**Dispersing Carbon Black Using** SMA® **Resins Or SMA® Imide Resins**

**Introduction**
SMA® Resins are a family of low molecular weight styrene/maleic anhydride copolymers and their derivatives. These resins can act as efficient polymeric surfactants in a variety of water-based dispersing and emulsifying applications. For example, SMA® Resins are well known as dispersing resins for pigments, where they provide benefits such as high dispersion stability and high pigment/dispersing resin ratios. To be used in this way, the SMA® Resins are typically hydrolyzed under basic conditions to form a SMA® carboxylate salt solution. To facilitate their use in water-base formulations, Sartomer produces, in addition to solid SMA® Resins, aqueous solutions of SMA® Resins as either their ammonium salts (H grades) or their sodium salts (HNa grades). The hydrolyzed SMA® solutions have anionic carboxylate functionality, and their use is typically limited to water solutions with pH > 7.

To broaden the utility of SMA® Resins, Sartomer offers a series of SMA® Imide Resins. SMA® Imides are low molecular weight styrene/maleimide copolymer which contain tertiary amine functional groups. Four grades are currently available for evaluation, SMA® 1000I, 2000I, 3000I, 4000I which have styrene/maleimide ratios of 1/1 to 4/1. SMA® Imide Resins dissolve in aqueous acid solutions. This dissolution is the result of protonation of the tertiary amine groups to form water-soluble trialkyl ammonium salt groups. Therefore, the water soluble SMA® Imide solutions have cationic, ammonium salt functionality, and their use is typically in water solutions with pH < 7.

This bulletin describes the ability of SMA® Resins and SMA® Imide Resins to disperse carbon black pigment under anionic and cationic conditions, respectively. The SMA® materials are found to be highly efficient dispersing agent when compared to several other commonly used materials.

**Test Methods and Materials**
The relative dispersing ability of the SMA® and SMA® Imide solutions were determined using a blender fluidity test. The objective of this work was to evaluate the behavior of different SMA® resins and to compare SMA® resins with a standard dispersing agent.

**Dispersing Agent Requirement (DAR) Test**
A standard dispersing test procedure was followed:

- Charge water in a 1 liter Waring blender bowl
- Add about one half of the dispersing agent concentration in liquid form and adjust the pH
- Add the carbon black with a low speed mixing
- Add the remaining dispersing agent and agitate at high speed

The end point criterion is the maintenance of uninterrupted fluidity for five minutes under high speed agitation.

The dispersing agent requirement as a percentage of the carbon black is then calculated as follows:

\[
\text{DAR} \% = \frac{\text{Dispersing agent solids}}{\text{carbon black}} \times 100
\]

In this procedure one has to avoid heat buildup, which tends to result in a lower dispersing agent requirement. Therefore, the bowl of the blender was cooled to eliminate this variable.
Several different carbon black grades were selected that differ in particle size, surface area and surface chemistry. As one would expect, grades with a higher surface area require more dispersing agent, and have a higher DAR.

Another important parameter is the DiButyl Phthalate Absorption number (DBPA). It is indicative of the structure of the carbon black, with higher numbers indicating carbon blacks which are more difficult to disperse. For example, Monarch 490 is more difficult to disperse than either Monarch 430 or Mogul L.

“Monarch” and “Black Pearl” refer to the physical forms of the carbon black. “Monarch” grades are fine powders, while “Black Pearls” are supplied in pellet form. Both were tested and no differences in the DAR values between pellets and powder forms were observed.

Monarch 280, 430, 490 and Mogul L were studied at a 30% carbon black loading. Monarch 1300 was tested at a loading of 15%. The pH of the formulation was held constant at 9 for the anionic SMA® resins and 4.5 for the SMA® Imide cationic resins.

(I) SMA® Resins for Anionic Carbon Black Dispersions

(A) Comparison between SMA® Resin Sodium Salts

For two representative carbon blacks, the DAR of SMA® 1000 < SMA® 17352 < SMA® 1440.
(B) Comparison of SMA® ammonium and sodium salt:

<table>
<thead>
<tr>
<th>Dispersing resins</th>
<th>Sodium(HNa) (%)</th>
<th>Ammonium (H) (%)</th>
<th>Carbon black Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMA® 1000</td>
<td>2.2</td>
<td>2.85</td>
<td>Monarch 430</td>
</tr>
<tr>
<td>SMA® 1440</td>
<td>3.55</td>
<td>3.3</td>
<td>Monarch 430</td>
</tr>
<tr>
<td>SMA® 17352</td>
<td>4.1</td>
<td>4.35</td>
<td>Monarch 490</td>
</tr>
</tbody>
</table>

Since the weight of the sodium is included in the DAR calculation, the SMA® 1000 sodium solution clearly gives better results. In the case of the SMA® esters, the gap is much smaller.

The conclusions are the followings:

- Sodium salt of SMA® has a better dispersing ability than ammonium salt.
- SMA® 1000 resin gives better performance compared to ester SMA® resin grades.

(C) Comparison between SMA® 1000 HNa and a reference resin

The dispersing agent requirement for SMA® 1000 HNa is equal to or lower than the reference resin for the range of carbon black grades.

Maximum Carbon Black Content

For two carbon blacks, the maximum carbon black loading was determined at a fixed dispersing agent concentration, using the same uninterrupted viscosity end point.

- **Carbon black** : Monarch 430, Dispersing agent loading : 2.8%
  - SMA® 1000 HNa 37%
  - Reference resin 35%

  In this test, SMA® 1000 HNa demonstrates superior ability to disperse carbon black at higher pigment loadings.

- Carbon black : Monarch 280, Dispersing agent loading : 2%
  - SMA® 1000 HNa 41%
  - Reference resin 37%
Viscosity Stability Versus Time
Two dispersions with 30% of Monarch 430, and respectively 2.5% of SMA® 1000 HNa and 2.6% of the reference resin were prepared. The viscosity was checked with a Brookfield viscosimeter after 1 day, 7 days, 21 days.

<table>
<thead>
<tr>
<th>Time</th>
<th>SMA® 1000 HNa</th>
<th>Reference resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 day</td>
<td>1100 mPa.s</td>
<td>50 mPa.s</td>
</tr>
<tr>
<td>7 days</td>
<td>1100 mPa.s</td>
<td>7300 mPa.s</td>
</tr>
<tr>
<td>21 days</td>
<td>1100 mPa.s</td>
<td>9000 mPa.s</td>
</tr>
</tbody>
</table>

While dispersions made with SMA® 1000 HNa have a higher viscosity, viscosity stability is better with SMA® 1000 HNa.

(2) SMA® Imides For Cationic Carbon Black Dispersions
SMA® Imide resins provide a unique combination between cationic character and hydrophobicity. They should therefore make cationic formulations with good water resistance.

As observed in the table below SMA® 1000 I and SMA® 2000 I are efficient dispersing agents for carbon black. Higher styrene content (1000 < 2000 < 3000) leads to higher dispersing agent requirement.

Comparison Using Monarch 490

<table>
<thead>
<tr>
<th>Dispersant</th>
<th>SMA® 1000 I H</th>
<th>SMA® 2000 I H</th>
<th>SMA® 3000 I H</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAR (%)</td>
<td>3.8</td>
<td>4.0</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Other carbon blacks

<table>
<thead>
<tr>
<th>Carbon black</th>
<th>SMA® 1000 IH</th>
<th>SMA® 2000 IH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monarch 430</td>
<td>2.85</td>
<td>2.95</td>
</tr>
<tr>
<td>Mogul L</td>
<td>4.9</td>
<td>5.6</td>
</tr>
<tr>
<td>Monarch 1300*</td>
<td>11.3</td>
<td>13.7</td>
</tr>
</tbody>
</table>

* DAR value with SMA® 1000 HNa is 11.2% for this carbon black.

It is therefore possible to obtain cationic dispersions with a reasonable amount of dispersing agent for a variety of carbon black grades.

Conclusions
SMA® 1000 is a very efficient dispersing agent for carbon blacks. This resin can be used to produce carbon black dispersions with high loading and low viscosity.

The SMA® base resins are more efficient than esterified resins.

Sodium solutions are more efficient than ammonium solutions.

The SMA® imides also perform well. This may open doors to a new line of cationic, hydrophobic carbon black dispersions.

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