Mixed Mineral Thixotropes
A New Class of Additives for Molded Thermoset Systems

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What is a thixotrope?

An additive that is designed to generate a shear thinning rheology with a delayed recovery in viscosity as the shear is relaxed.
What is a mixed mineral thixotrope (MMT)?

MMT’s are a new class of additive that are characterized by high efficiency and ease of incorporation. Furthermore (and perhaps most importantly), they develop application properties (such as sag resistance) before the onset of appreciable viscosity. We say that MMT’s have a heightened property response/viscosity ratio. They are designed to compete in a very cost effective manner – primarily against fumed silicas and organoclays.

MMT’s take advantage of fundamental morphological differences between different mineral types to generate easy dispersing products. The efficiency improvements come from the difference in viscosifying mechanisms which generates an impressive synergy between the different minerals employed.
The primary mineral is sepiolite. Smaller amounts of proprietary minerals are used to effect dispersion and efficiency of the MMT. Typically, quaternary ammonium salts are used as surface treatments.
Difference vs. Conventional Organoclay

Conventional Organoclay

MMT

MMT = Mixed Mineral Thixotrope
Bulk Density

- Fumed Silica: 50 g/l
- MMT: 130 g/l
- Organoclay: 400 g/l
Which types of systems can utilize MMT’s?

Initial work focused on unsaturated polyester resins and epoxy resin containing systems. These are typically high build coatings. Recent developments have shown that MMT’s can also be successfully used in a variety of thin film applications such as decorative enamels, thermoset systems, and automotive color coats.
How do I use MMT’s?

In solvent-containing systems that can tolerate such processing, always add the MMT to the solvent. If solvent is not available, add the MMT to (in order of preference):

1) Reactive diluent
2) The lowest viscosity resin

MMT’s will exhibit decreasing efficiency as you descend the above “preference ladder”, but will almost always be more efficient than currently employed thixotropes. Cowles type shear will suffice in all applications for dispersing MMT’s. Other incorporation methods can also be used.

In the case of fumed silicas, MMT’s will typically exhibit efficiencies that are 30 to 40% improved. For organoclays, the improvement may be 50% or more. But remember, MMT containing systems will be at a lower viscosity to achieve the same sag resistance.
How do I use MMT’s (continued)?

In many systems, the use of a “rheological enhancement” additive (such as BYK R-605) is recommended to decrease the total amount of additives that are used in the system. BYK R-605

A typical generic formula might look something like this:

Solvent
MMT

*MIX 5 minutes at high speed*

Wetting agent
Pigments

*GRIND*

Letdown
BYK R-605
How do I use MMT’s (continued)?

The use of BYK R-605 can reduce the amount of MMT you use by as much as 30% and provide you with a more stable system. It is recommended that you evaluate the use of such synergistic enhancers when you are studying the use of MMT’s in your coatings system. Materials such as BYK R-605 should be used at 10% of the weight of the MMT additive.
# Effect of Enhancer on MMT in Unsaturated Polyester

<table>
<thead>
<tr>
<th>Treatment</th>
<th>1 rpm</th>
<th>10 rpm</th>
<th>100 rpm</th>
<th>TI (10/100)</th>
<th>Sag</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMT 0.5%</td>
<td>2000</td>
<td>600</td>
<td>310</td>
<td>1.94</td>
<td>0</td>
</tr>
<tr>
<td>MMT 0.5% + BYK R-605</td>
<td>6000</td>
<td>1400</td>
<td>480</td>
<td>2.92</td>
<td>150</td>
</tr>
<tr>
<td>MMT 0.75%</td>
<td>2000</td>
<td>800</td>
<td>370</td>
<td>2.16</td>
<td>150</td>
</tr>
<tr>
<td>MMT 0.75% + BYK R-605</td>
<td>8000</td>
<td>1800</td>
<td>560</td>
<td>3.21</td>
<td>250</td>
</tr>
<tr>
<td>MMT 1.0%</td>
<td>3000</td>
<td>1100</td>
<td>420</td>
<td>2.62</td>
<td>200</td>
</tr>
<tr>
<td>MMT 1.0% + BYK R-605</td>
<td>12000</td>
<td>2400</td>
<td>680</td>
<td>3.53</td>
<td>350</td>
</tr>
</tbody>
</table>
=> up to 15% pregel possible - still pourable
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Off White</td>
</tr>
<tr>
<td>Form</td>
<td>Fine Powder</td>
</tr>
<tr>
<td>Mixed Minerals</td>
<td>Proprietary Blend, Patented</td>
</tr>
<tr>
<td>Moisture Content</td>
<td>4%</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>8 lbs / ft³</td>
</tr>
<tr>
<td></td>
<td>130 kg / m³</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.5 - 1.7 g / cm³</td>
</tr>
</tbody>
</table>
Conventional

MMT's
ISOPHTHALIC

Formulation
55% Iso
45% Styrene
7% Tween®20 on Rheological
.5% Cobalt/DMA (8/1) on Resin

Viscosity (Centipoise)

Shear Rate (1/sec)
**DCPD RESIN**

**RECOVERY BEHAVIOR**

**UNFILLED—65% SOLIDS**

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**65% DCPD Unfilled**

<table>
<thead>
<tr>
<th>Brookfield Viscosities</th>
<th>Sag Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>6rpm 60rpm Mil thickness</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MMT</th>
<th>1.0%</th>
<th>2300</th>
<th>570</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7%</td>
<td>1200</td>
<td>370</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>0.5%</td>
<td>600</td>
<td>350</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

| AEROSIL 200 | 1.0% | 4000 | 940 | 4 |

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**DCPD RESIN**

**RECOVERY BEHAVIOR**

**UNFILLED—65% SOLIDS**

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Figure 1: 0.5% FUMED SILICA
8 mils (203 microns) sag resistance
Figure 2:
0.5% CONVENTIONAL ORGANOCLAY
4 mils (102 microns) sag resistance
Figure 3: 0.3% MMT
8 mils (203 microns) sag resistance
1% Fumed Silica
Powder Addition

350 µm

1% MMT
Powder Addition

300 - 350 µm

1% MMT
Pregel Addition

> 500 µm

pregel preferred
1% Fumed Silica
Powder Addition

0.75% MMT
Pregel Addition

0.5% MMT
Pregel Addition

savings up to 50%
Improved Sag

Relaxation Time
1% Tickener (Powder Addition), 0.1% Byk R605 (Enhancer)
in Palatal P4-01 (Unsaturated ortho-Polyester Resin)

- Fumed Silica
- MMT

Viscosity recovery at 1 sec⁻¹
Shear thinning at 1000 sec⁻¹

Time (sec)
Viscosity Recovery (mPas)
<table>
<thead>
<tr>
<th></th>
<th>Load</th>
<th>Brookfield Viscosity (cps)</th>
<th>Sag (mils)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>6 rpm</td>
<td>60 rpm</td>
</tr>
<tr>
<td><strong>64.9% Solids Orthophthalic Resin</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MMT</td>
<td>0.5%</td>
<td>2,500</td>
<td>600</td>
</tr>
<tr>
<td>MMT</td>
<td>1.0%</td>
<td>3,500</td>
<td>900</td>
</tr>
<tr>
<td>Fumed Silica</td>
<td>1.0%</td>
<td>2,700</td>
<td>800</td>
</tr>
<tr>
<td><strong>69.4% Solids Orthophthalic Resin</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MMT</td>
<td>0.54%</td>
<td>2,800</td>
<td>900</td>
</tr>
<tr>
<td>MMT</td>
<td>1.00%</td>
<td>4,600</td>
<td>1,400</td>
</tr>
<tr>
<td>Fumed Silica</td>
<td>1.00%</td>
<td>3,900</td>
<td>1,100</td>
</tr>
<tr>
<td><strong>64.9% Solids Dicyclopentadiene (DCPD) Resin</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MMT</td>
<td>0.35%</td>
<td>2,625</td>
<td>878</td>
</tr>
<tr>
<td>Fumed Silica</td>
<td>0.60%</td>
<td>2,600</td>
<td>950</td>
</tr>
</tbody>
</table>
### Evaluation of Thixotropes in Filled Epoxy Resin Systems

A side: 100 parts Epon 828, 25 – 50 parts filler; B side: 58 parts Ancamine® 2280

<table>
<thead>
<tr>
<th>Extender</th>
<th>Thixotrope</th>
<th>Loading</th>
<th>10 rpm Viscosity</th>
<th>Sag Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>MMT</td>
<td>1.5%</td>
<td>100,000</td>
<td>20</td>
</tr>
<tr>
<td>TiO₂</td>
<td>FS – Hydrophobic</td>
<td>2.0%</td>
<td>135,000</td>
<td>20</td>
</tr>
<tr>
<td>TiO₂</td>
<td>FS - Hydrophilic</td>
<td>2.5%</td>
<td>140,000</td>
<td>20</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>MMT</td>
<td>1.3%</td>
<td>60,000</td>
<td>10</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>FS – Hydrophobic</td>
<td>1.6%</td>
<td>80,000</td>
<td>10</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>FS - Hydrophilic</td>
<td>2.4%</td>
<td>100,000</td>
<td>10</td>
</tr>
<tr>
<td>Silica Flour</td>
<td>MMT</td>
<td>1.0%</td>
<td>80,000</td>
<td>10</td>
</tr>
<tr>
<td>Silica Flour</td>
<td>FS – Hydrophobic</td>
<td>1.4%</td>
<td>70,000</td>
<td>10</td>
</tr>
<tr>
<td>Silica Flour</td>
<td>FS - Hydrophilic</td>
<td>2.4%</td>
<td>90,000</td>
<td>10</td>
</tr>
</tbody>
</table>

Lower Loading + Lower Viscosity + Same Sag = Increased Performance
**HIGH SOLIDS, HIGH BUILD EPOXY FORMULATIONS**

Viscosity & Sag Resistance of Thixotropic Additives

<table>
<thead>
<tr>
<th>THIXOTROPIC ADDITIVE</th>
<th>VISCOSITY, centipoise</th>
<th>SAG</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 rpm</td>
<td>10 rpm</td>
<td>20 rpm</td>
<td>50 rpm</td>
</tr>
<tr>
<td>MMT</td>
<td>6600</td>
<td>3700</td>
<td>2100</td>
<td>1040</td>
</tr>
<tr>
<td>Claytone® APA</td>
<td>7800</td>
<td>4300</td>
<td>2400</td>
<td>1180</td>
</tr>
<tr>
<td>Aerosil 200</td>
<td>14000</td>
<td>7600</td>
<td>4150</td>
<td>1920</td>
</tr>
<tr>
<td>Cab-O-Sil TS720</td>
<td>4400</td>
<td>2450</td>
<td>1450</td>
<td>750</td>
</tr>
</tbody>
</table>

Lower Viscosity, but exceptional Sag Resistance
Viscosity Stability at Equal Sag Performance

1 rpm Viscosity, cps

- 1.9 FS/PS
- 1.14 MMT
- 1.14 MMT + Byk

Initial: 32000
2 weeks: 28000
4 weeks: 24000
7 weeks: 20000
Graph 3
31051-00 48 Hours

% Syneresis vs % Load

A-200
HDK N20
MMT
MMT + Byk

0.0 0.2 0.4 0.6 0.8 1.0 1.2
0.0 5.0 10.0 15.0 20.0 25.0 30.0

SOUTHERN CLAY PRODUCTS
ROCKWOOD ADDITIVES
Epoxy Floor Coating Containing Quartz Sand
Based on POLYPOX E 403

- MMT
- Organoclay
- Fumed Silica
- Control blank
Resin / LP (Garamite 1210 (0-1.25% BOP))
No Garamite

Garamite

0 % BOP

1.0 % BOP
Paste Moldings with and without Garamite 1210

Garamite

No Garamite
Resin/LP/Glass Bubbles with and without Garamite 1210

No Garamite

Garamite

0 % BOP

0.25 % BOP
Resin/LP/Glass Bubbles with and without Garamite 1210