertaken using sodium lauryl sulfate (SLS). Presumably this is because SLS is effective and inexpensive. (Also, for laboratory work, pure SLS is available). Calfaxes®, however, are becoming more popular owing to their superior properties. A range of other surfactants has been used in EP, including ammonium lauryl sulfate (ALS), soaps such as potassium oleate and alkyl naphthalene sulfonates.

Calfax® products can be used in numerous EP systems, the main applications, however, are in;

- Polystyrene
- Polystyrene-butadiene (SBD)
- Polyvinyl or vinylidene chlorides (PVC)
- Polyvinyl acetate (PVA) latexes

The uniqueness of the Calfax® surfactants is based on the high charge associated with the disulfonate functionality combined with the large hydrophilic “footprint” associated with the diphenyl oxide disulfonate head group.

A study carried out at the Emulsion Polymers Institute at Lehigh University published in 1990 addressed the use of, in this case, Calfaxes® in SBD emulsion co-polymerization.

Calfax® results were compared with SLS. The papers detail the effects of the length and substitution pattern of the alkyl side chains on three important factors.

- The “efficiency” of the surfactant - defined as “the bulk concentration of the surfactant required to lower the interfacial tension (between water and the monomer) by a significant amount (20 dynes/cm).”
- The free energy of adsorption ($\Delta G_{0ads}^0$) - a measure of how strongly the surfactant adsorbs at the surface or interface.
- The critical micelle concentration (CMC) - the surfactant concentration at which micelles start to form.

The efficiency is numerated as the negative log of the concentration ($-\log C_{(n=20)}$) and is written as $pC_{20}$. Lengthening or branching the chain increases this value ($C_{16} > C_{10}$ and br. $C_{12} >$ lin. $C_{12}$). Due to the larger hydrophilic group at the surface interface, all Calfaxes® have a significantly higher efficiency than SLS (as much as a factor of 40 with br. $C_{12}$).

The strength of surface or interface adsorption similarly increases with chain length and branching. This increase is indicated by a decrease (increase in negative value) of $\Delta G_{0ads}$. The CMC decreases with chain length and branching. The CMC of the
branched C_{12} material is one tenth that of SLS. As a practical matter, in emulsion polymerization and latexes, these physical attributes of the Calfax® surfactants manifest themselves in several ways.

**Latex Stability**

Stability of a latex is important during all phases of production from the emulsion polymerization process itself through the subsequent pumping, handling, and storage of the product.

Latex stability during the polymerization process can be assessed by the amount of coagulum (waste) left in the reactor at the end of the reaction. Studies\(^1\) have shown that use of Calfax® surfactants in SBD processes result in significantly less waste formation than either SLS or LAS (1.6% for DB-45 vs. 21.9% for SLS). An order of magnitude difference was noted between LAS and the linear C_{16} Calfax®. The same order of improvement was noted between the branched C_{12} Calfax® and SLS in PVC manufacture.

The improved mechanical stability of Calfax® stabilized SBD latexes over those using SLS or LAS has been shown by the failure of the latter two to remain liquid under high shear conditions while the former showed little to no coagulation after 30 minutes. Calfax® stabilized latexes will, therefore, outperform others under pumping and handling conditions found in the industry.

Storage stability has been studied with both PVC and polystyrene latexes where Calfax® stabilization led to retention of low viscosity for more than 45 days, while similar systems stabilized with SLS or LAS set up within one week.

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Particle Size Distribution

Since the particle size and distribution of the final latex greatly affects latex performance, control over these parameters is vital.

For the most part the particle size of the polymer beads in the resultant latex will be inversely proportional to the surfactant concentration, provided that concentration is above the CMC. Generally, the end product made from latexes, whether they be coatings, foams, or materials such as synthetic rubber, require evaporation of the suspendant water. Anything that remains besides the desired polymer, including surfactant, can have deleterious effects on this end product. Thus, a more efficient surfactant with a lower CMC which requires lower concentrations to achieve the desired particle size will prove advantageous. As shown above, Calfaxes® are amongst the most efficient surfactants available. In an SBD latex, for example, a 200 nm particle size can be achieved at around one fourth the concentration of the C₁₆ Calfax® as with SLS.² All Calfaxes® produce narrow particle size distributions.

Other Advantages

Use of Calfaxes® does not result in any loss of monomer conversion from the usual high levels achieved with SLS and LAS. For the same solids contents, Calfaxes® generally produce latexes with lower viscosities and higher surface tensions than other surfactants. Finally, latexes stabilized with Calfaxes® have a higher resistance to coagulation by polyvalent metal ions than those using other materials.

To sum up, Calfax® DPOdisulfonates produce more stable latexes which are easier to handle with less surfactant for a given particle than other commonly used surfactants.