Cray Valley Products
For Paper Sizing

SMA® Resins
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**Introduction**

SMA® Resins can be used in the surface sizing process of paper manufacturing to produce a product with greatly improved properties. In combination, with starch, SMA® Resins produce paper with:

- improved water resistance (low COBB values)
- greater ink resistance (high HST values)
- better printability, including for ink jet or laser printing
- lower air porosity

SMA® Resins are compatible with most sizing formulations and equipment, and bring the following benefits to the manufacture process:

- can be used on alkaline, neutral or, when alum is used at a level of at least 2 kg per ton, acidic papermaking machines
- reduces the sizing viscosity, including formulations that contain pigment dispersions
- improves drying speed
- minimizes drawbacks of alkaline internal sizing by limiting internal sizing reversion and increasing the coefficient of friction
- can reduce internal size levels to obtain a cleaner white water system with fewer deposits

**SMA® Resin Products**

SMA® Resins are a family of low molecular weight styrene-maleic anhydride copolymer products. They are available in two physical forms:

**Solid Resin**

SMA® 1000, SMA® 2000, SMA® 3000, SMA® 2625 and SMA® 17362 in flake (F grades) or powder (P grades) forms.

**Hydrolyzed To Aqueous Solutions**

As their ammonia salt solutions (SMA® 1000H, SMA® 2000H, SMA® 3000H, SMA® 2625H and SMA® 17362H) or their sodium salt solutions (SMA® 1000HNa, SMA® 2000HNa and SMA® 3000HNa).

A summary of the properties of these different grades can be found in the Sartomer Product Bulletin “SMA® Multi-Functional Resins.”

**Selection Of Starch**

Anionic, amphoteric, oxidized, or slightly cationic starches can be used with SMA® Resins, so the starch can be selected for optimal performance. Excellent results are obtained with a good film forming starch, such as a medium viscosity ethylated starch.

**SMA® Resins - Starch Formulations**

The required concentration of SMA® Resin depends mainly on the desired level of sizing, on paper absorption properties, and on the presence of aluminium sulphate. A typical composition for a surface sizing solution (solids content in wt. %) is:

- SMA® Resins: 0.2 to 2 %
- Starch: 4 to 10 %
- Water: remaining part.

It may be necessary to adjust the solids content and the SMA®/Starch ratio, depending on the viscosity and the size-press technique used.

Generally, the SMA® Resin content does not exceed 15 % of the dry starch content. The SMA® Resins content will generally be between 0.5 and 1.5 Kg per ton of paper. Thus, a 66 g/m² paper should contain only between 30 and 130 mg of SMA® Resin per square meter.

**Preparing SMA® Resin - Starch Sizing Solutions**

There are a number of options for the process to prepare SMA® Resin – Starch Solutions:

1.) You can purchase the SMA® Resin as a hydrolyzed, aqueous solution grade. The sizing solution can then be easily prepared by blending the SMA® solution with pre-digested starch. Either a H grade (ammonia salt) or a HNa grade (sodium salt) can be used, or a mixture of the two. Depending upon the drying conditions, use of the H grade can give paper with better water
resistance and sizing response (higher HST values). SMA® HNa grades generally give higher Gurley densometer values (lower porosity).

2.) You can purchase the SMA® Resin as a solid grade, hydrolyze the resin to an aqueous salt solution and then blend that solution with the starch as in Process 1. Please refer to the Sartomer Technical Bulletin “Solubilizing SMA® Resins In Water” for details on how to carry out the hydrolysis reaction.

3.) You can purchase the SMA® Resin as a solid grade and concurrently hydrolyze the resin and digest the starch in a one-step, one-reactor process. In this process, the SMA® Resin and starch are dispersed in water and base (typically ammonium or sodium hydroxide solution) is added so as to reach and maintain a pH of greater than 8.0. The process is commonly carried out at 85°C, with good agitation, and takes for 1-3 hours to effect the digestion and resin solubilization. The desired solids level can be obtained by diluting with water as long as the pH is maintained at 8.0-9.0.

Performance Evaluation

1) Water Resistance (COBB value)
Figure 1 shows that SMA® 2000H and SMA® 3000H give very good COBB values after 15 seconds, better than the two competitive resins. A pilot paper machine was used to produce the base paper which was then sized on line using a pilot size-press with aqueous solutions containing either starch (as a control) or starch + resin, then followed by drum drying.

Base paper: Hardwood/softwood = 1/1(bleached Kraft)
Clay, N°.2 = 15 %
Titanium dioxide = 0.5 %
Rosin = 0.5 %
Alum = 0.5 %
Stock pH = 4.0 - 4.5
Mean basis weight = 72 g/m²

Size press solution: Hydroxyethyl cornstarch + SMA® Resin = Total Solids = 10% resin content.

Approximate pick-up = 4.5 % of paper weight = 4% based on starch.

Figure 2 gives results with a 66 g/m² non internally sized paper, which has been surface sized using a native potatoe starch as control.

2) Ink jet printability
To evaluate the ink jet printability of papers treated with SMA® resins, the print quality of documents printed on different papers using a commercial ink jet printer was compared.
The wicking properties of black print were evaluated by printing characters on different papers. SMA® 3000 resin sized alkaline paper, internally sized with ASA, (Figure 3A) was compared to a commercial grade of premium ink jet paper (Figure 3 B). Printing of the SMA® 3000 sized paper is noticeably sharper.

Bleeding during color printing is due to a diffusion of one color ink into adjacent colors. This was evaluated by an analysis of the sharpness of composite black printing on a yellow background.

The pictures in Figure 4 compare the print quality when SMA® 3000H is applied to an alkaline paper, internally sized with AKD, with the same paper without the size-press treatment.

With SMA® 3000H, the bleeding of the color printing was reduced and a good printing quality for a ink jet application was obtained.

3) Air Porosity of Paper
A Gurley densiometer was used to test the air porosity of paper surface sized with SMA® Resins in comparison to paper sized with a competitive resin. The results summarized in Table 1 clearly indicate that SMA® Resins give paper with air porosity equal to or lower to air porosity of the competitive paper.
Conditions: Alkaline base paper, 95 kg per ton of filler, 0.454 kg per ton of AKD (internal sizing agent), 2.7 kg per ton of alum, 114 g/m² resin pick-up, or 3.18 kg per ton.

Table 1: Air porosity performance

<table>
<thead>
<tr>
<th>Resin</th>
<th>Gurley densometer (sec/100 cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMA® 1000H</td>
<td>64</td>
</tr>
<tr>
<td>SMA® 2000H</td>
<td>66</td>
</tr>
<tr>
<td>SMA® 3000H</td>
<td>67</td>
</tr>
<tr>
<td>Competitor Resin</td>
<td>68</td>
</tr>
</tbody>
</table>

4) Coefficient of friction (COF)

One of the major advantages of using SMA® sizing formulations in alkaline papermaking is that they increase the coefficient of friction. The COF properties of paper made with a variety of sizing agent are compared in Table 2. While all surface sizing agents increase the COF relative to the non-sized control, not all formulations improve the COF relative to sizing with ethylated starch. The sizing formulations that contain SMA® H grades provide the largest increases in COF compared to those which contain SMA® HNa grades or other resins, such as acrylates or polyurthanes.

Table 2: Effects of various surface sizing agents on coefficient of friction (COF)

<table>
<thead>
<tr>
<th>Surface Size</th>
<th>COF (unitless)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.59 kg per ton size, medium viscosity ethylated starch</td>
</tr>
<tr>
<td>None</td>
<td>0.36</td>
</tr>
<tr>
<td>Ethylated Starch only</td>
<td>0.44</td>
</tr>
<tr>
<td>SAA</td>
<td>0.43</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>0.39</td>
</tr>
<tr>
<td>SMA® 3000HNa</td>
<td>0.40</td>
</tr>
<tr>
<td>SMA® 1000H</td>
<td>0.46</td>
</tr>
<tr>
<td>SMA® 2000H</td>
<td>0.49</td>
</tr>
<tr>
<td>SMA® 3000H</td>
<td>0.48</td>
</tr>
<tr>
<td>Competitor Resin</td>
<td>0.45</td>
</tr>
</tbody>
</table>

with the SMA® Resin, giving a much higher improvement in COF compared to an ethylated starch sizing.

Conditions for this study were alkaline base paper, 136 kg per ton of calcium carbonate, 1.13 kg per ton of AKD, 2.27 kg per ton of alum, 75 g/m², surface size pick-up 1.59 kg per ton.

Conclusions

SMA® Resins are versatile products, either ready for use in ammonium or sodium salt aqueous form (SMA® H or HNa), or available in anhydrous form (SMA® P or F).

At an average concentration of 0.5 to 2 kg per ton of paper, SMA® Resins allow the manufacturer to adjust various properties in order to obtain the required performance:

SMA® Resins will help overcome drawbacks of alkaline internal sizing, and also reduce internal size level thus resulting in the possibility of reducing the total sizing cost.

The different combination of SMA® grades and types of starches provide a range of possible sizing formulations which can be adjusted to give optimal performance for a particular desired property, be it water resistance, ink resistance, porosity or COF.
**Introduction**

The paper industry is always balancing the often competing objectives of improving quality and reducing costs. Surface treatment of the paper is a reliable and economical way to improve the quality of paper.

Starcote® dispersions can be used as surface treatment agents to improve various surface properties of paper, such as printability, hydrophobicity, toner adhesion, reduction of linting and curling.

**What are Starcote® Dispersions**

Starcote® dispersions are core-shell styrene acrylic dispersions with a low particle size. The core is made with hydrophobic monomers (styrene, acrylic esters) and the shell is made with low molecular weight SMA® Resin. The structure is described in Figure 1. As shown in this figure, the majority of the SMA® Resin introduced in the polymerization is chemically anchored to the particles while a small fraction remains free in the aqueous phase. This unique structure permits Starcote® dispersions to take advantage of the best properties of both aqueous SMA® Resins solutions and aqueous polymeric dispersions. The SMA® Resins give a high affinity to the paper fibers and excellent functionality to reactive with inorganic crosslinkers. However, because the SMA® Resins are used to produce polymeric dispersions, the resulting formulation provides a high solid content, low foaming, and good film forming properties. The hydrophobic properties of Starcote® dispersions come from both SMA® Resins and the hydrophobic monomers used in the polymerization.

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Cray Valley offers 2 grades of Starcote® dispersions with the following characteristics:

<table>
<thead>
<tr>
<th></th>
<th>STARCOTE® 6100</th>
<th>STARCOTE® 7000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid content (%)</td>
<td>23</td>
<td>40</td>
</tr>
<tr>
<td>pH</td>
<td>&lt; 9.5</td>
<td>&lt; 9.5</td>
</tr>
<tr>
<td>Viscosity (mPas)</td>
<td>&lt; 100</td>
<td>&lt; 1000</td>
</tr>
<tr>
<td>Freezing-thaw stability</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Mechanical stability</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

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![Figure 1: Starcote® Structure](image)
How to use Starcote® Dispersions

Starcote® dispersions can be used in surface sizing in combination with starch (and optionally with an optical brightener) to increase water and ink resistances as well as printability and toner adhesion. A typical sizing formulation contains 2 to 10% of the dry sizing agent relative to the dry starch content. The level of Starcote® required is linked to the level of internal sizing agent used in the sheet.

Starcote® can also be used in pigmented sizing or coating formulations to increase the water resistance. The level of Starcote® needs to be optimized according to the formulation and level of performance expected. Starcote® dispersions have very good compatibility with all the components used in the coatings formulation. They help to disperse the pigments and to reduce the tackiness of the coating due to their hard shell structure.

Some of these properties are described in the following examples or/and industrial case studies.

Performance of Starcote® Dispersions

Water resistance

One of the main functions of a surface sizing agent is to increase the water resistance of paper or paper board, especially if the paper or paper board is produced with a low level or no internal sizing agent. Water resistance is classically measured with a Cobb test. The water resistance improvement available by using Starcote dispersions is described in the three following examples:

Example 1:
A pilot trial was made with a wood free fine paper, sized with 1 Kg/ton of ASA and which contained 13% CaCO₃. The surface sizing agents were introduced in an 8% starch solution. The size pick up was 1 Kg dry of surface sizing agent / ton of paper with a classical size press.

Even at this low pick up, Starcote® dispersions give very good sizing properties, Figure above. Water contact angle measurements at the surface of the treated papers, another way to demonstrate the hydrophobicity of the treated surface, (Figure below for Starcote® 6100).
Example 2: This example employs a pigmented sizing formulation, containing:
- 100 parts of talc
- 100 parts of starch
- 0 or 10 part of surface sizing agent

The final concentration of the pigmented sizing formulation was about 25% and the formulation was applied on one side of an unsized alkaline fine paper with a film press equipment. The pick up was 5 g/m², which corresponds to 3 Kg/ton of dry surface sizing agent.

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>Starch only</th>
<th>Starcote® 6100</th>
<th>Competitive styrene acrylics dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobb₆₀ (g/m²)</td>
<td>100</td>
<td>24</td>
<td>30</td>
</tr>
</tbody>
</table>

This pigmented surface treatment efficiently fills the voids of the paper surface and increases the water resistance. Thus, it will reduce the penetration of subsequent coating as well as provide good adhesion between the paper and this further coating. This last property is mainly due to the reactivity of SMA® molecule.

**Ink jet printability**
Surface sizing agents are critical components to improve the ink jet printability of paper. It controls the ink absorption of the paper, especially reducing the horizontal penetration of the ink as it can be observed in the following wicking test example:

- **paper before size-press treatment**
- **paper treated with STARCOTE**

Providing additional ink resistance to the paper, Starcote® dispersions also improve the bleed through of the paper, as well as the optical density of the printed image.

**Toner adhesion**
Paper performance in copier and laser printer is influenced by surface sizing agents. The toner adhesion of papers treated with Starcote® is improved, thanks to the chemical affinity of the product to the toner particles.

The following Figure shows the surface of an AKD sized fine paper after a laser printing and a tape peel test. The presence of Starcote® greatly improves the fixation of toner to the paper surface.
Industrial Case Studies:

1.) On A Test Liner to improve COBB test and final ink jet printability
On a two-layer (Kraft and Wood free pulp) test liner machine, equipped with a Film-press (SYM-SIZER) which runs at 500 m/min, a combination of Starcote® and corn starch (starch @ 13% + Starcote® @ 1% in size-press solution) is applied on a test liner (140 g/m²) to improve Cobb tests and ink-jet printability. The results obtained (Cobb 30 min < 100 g/m² and Cobb 1 min < 30 g/m²) allow this test liner to be used for a final high quality corrugated board for packaging application. This packaging corrugated board is printed with flexographic or ink-jet printer.

2.) On a base paper as A Pre-coating treatment for a final wet-strength label paper
On a paper machine, equipped with a gate-roll system, a combination of Starcote®, tapioca starch (17%) and additives is applied as a pre-coating treatment to improve an optimal coating deposition made off-line. A final good sizing level (Cobb 1 min < 20 g/m²) is obtained even if a high viscosity starch solution is used according to the Gate-Roll system requirements.

3.) On Liner board made with recycled paper to improve water resistance
Starcote® is used in a pigmented sizing formulation, with Kaolin as a main component and a mixture of SBR and starch as a binder. The level of Starcote® is adjusted in order to obtain a Cobb 1 min < 20 g/m² on board with high grammage (200 to 350 g/m²). Starcote® exhibits also a very good mechanical stability on the high shear filter present in this paper mill.

Conclusions
The sizing properties of Starcote® are very efficient on all types of paper (wood free alkaline paper, internally sized paper, non sized paper, mechanical paper and waste de-inked paper) and all kinds of surface sizing equipment (size-press, gate roll and film press).

Used in conjunction with starch, Starcote® improves the ink jet printability as well as the toner adhesion of treated papers.

In addition to the standard surface sizing applications, Starcote® dispersions can also be used in pigmented sizing or coating formulations to improve the water resistance. Finally, Starcote® can act as a barrier coating to improve coating holdout.
The addition of aqueous solutions of the sodium or ammonium salts of SMA® Resins to paper sizing formulations can, under certain conditions, lead to the formation of a small amount of foam. This foaming tendency is due to the surface tension reducing effect of SMA® Resins, and is most likely to occur under high shear operations such as circulation of the sizing solution through pumps, lines or the size-press. To solve the foaming issue, we recommend to add a selected anti-foam agent to the resin solution during the surface sizing introduction.

### Anti-foam Agent Addition - Recommended Procedure.

A standard laboratory test (see details in the Appendix) to evaluate the efficiency of a large number of anti-foam agents in preventing SMA® related foaming. While it may be necessary to adapt the anti-foamer quantity to the specific use conditions (amount of starch, size-press design, speed and time of the solution circulation, temperature, quality of the water, etc...), in general, the optimal amount of anti-foamer is 0.1 to 0.5% of the weight of the surface sizing agent introduced in the formulation.

Within this optimal concentration range, the recommended products listed below do not change the sizing performances on a classical writing/printing paper substrate.

For your benefit, we include below not only a list of recommended anti-foam agents, but also a second list of anti-foam agents which we tested and found to be ineffective in eliminating foaming and which we therefore do not recommend. These lists are by no means exhaustive, and if you wish to use a different anti-foam agent, our laboratory is ready to help you in its evaluation.

#### Recommended Anti-Foam Agents:

- ANTAPHRON NE 4561 (Huls AG)
- HTI 9074 (Hopton Technology)
- NOPCO NXZ & 8034* (Henkel)
- FOAMASTER 340 (Henkel)
- BEVALOID 2540 & 1428/01* (Bevaloid)
- DISCOTECH 5517 & 5980* (Callaway)
- RESPUMIT NF NEW (Bayer Corp.)
- VIRCO SP - 952 (Virkler)

* These anti-foam agents are partially miscible in the sizing solution, and are most effectively used when added just before the solution enters the size-press.

#### Non-Recommended Anti-Foam Agents:

- NOPCO 267A (Henkel)
- FOAMASTER C14 & MPE 847 (Henkel)
- ETINGAL L & S (BASF)
- PARACUM 21/012, 44 PDI, 81/168 & 24SW (Dr. Kolb AG)
- Triton DF 12 (Rohm & Haas)
Appendix. Laboratory Evaluation Of SMA® Foaming Tendency

We have used a laboratory test to simulate the high shear conditions encountered during paper sizing applications. This allows us to evaluate the tendency of SMA® to cause foaming and the efficiency of anti-foam agents to reduce this foaming.

The test is based upon a standard model of a recycle circuit (AFNOR T 73-412), with the following procedure:

1. Load apparatus with 250 ml of solution (SMA® + anti-foam agent)
2. Pump solution through a high shear circuit for 2 min.
3. Stop pump and measure the initial volume of foam (V₀)
4. 1 Min. after stopping pump, measure volume of foam (V₁)
5. 3 Min. after stopping pump, measure volume of foam (V₂).
6. 5 Min. after stopping pump, measure volume of foam (V₃).

Using this test, we first measure the volume (V₀) of foam generated by dynamic circulation of a SMA® solution through a pump and high shear circuit, and then measure the stability of this foam over a 5 min. period (V₁, V₂ and V₃).

Typical results obtained using SMA® 3000 solutions are in the following Table:

<table>
<thead>
<tr>
<th>Product / Vol. of foam</th>
<th>V₀</th>
<th>V₁</th>
<th>V₂</th>
<th>V₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMA® 3000H (1%)</td>
<td>200 ml</td>
<td>180 ml</td>
<td>160 ml</td>
<td>150 ml</td>
</tr>
<tr>
<td>SMA® 3000H + starch</td>
<td>220 ml</td>
<td>210 ml</td>
<td>185 ml</td>
<td>160 ml</td>
</tr>
<tr>
<td>SMA® 3000H/AF</td>
<td>5 ml</td>
<td>5 ml</td>
<td>0 ml</td>
<td>0 ml</td>
</tr>
<tr>
<td>SMA® 3000H + NOPCO 8034</td>
<td>10 ml</td>
<td>5 ml</td>
<td>0 ml</td>
<td>0 ml</td>
</tr>
</tbody>
</table>

SMA® 2625H and SMA® 3000HNa solutions show the same foaming and foam stability properties when subjected to the these test conditions.

The presence of starch, as in size-press formulations, slightly increases both the foam volume and its stability. Therefore, the concentration of anti-foam agent in starch-containing formulations is generally nearer to the high recommended level (to 0.5%).

These results confirm that SMA® solutions have a tendency to foam, and that this foam is stable. Due to the stability of the foam, the most effective approach to eliminating foaming issues is to prevent foam formation by using one or both of the methods described in this brochure.
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