

Styrene Maleic Anhydride Ester Copolymers and the New SMA 1550H – Pigment Dispersants for Waterborne Inks and Coatings



Benefits

- Improved color strength
- Improved dispersion stability and viscosity control
- Excellent compatibility with emulsions and solution resins
- Excellent gloss

Target Markets

- Water-based inks

Additional Information

MSDS/TDS: SMA 1440H, SMA 17352H, SMA 1550H

Description

Optimizing pigment dispersion is a vital aspect of performance in water-based inks and coatings. The elements of dispersion are (1) wetting of pigment agglomerates, (2) separation of the agglomerates into discrete primary particles, and (3) maintenance of particle separation. Often, dispersion formulations can possess adequate pigment wetting, but not long-term stability (maintenance of particle separation). This creates problems such as gelling and loss of color, gloss, or transparency (or opacity in the case of opaque pigments). The key to attaining good performance is to utilize a dispersant with chemical moieties that have an affinity for the pigment surface, thus enhancing pigment wetting. Furthermore, the architecture of these polymers needs to be designed so that adequate steric stability is obtained, which provides good long-term dispersion stability by maintaining particle separation. SMA[®] dispersants are low molecular weight styrene and maleic anhydride ester copolymers, as shown in Figure 1, have (1) ester side chains with strong affinity for pigment surfaces, (2) 8-9 anionic acid groups to provide electrostatic stability in water based dispersions, and (3) a polymeric backbone to provide steric stability.

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SMA® 1440H and SMA 17352H have long been recognized as industry-standard pigment dispersants for water-based coatings and inks. Ink manufacturers have developed commercial formulations in which SMA 1440H has been shown to perform as an all-inclusive, one-component dispersant in acrylic emulsion/resin blend formulations, replacing as many as 4-5 other types of dispersants. Because of the unique anionically charged chemical structure of SMA esters and complementary design of hydrophilic-hydrophobic properties, SMA 1440H and 17352H efficiently disperse and stabilize many types of organic and inorganic pigments, developing the strongest color from a given amount of pigment. SMA esters are polyelectrolyte resins, which become water insoluble as the paint film cures, and therefore contribute to film reinforcement. SMA 1440H and SMA 17352H are the ammonia solutions of SMA 1440F and SMA 17352F/P, respectively.

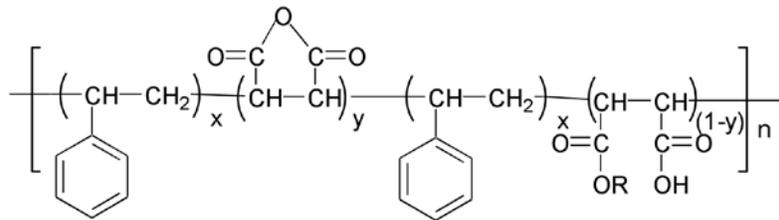


Figure 1 – Structure of SMA Ester Copolymer

More recently, a new SMA-based derivative, SMA 1550H, has been developed that gives even better performance than both SMA 1440H and SMA 17352H.

In this study, the SMA derivatives were compared against the ammonia solutions of a standard styrene acrylic dispersant (Acrylic A) and a higher-performance styrene acrylic dispersant (Acrylic B). The solution properties of all the dispersants are shown in Table 1.

Table 1 – SMA and Acrylic Pigment Dispersants

| Product | Solids (wt. %) | pH |
|-----------------|----------------|-----------|
| SMA 1440H | 33 | 8.0 – 9.5 |
| SMA 1550H | 30 | 8.0 – 9.5 |
| SMA 17352H | 25 | 8.0 – 9.5 |
| Acrylic A NH4OH | 30 | 8.0 – 9.5 |
| Acrylic B NH4OH | 30 | 8.0 – 9.5 |

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All of the dispersants were tested in each of the pigments shown in Table 2 at the specified pigment solids and dispersant levels.

Table 2 – Pigment properties

| Pigment Number | Manufacturer | Pigment Loading | Dispersant Loading |
|-------------------|-------------------|-----------------|--------------------|
| Pigment Red 57:1 | Tri-tex/Biz Bees | 37% | variable |
| Pigment Blue 15:3 | Biz Bees Thailand | 37% | variable |
| Pigment Yellow 83 | Tri-tex Canada | 37% | variable |

Dispersion Procedure

The pigment dispersions were prepared using the following method. To a 4-ounce Nalgene bottle containing 100 g of 0.1 mm zirconium beads, the dispersion ingredients were added: pigment, water, dispersant, and Surfynol® DF-58 defoamer from Air Products. The lid of the Nalgene container was then screwed on tightly and sealed with electrical tape. The individual containers were placed into a one-gallon can. Two of these cans were loaded onto a Red Devil Shaker. In this way numerous dispersions could be prepared simultaneously. The dispersions were shaken for 30 minutes. After 30 minutes, the dispersion properties were measured and specific amounts were added to the emulsion/solution acrylic ink resin blend to evaluate the ink properties.

Dispersion Properties

Color Development

One percent of the concentrated pigment dispersions was added to clear acrylic emulsion/solution acrylic ink resin blends, and 2-mil wet drawdowns on clear glass were prepared. Color values were measured on dry films using a colorimeter with glass panels sitting on a white background.

Viscosity Stability

Brookfield viscosities were measured at various shear rates on the initial dispersions and after aging for 10 days at 50 °C. For ease of incorporation into inks and good shelf stability, the best dispersions have the lowest viscosity values that remain stable after aging.

Results

Pigment Blue 15:3

For Pigment Blue 15:3, only the new SMA 1550H dispersant and the Acrylic B were capable of giving dispersions that had measurable viscosities. Dispersions were let down into the acrylic binder and the drawdowns are represented below in Figure 2. SMA 1550H dispersant develops similar color at half the use level of Acrylic B.

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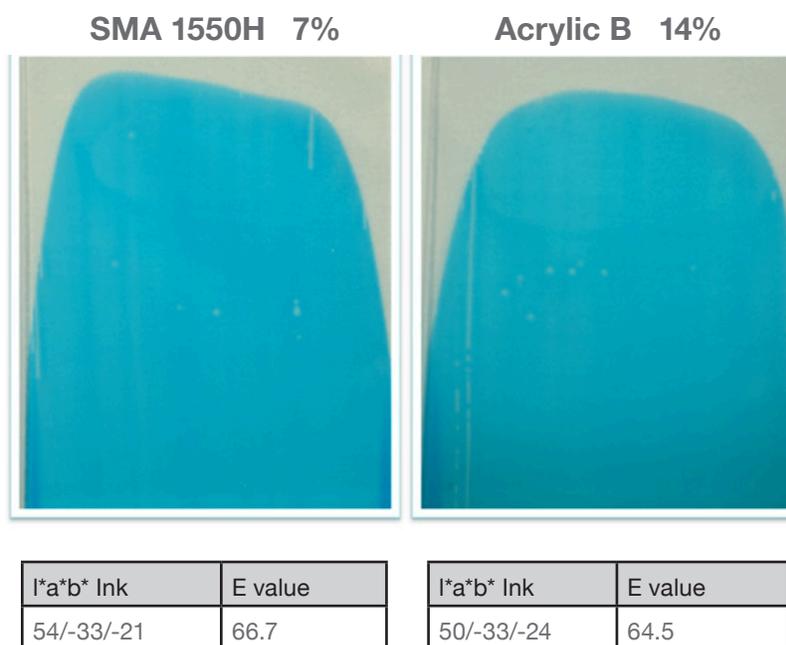


Figure 2 – Drawdowns and l,a,b values for dispersions let down into ink acrylic resin

Viscosity Stability

Both the SMA 1550H and the Acrylic B gave viscosities less than 100 cps, as shown in Figure 3, which will allow the dispersions to be easily incorporated into the solution/emulsion acrylic letdown resin blend. However, the Acrylic B gave a smaller change in viscosity after aging, demonstrating better viscosity stability.

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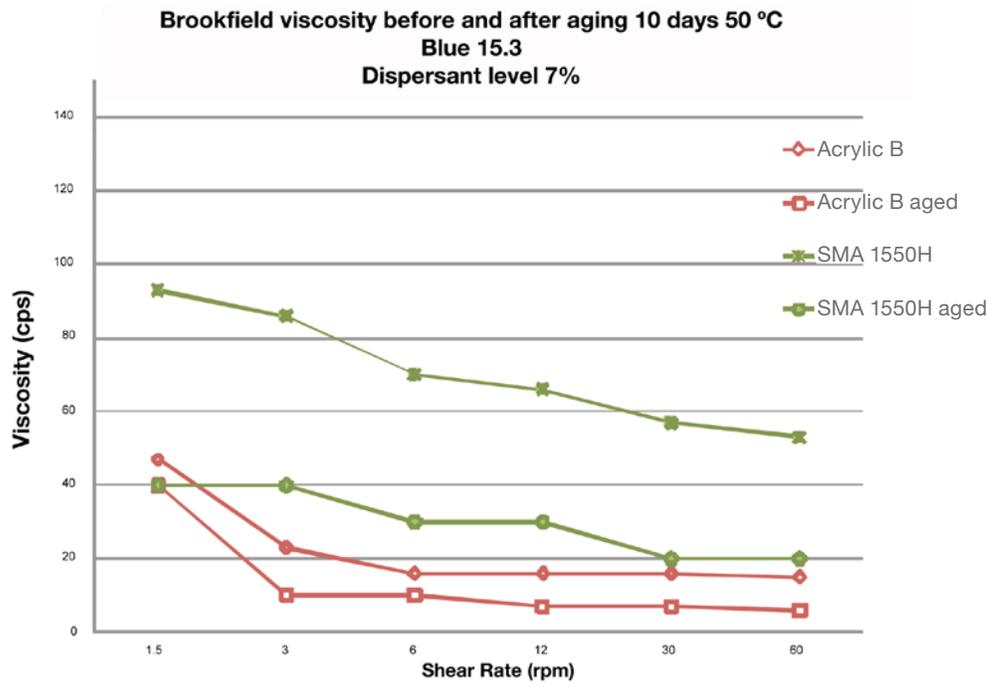


Figure 3 – Pigment Blue 15:3 Dispersions – Viscosity versus shear rate

Pigment Red 57:1

For Red 57:1, only SMA 1550H and Acrylic A gave dispersions that had measurable viscosities before and after aging. These dispersions were let down into the acrylic binder and the drawdowns of the finished inks are represented in Figure 4. Both dispersants gave similar l,a,b color values showing excellent red color development.

SMA 1550H 21%



Acrylic A 21%



| l*a*b* Values | l*a*b* Values |
|----------------------|----------------------|
| 39/41/5 | 41/43/3 |

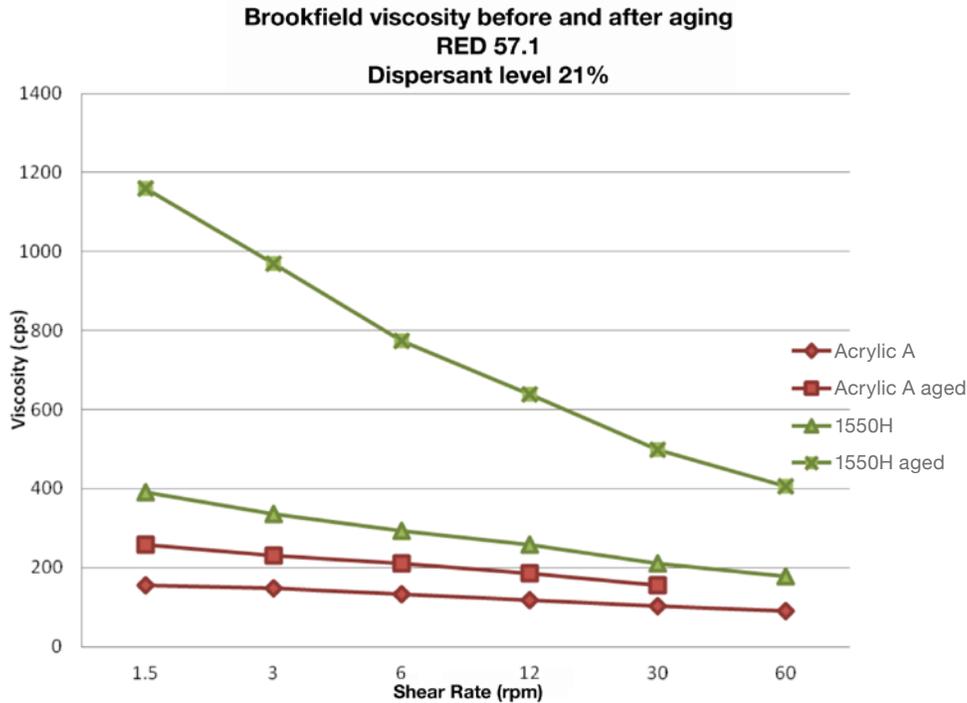
Figure 4 – Drawdowns and l,a,b values for dispersions let down into ink acrylic resin

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Viscosity Stability

Acrylic A gave the lowest viscosity and the value increased slightly after aging as shown in Figure 5. SMA 1550H gave a low initial viscosity; however, the viscosity tripled after aging at 50 °C for 10 days. Overall, for Pigment 57:1, SMA 1550H gave excellent color development, but Acrylic A gave the best combination of color development and



viscosity stability.

Figure 5 – Pigment Red 57:1 Dispersions – Viscosity versus shear rate

Pigment Yellow 83

For Yellow 83, SMA 17352H, SMA 1550H, and Acrylic A and B all gave dispersions that had measurable viscosities before and after aging. All of the dispersions were let down into the acrylic binder and the drawdowns of the finished inks are represented in Figure 6. All of the dispersants gave l,a,b color values that were similar but the SMA 17352H had the highest b value, indicating the best yellow color development.

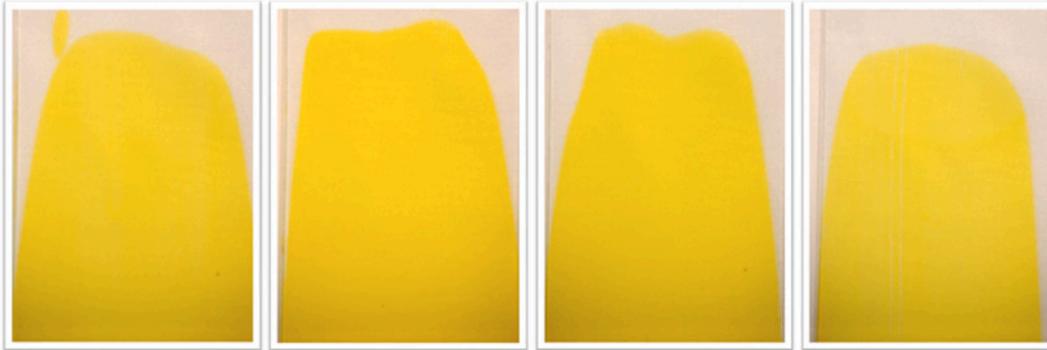
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SMA 17352H 14% SMA 1550H 14% Acrylic A 14% Acrylic B 14%



| I*/a*/b* values | I*/a*/b* values | I*/a*/b* values | I*/a*/b* values |
|-----------------|-----------------|-----------------|-----------------|
| 74/2/47 | 73/3/48 | 73/3/49 | 73/2/46 |

Figure 6 – Drawdowns and I,a,b values for dispersions, all with 14% dispersant, let down into ink acrylic resin

Viscosity Stability

Brookfield viscosities are shown in figure 7. Acrylic A gave the lowest viscosity and the value increased slightly after aging. However, the SMA 17352H also gave a very low viscosity and the values did not change at all after aging at 50 °C for 10 days, demonstrating superior storage stability. The Acrylic B and the SMA 1550H gave slightly higher initial viscosities, but the aged viscosities for these dispersions were much higher. Overall, for Pigment Yellow 83, the SMA 17352H gave the best combination of color development and viscosity stability.

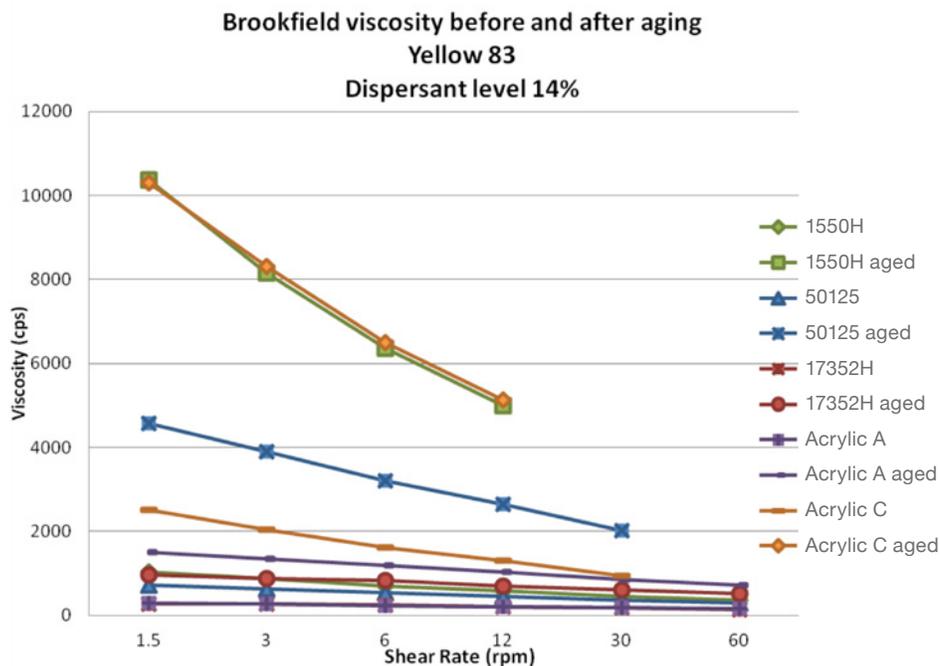


Figure 7 – Pigment Yellow 83 Dispersions – Viscosity versus shear rate

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Summary

In this study, SMA esters and a new SMA derivative, SMA 1550H, were compared against an industry-standard Acrylic A dispersant and a higher-performance Acrylic B dispersant. The performance of the dispersants varied for the three organic pigments Blue 15:3, Red 57:1 and Yellow 83. For Blue 15:3, the new SMA 1550H gave the best combination of color development and viscosity stability. For Red 57:1 the Acrylic Resin B gave the best combination of properties. For Yellow 83, SMA 17352H gave the best combination of properties. The most universal performance came from the SMA 1550H which gave excellent results in Blue 15:3, very good results in Red 57:1, and good results in Yellow 83.

Future Studies

The fact that SMA 1550H was the only dispersant that was capable of dispersing the three organic pigment shows that it is universal compared to previous SMA esters. Additional pigments will be studied along with additional ink properties to further explore the robustness of this new dispersant.

For more information, please visit www.crayvalley.com

About Total Cray Valley

Total Cray Valley is the premier global supplier of specialty chemical additives, hydrocarbon specialty chemicals, and liquid and powder tackifying resins used as ingredients in adhesives, rubbers, polymers, coatings and other materials. Total Cray Valley has pioneered the development of these advanced technologies, introducing hundreds of products that enhance the performance of products in energy, printing, packaging, construction, tire manufacture, electronics and other demanding applications.

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