A New Generation of Gypsum Dispersing Agents

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Abstract:
As global energy costs continue to increase there is an ever growing need to reduce energy consumption in the production of wallboard and other gypsum-based products. A new generation of commercially available colorless dispersants based on polycarboxylate comb copolymers has been developed that produces flows at lower water use levels than obtainable with conventional dispersants. At conventional water use levels, dispersant dosage is reduced by up to 80%, while maintaining flow.

This paper compares the performance of this new generation of dispersants to the conventional dispersants. A focus is placed on the performance in synthetic gypsum. Dispersant dosage versus performance, set times and hydration rates, are discussed. A discussion on how changes to the structure of this new generation of dispersants affect performance is also discussed.

Introduction
As energy costs continue to increase there is an ever increasing need to reduce the water to stucco ratio, thereby reducing the time that the wallboard needs to spend in the drying oven. The conventional dispersants used today are cost effective at reducing water demand. However, the performance of the conventional dispersants plateaus after which adding additional dispersant does not improve flow. A new generation of colorless dispersants has been developed that extends the range of water to stucco ratios beyond what is attainable with conventional dispersants. In the standard range of water reductions, these new dispersants give flow equivalent to those obtained with conventional dispersants at only 20 – 40% of the dosage. When dosed to give equivalent flow performance, the associated properties (set time, hydration rate, etc.) are comparable to that obtained with conventional dispersants. The performance of
these new dispersants has been proven in commercial wallboard production for over a year.

**Energy Costs – The Need to Reduce Water Levels**

In North America natural gas is the principal source of energy used in the production of wallboard. Natural gas also plays a key role in wallboard production in other parts of the world. Historically the average natural gas cost to industrial applications in the United States, including wallboard production, has averaged $2.50 - $3.00 per thousand cubic feet.\(^3\)

Since 2000, the cost for natural gas has risen considerably. With growing demand, especially from new electricity generation plants, the natural gas demand in North America is increasing faster than production. As the result of this growing demand combined with stored reserves being well below historical levels, natural gas is expected to remain high for the foreseeable future.\(^4\) Spot natural gas price is expected to range between $5.00 and $6.60 per thousand cubic feet through the end of 2004, peaking over $6.00 this winter.\(^5,6\) The long term outlook calls for natural gas demand to continue to increase with long term pricing in excess of $7.00 per thousand cubic feet.\(^7\)

Figure 1 shows how natural gas cost impacts the cost to produce wallboard.\(^8\) Historically the natural gas-based energy cost to dry wallboard moved in the range of $5 - $6 per thousand square feet. At various times in the past two to three years this cost has peaked at $10 per thousand square feet. Based on the Energy Information Administration's price calls to the end of 2004, we estimate that this cost will remain in the $8 – $9 per thousand square feet range. This represents nearly an 80% increase in the energy cost to dry wallboard. If there is a time to reduce water levels, it is now.

Using a very detailed model that was developed with a leading industry expert, we have modeled how reducing water content improves the financial performance of a nominal wallboard plant.\(^9\) We assumed a natural gas price of $5.50 per thousand cubic feet, the expected midpoint of the near-term forecasts. Higher natural gas prices will only strengthen the case for further water reductions. We also assumed that the plant is currently using a conventional dispersant and that the additional water reduction is achieved by using a dispersant based on the new technology, in addition to the conventional...
dispersant. Additional plant characteristics are summarized in Figure 2.

The improved profitability and unit cost savings are summarized in Table 1. It is clear than moving to lower water levels through the use of dispersants, both conventional and new, will both reduce unit costs and improve overall plant profitability. The new dispersant technology described in this paper allows water reductions not typically achievable with the conventional dispersants.

**Technology Overview**

Simple polycarboxylates are known to improve the flowability of gypsum slurries. This improved flow is mainly due to set inhibition as opposed to colloidal dispersion. In the 1980’s a new family of modified polycarboxylates were developed that have a “comb” structure as shown in Figure 3. These new polymers have a polycarboxylate backbone and polyether “teeth”. These polymers were first developed for use as concrete water reducers.\(^{10}\) These polymers proved to be excellent dispersants and are now widely used in the production of concrete. The superior dispersive power is the result of dual forces, both steric and electronic repulsion, as shown in Figure 4.

![Comb Polymer Structure](image)

Recently, the gypsum industry has begun to take a look at these new dispersants.\(^{11,12}\) The comb polymers sold into the concrete market that have been optimized to disperse cement are not directly useable in gypsum-based applications. Modifications to basic polymer structure are required for these polymers to deliver the required performance in gypsum-based applications. Changes to molecular weight, “tooth” composition and length, “tooth” density, and backbone composition all affect performance. We will describe how some of these changes affect performance in this paper.

**Methods and Materials**

**Flow – Method A.** Method A was used for both natural and synthetic gypsum. The dispersing ability of the dispersant candidates was measured utilizing a water reduction test patterned after ASTM C472. This test is used to determine the amount of water that is required to produce a gypsum composition of a specific viscosity. The desired viscosity reflects the fluidity necessary to obtain proper flow of the gypsum slurry in the manufacturing process. This amount is called the “consistency,” and it is defined as the

<table>
<thead>
<tr>
<th>Water Reduction</th>
<th>5%</th>
<th>10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production Cost</td>
<td>-$0.40/MSF</td>
<td>-$0.68/MSF</td>
</tr>
<tr>
<td>Productivity</td>
<td>+5%</td>
<td>+11%</td>
</tr>
<tr>
<td>EBIT (earnings before interest and tax)</td>
<td>+$1.4 MM/yr</td>
<td>+$2.7 MM/yr</td>
</tr>
<tr>
<td>ROCE (return on capital employed)</td>
<td>+4%</td>
<td>+7%</td>
</tr>
</tbody>
</table>

Table 1 - Plant Profitability
volume of water required to produce the desired viscosity for 100 g of calcined gypsum (CaSO₄½ H₂O).

Consistency = ml H₂O/100 g gypsum

Gypsum compositions were prepared by swiftly adding 50 g of the calcined gypsum into an 8 ounce expandable polystyrene cup containing either water alone or an aqueous solution containing the dissolved dispersant candidate. The gypsum composition was gently hand-agitated for 60 seconds using a 3/4 inch metal spatula in order to provide uniform wetting of the calcined gypsum. This was immediately followed by more vigorous mixing, using the same spatula, for 30 seconds at a rate of about 160 strokes/minute. Then, the gypsum composition was immediately poured out of the cup in one continuous motion from a height of 90 mm onto a clean, glass plate. The diameter of the resulting circular patty was then measured. The desired slurry viscosity for these experiments produced a test patty that measured 90 mm in diameter. The consistency was then calculated to be two-times the volume of water needed to produce this test patty diameter.

Flow – Method B. An modified procedure was used to mix and measure flows for slurries prepared using number one molding plaster.

Initial Set. The initial set time is patterned after a procedure described in ASTM C266. The method involves preparing gypsum compositions in a manner essentially similar to the method described above for determining consistency. To test the initial set time, the cup remains upright on the lab bench top. A 300 g mass, 1 mm diameter Vicat needle is then positioned normal to the exposed, top surface of the gypsum slurry and is allowed to repeatedly fall freely with the force of gravity. The initial set time is defined as the instant at which the Vicat needle stops penetrating completely through the slurry.

Hydration Rate - The time-dependent change in temperature of the thermally insulated slurry is measured using a Type K thermocouple.

The remaining gypsums, which are used all currently used in wallboard production, were obtained from wall board producers in North America and Europe. (See Table 2.)
Table 2 - Gypsiums

<table>
<thead>
<tr>
<th>Type</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSG-A</td>
<td>Synthetic N. America</td>
</tr>
<tr>
<td>DSG-B</td>
<td>Synthetic N. America</td>
</tr>
<tr>
<td>NG</td>
<td>Natural Europe</td>
</tr>
<tr>
<td>MP</td>
<td># 1 Molding Plaster N. America</td>
</tr>
</tbody>
</table>

The dispersants used in this study are summarized in Table 3. The naphthalene sulfonate formaldehyde and sodium lignosulfonate are grades commonly used commercially for wallboard production. The polyacrylic acid, 2,000 MW, was obtained from Aldrich Chemical Company. Comb polymer CP-A is Ethacryl G available from Lyondell Chemical Company. Comb polymers CP-B and CP-F, along with the other comb polymers used in this study are products in development by Lyondell Chemical.

Table 3 - Dispersants

<table>
<thead>
<tr>
<th>Type</th>
<th>Form</th>
<th>Availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS Sodium Lignosulfonate</td>
<td>Aqueous Solution</td>
<td>Commercial</td>
</tr>
<tr>
<td>NSF Naphthalene Sulfonate Formaldehyde</td>
<td>Aqueous Solution</td>
<td>Commercial</td>
</tr>
<tr>
<td>CP-A Comb Polymer</td>
<td>Aqueous Solution</td>
<td>Commercial</td>
</tr>
<tr>
<td>CP-B Comb Polymer</td>
<td>Aqueous Solution</td>
<td>Developmental</td>
</tr>
<tr>
<td>CP-F Formulated Comb Polymer</td>
<td>Solid</td>
<td>Developmental</td>
</tr>
<tr>
<td>PAA Polyacrylic Acid</td>
<td>Solid</td>
<td>Commercial</td>
</tr>
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</table>

Polymer Structure versus Performance
Unlike dispersants which are based on natural products, the dispersant producer has tremendous flexibility when it comes to optimizing the molecular structure of this new family of comb polymer dispersants. A summary of the structural variables available to the producer to optimize performance are summarized in Table 4. We continue to investigate how modifications to the comb polymer structure and composition affect performance in gypsum. For the purposes of this paper, we will briefly discuss how two types of changes, “tooth” density and overall molecular weight, affect performance. We will also compare two different carboxylate backbones. To get a better measure of the dispersive power of the polymers the studies were conducted using number 1 molding plaster. This was done to minimize any secondary effects caused by interactions of the polymers with impurities in the stucco.
Table 4 - Comb Polymer Structural Variables

<table>
<thead>
<tr>
<th></th>
<th>Typical Range</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Overall Molecular Weight</strong></td>
<td>10,000 – 200,000</td>
</tr>
<tr>
<td><strong>Backbone Composition</strong></td>
<td>Acrylic Acid / Methacrylic acid /</td>
</tr>
<tr>
<td></td>
<td>Allyl Alcohol / Styrene / AMPS / N-vinyl Pyrrolidone / Maleic Acid / Unsaturated sulfonic acids / Unsaturated Phosphonates Derivatives of the above &amp; numerous others</td>
</tr>
<tr>
<td><strong>“Tooth” Density</strong></td>
<td>10% - 90%</td>
</tr>
<tr>
<td><strong>“Tooth” Composition</strong></td>
<td>Ethylene Oxide / Propylene Oxide / Butylene Oxide Ratios and Random vs Block</td>
</tr>
<tr>
<td><strong>“Tooth” Molecular Weight</strong></td>
<td>500 – 6,000</td>
</tr>
</tbody>
</table>

Figure 5 compares how changing the overall molecular weight and tooth density affects flow performance. Each circle represents a different polymer. All of the dispersants were dosed at the same level. **Series A** and **M** represent the two different backbones. The diameter of the circle indicates the relative flow increase over the control with no dispersant. Two conclusions can be drawn from the limited data set presented here. First, within the range of molecular weights and tooth densities studied, the maximum flow is obtained at low tooth density and low molecular weight. Second, the **Series A** polymers have better flow than the **Series M** polymers.

We selected one of the better performing polymers from each backbone type for further study, **CP-A** and **CP-B**. The dispersing powers of these two polymers are compared to that of naphthalene sulfonate formaldehyde and lignosulfonate in Figure 6. Both of these polymers have greater dispersing performance than the conventional dispersants.

Both **CP-A** and **CP-B** can only be prepared as aqueous solutions and for some non-wallboard applications there is a need for a dry powdered product. **CP-F** is a developmental formulated comb polymer, which can be produced as a dry powder. While the dispersing power of **CP-F** is less than both **CP-A** and **CP-B**, its dispersing power is still greater than the conventional dispersants, **NSF** and **LS**.

While this paper is focused on the performance of this new family of dispersants in synthetic gypsum, these polymers are also very effective in natural gypsum. An example of the typical performance of one of these polymers, **CP-A**, is shown in Figure 7.
Performance in Synthetic Gypsum

The focus of this paper is on how these new polymers perform in synthetic gypsum. The results presented focus on the direct comparison of two of these new polymers to the conventional dispersants for two different synthetic gypsums. The key performance properties of set time, hydration rate and flow will be reviewed.

As in both molding plaster and natural gypsum, the two comb polymers, CP-A and CP-B, exhibit greater water reducing ability, than the conventional dispersants in both of the synthetic gypsums. (See Figures 8 and 9.) While the performance of CP-B plateaus, though to a lesser degree than the conventional dispersants, the performance CP-A continues a steady increase with increasing dosage. These new dispersants allow for water reductions that are beyond what is typically obtainable with the conventional dispersants.

At dosages less than 0.05 wt%, both CP-A and CP-B have set times comparable to the conventional dispersants. (See Figures 10 and 11.) At a nominal dosage of 0.1%, CP-A begins to show slightly longer set times. As with the conventional dispersants, the set times of gypsums containing CP-B show little to no change with increasing dosage.

The two comb polymers, CP-A and CP-B are modified polycarboxylates. The performance of a simple unmodified polyacrylic acid, PAA, is shown in Figures 9 and 11. While PAA appears to be a powerful dispersant, the flow improvement is not the result of its dispersancy, but instead is mainly due to it being a powerful retarder, to such a degree that the gypsums containing PAA did not set.
Figure 8 - Comparative Water Reducing Power in DSG-A

Figure 9 - Comparative Water Reducing Power in DSG-B

Figure 10 - Set Times in DSG-A

Figure 11 - Set Times in DSG-B
A dispersant’s effect on hydration rate is key to understanding its performance. Hydration rate is tied to both setting and strength build. Within the dosage range studied, naphthalene sulfonate formaldehyde, NSF, has little to no effect on the hydration rate as compared to the control without any dispersant. (See Figure 12.) Except for at the 0.10% dosage where it is slightly slower, CP-B has a faster hydration rate than that of the control. At dosages of 0.05% and lower, CP-A has a hydration rate comparable to the control. At higher dosages, CP-A slows the rate of hydration. Comparison of both CP-A and CP-B to the conventional dispersants, lignosulfonate (LS) and naphthalene sulfonate (NSF), all at 0.05%, shows no initial difference in hydration rate from each other and the control. As the hydration process proceeds, the hydration rate for gypsum containing CP-A slows slightly. This slight reduction in hydration rate can easily be off set, if necessary, by adding a small amount of a conventional accelerator.

The comparisons shown thus far have focused on comparisons based on equivalent dosages. However, to better demonstrate the performance of the new dispersants at a set level of water reduction, we adjusted the dosage of each dispersant to obtain the same nominal flow. The water to stucco ratio was 0.6, representing a 5% water reduction over the control. The dispersant dosages were then adjusted to give the same flow as the control. The required dosages in each of the gypsumps, DSG-A and DSG-B, are shown in Figure 13.
Figure 13 - Required Dosages at 5% Water Reduction

Figure 8 - Set Times at 5% Water Reduction

Figure 15 - Hydration Rates at 5% Water Reduction
In the two gypsums used in this study, the required dosages of dispersant was reduced by 55 – 70% with the new dispersants as compared to lignosulfonate.

In DSG-A, CP-A showed at slight retardation in set as compared to lignosulfonate. (See Figure 14.) In DSG-B both comb polymer dispersants, CP-A and CP-B, showed a slight acceleration in final set as compared to lignosulfonate. The hydration rates are consistent with the set time measurements. CP-A has a slightly slower hydration rate than both of the conventional dispersants in DSG-A. Both CP-A and CP-B have faster hydration rates than lignosulfonate ion DSG-B. The small differences in performance observed in the two different gypsums are consistent with what we have observed in our broader studies. Similar to the conventional dispersants, these new comb polymer dispersants will show some differences in performance with different gypsums. While in some cases CP-A showed a slight retardation, looking at the full set of data, we conclude within in the dosage range studied that on average that the set times are comparable to the conventional dispersants. CP-B induces better setting characteristics than CP-A.

Summary and Conclusions

A new family of gypsum dispersants has been developed by uniquely modifying the comb polycarboxylates originally developed for use as concrete water reducers. With forecasts calling for energy costs to remain above historical levels, wallboard plants must reduce energy consumption. Moving to lower water to stucco ratios through the use of dispersants reduces production costs through energy savings. Moving to lower water levels also increases both overall plant profitability and return on investment by increasing productivity.

These new comb polymers are true dispersants unlike simple polycarboxylates, which improve flow mainly through set inhibition. The very flexible polymer technology offers the dispersant producer a vast range to options to modify the polymer structure and composition to improve not only the dispersancy of the polymer, but also its secondary performance properties such as hydration rate and set time.

These new dispersants are virtually colorless, thereby virtually eliminating the staining that is the direct result of using the more highly colored conventional dispersants. At typical use levels, the effects on hydration rate and setting induced by these new dispersants are comparable to those of the conventional dispersants. At dosage levels beyond the typical use levels one of the new polymers studied induced a slight set retardation. This can be overcome, if necessary, by using a standard set accelerator. The new comb polymers are highly efficient dispersants, typically reducing the amount of dispersant needed by 50 – 80%. In addition, these new dispersants extend the range of water reduction beyond what is typical obtainable with the conventional dispersants.
These new polymers have been used in commercial wallboard and in other gypsum-based applications for over a year. Improvements will continue to be made to the technology that will offer wallboard producers, along with producers of other gypsum products, even greater performance and flexibility.

References

1 This paper has been edited from the original form.
2 US Patent No. 6527850
4 Reisch, M. S.; Running Low on Gas; Chem. & Eng. News; 19 (July 14, 2003)
5 Short-Term Energy Outlook – June 2003; Energy Information Administration (EIA)
6 Trapmann, W.; EIA’s Outlook on Gas pricing and Storage Deliverability presented at Infocast Conference, June 17, 2003
7 Mariner-Volpe, B.; EIA’s Outlook on Natural Gas presented to the Arkansas Public Service Commission, June 3, 2003
8 Calculations assume a nominal wallboard plant producing 12.5 mm board with a water to stucco ratio of 0.65. Only costs to dry the board are considered.
9 The model takes into account plant design, line speed, drier capacity etc. All raw material, labor, utility and all fixed costs are considered. Current board pricing along with distributor margins and distribution costs are also considered in the model. The model assumes a 7% depreciation on plant capital and a tax rate of 35%.

2541-V2-0604
superseded by 2541-V1-0903