**SMA Resins: a Polymeric Surfactant for Emulsion Polymerisation**

**Presentation of SMA Resins**

SMA resins are low molecular weight copolymers of STYRENE - MALEIC ANHYDRIDE. SMA 1000, 2000, 3000 and 4000 are copolymers with a styrene / maleic anhydride ratio equal to 1/1, 2/1, 3/1 and 4/1 respectively.

The alkali salts of these copolymers in aqueous solutions (ammonium, sodium, potassium salts,...) are used as polymeric surfactants in the emulsion polymerisation process.

The alkali salts of the SMA resins are soluble in all proportions in water. They are sensitive to strong acids and can precipitate at pH below 6.

**Advantages to use SMA as a polymeric surfactant**

1) **Quality improvement of acrylic dispersions**

   **A - Low particle size - specific rheological properties**

   The particle size of these dispersions is very small, with a narrow distribution so that the rheology of the latex is well controlled. This property is evident in all coating formulations where a Newtonian behaviour is requested.

   **B - Acrylic dispersion stability**

   By using SMA resins as a polymeric surfactant in an emulsion polymerisation process, alone or in combination with other surfactants, the stability of the dispersion under different kinds of stress (chemical, high shear or freeze/thaw) is significantly improved. The presence of SMA copolymer, adsorbed at the surface of the particles of an acrylic dispersion, enhances the stability of the latex by an increase of electrostatic repulsion (See “Electrostatic stabilisation of acrylic emulsion by SMA). This advantage is very important for inks and lacquers applications where the shear stress, during the printing process, is very high (> 1 000 000 s-1).

   **C - NO VOCs - Solvent free formulation**

   By using SMA resins as a polymeric surfactant, the use of classical surfactants can be eliminated. Thus the latex synthesised is zero VOC.

   Moreover, the latex polymer emulsion can be prepared from a variety of monomers. The proportions of the various monomers are adjusted to yield polymers with the right Tg, and thus to obtain a good film formation. This gives an advantage in comparison with hard polymers for which glycol ethers and other organic solvents must be added to ensure good coalescing at ambient temperature.
Principal characteristics of the ammonium salt solutions of SMA resins

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<tr>
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<th>SMA1000H</th>
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<tbody>
<tr>
<td>Aspect</td>
<td>Yellowish, Transparent and fluid liquid</td>
<td>Yellowish, Transparent and fluid liquid</td>
<td>Yellowish, Transparent and fluid liquid</td>
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<td>Charge</td>
<td>Anionic</td>
<td>Anionic</td>
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<td>pH</td>
<td>&lt;9.5</td>
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<td>Viscosity at 30°C (mPa.s)</td>
<td>&lt;1200</td>
<td>&lt;500</td>
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2) **Higher performance of the final coating**

**A - Hardness**
Due to their high Tg (> 120°C for the base resins), the SMA resins, partially incorporated into the polymer backbone, improve the *hardness of the coating*.

**B - High heat resistance**
An overprint varnish, based on a latex synthesised in the presence of SMA resins, can show *high heat resistance properties* (no blocking during face-to-face test at 200°C, 200 kPa, 2 seconds dwell). This property is due to the high Tg of the SMA copolymers and could be applicable for different types of water based coating (inks, OPV or lacquers for example).

**C - High Gloss**
The presence of a styrene copolymer like SMA resins in the final coating formulation and the very low average particle size of latex made with SMA resins, *increases the gloss to a significantly high level* in comparison with other hard resins system or latex based on classical surfactants.

**D - Water Resistance**
The total replacement of the classical surfactant by SMA resins can *strongly enhance the water resistance of the final film*, after a drying step efficient enough to evaporate the ammonia used during the hydrolysis of the SMA resins.

3) **Better runnability during the coating process**
The presence of SMA resins into the final coating can help to *resolubilize the coating deposit*, on the printer rolls for example, after a break during the production. Due to the solubility of SMA resins in an alkaline solution, the latex can be easily resolubilised. This property is very important for ink and OPV applications but also for floor polishes formulations.

**An example of polymerisation with SMA resins**
The following formulation is just a guideline to show how an SMA resin solution can be used as a polymeric surfactant in a classical emulsion polymerisation process.

**With SMA resins as polymeric surfactant alone**

**Components**
- SMA1000 H: 65 g
- Water: 27 g
- Monomers (Styrene/acrylates): 35 g
- (NH4)2S208: 1 g
- Water: 2 g
**Emulsion polymerisation process**

SMA 1000 H resin solution and water were added to a kettle equipped with a stirrer, condenser, dropping funnel and nitrogen inlet. The mixture was heated to 85°C with stirring and the kettle was purged with nitrogen. When the reaction temperature was reached, the monomers and the initiator were added at a constant rate (3-4 hrs.) to maintain a reaction temperature of 80-85°C. When monomer addition was complete, a temperature of 85°C and stirring were maintained for 1 hour.

The resultant styrene/acrylate latex has a very low particle size (66 nm). This latex exhibits an excellent freeze/thaw, mechanical and storage stability.

This type of latex can be used for different coatings like Over Print Varnish, flexographic inks where a high gloss, good mechanical stability and resolubility is required.

**Conclusions**

The chemical structure of SMA resins induce a very specific behaviour of the alkaline solutions of these polyelectrolytes, identical to a classical anionic surfactant’s behaviour. These surface tension properties allow you to use SMA resins as a polymeric surfactant in the classical emulsion polymerisation process.

In this way, firstly a very stable dispersion with small particles size and well controlled rheological behaviour can be obtained.

Secondly the presence of SMA resins as a polymeric surfactant is displayed by the final coating properties: high thermal resistance, high gloss and hardness of the film together with good water resistance if sufficient drying conditions are provided.

Another benefit of SMA resins, in replacement of classical surfactants, is a better runnability of the coating formulations (printing inks or OPV, for example) due to an excellent resolubility of the coating deposits which reduces the machine cleaning time and ultimately saves time and money in the printing process.