EH&S Impact of Common Water Resistant Additive Technologies in Gypsum Board

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About Henry Company

• Manufacturer of Aqualite Wax Emulsions for the Gypsum Board Industry
• Henry sells Aqualite direct in all the Americas
• Partnered with H&R for manufacturing, sales, and distribution in Europe and Asia Pacific of Aqualite
• Currently developing next generation Aqualite wax emulsion products and additional products to aid processing and provide cost savings in gypsum board plants worldwide
• A leading innovator of Building Envelope Systems®, addressing the principles of integrating air/vapor barrier, roofing and waterproofing systems to ensure superior building performance
Presentation Outline

• Introduction
• Wax Emulsion, Siloxane, and Gypsum Chemistries
• Wax Emulsion and Siloxane in the Manufacturing Process
• Product Storage and Disposal
• Occupational and Regulatory Issues
• Impact on EPA Title V Air Emissions Permits
• New Lab VOC Method
• Results
• Conclusions
Introduction

• Two major methods of imparting water resistance (WR) to gypsum boards are incorporation of wax emulsions and siloxanes

• US market share is approximately 55% wax emulsion / 45% siloxane

• Chemistries and WR mechanisms of each are different

• Wax emulsions commonly considered to be the simplest and safest
Introduction (cont…)

• Siloxanes can be cost effective but present explosion/fire hazards, complex processing conditions, and generate significant VOCs and PM emissions

• A new lab simulation was developed to allow quantification and speciation of VOCs from both wax emulsion and siloxane

• Current assumptions about the overall safety and emissions from the use of wax emulsions and siloxane may be incorrect
Wax Chemistry

- Waxes have been used since early history in many applications including art, lubrication, protection of surfaces, cosmetics, and pharmaceuticals
- There are many types of natural and synthetic waxes
- Waxes are often blended to achieve the desired cost for performance requirements
- Waxes are typically long chain aliphatic molecules with minimal reactivity and hazards in handling
Wax Chemistry (cont…)

- Waxes for gypsum board applications are typically melt blended then emulsified in water to allow room temperature transport to gypsum board plants plus increases the compatibility with aqueous gypsum based slurries.
- Wax emulsions often increase board strength in addition to providing WR properties to gypsum board.
Siloxane Chemistry

- Silanes, siloxanes, and siliconates have historically been used to add WR to masonry and gypsum based materials.
- Polymethylhydrogensiloxane (PMHS) is the family of siloxanes commonly used by the gypsum board industry to impart WR.
- PMHS is a product made by reaction of methylhydrogendichlorosiloxane which is an undesirable by-product produced when making siloxanes.
Siloxane Chemistry (cont...)  

- PMHS reacts with water to further polymerize and releases Hydrogen gas  
- The reaction of PMHS in gypsum board liberates high levels of VOC and PM, especially PM 10 (less than 10 microns) and PM 2.5 (less than 2.5 micron)  
- Siloxanes are often provided containing additives which contribute to the overall VOCs emitted
Gypsum Chemistry

- Industrial Gypsum Chemistry Cycle
Wax and Siloxane in Manufacturing Process

- Wax and siloxane are added to the process at the pin mixer.
- The setting stucco crystallizes to the dihydrate form.
- Siloxane can interfere with the crystallization process and impact board strength and set time.
- Siloxane can also react too slowly and not produce good WR numbers out of the kiln.
- Siloxane WR mechanism is from coated pores that repel liquid water.
Wax and Siloxane in Manufacturing Process (cont…)

- Wax does not interfere with the crystallization process and WR effect is immediate
- Wax particles lock into the gypsum matrix as they melt and flow
- Wax WR mechanism is from blocked pores but does not block water vapour
- Due to the difference in mechanisms and the reaction rate of siloxane, wax emulsions are more forgiving in the broad range of stucco types and purities
Wax and Siloxane WR Mechanisms

**Wax**
- Block pores of matrix
- Tortuous route of water
- Permeable to water vapor

**Siloxane**
- Thin “monomolecular” layer on walls of pores of matrix
- Blocks liquid water
- Permeable to water vapor
Wax and Siloxane WR Mechanisms (cont...)

**Wax**
After external compression forces: wax supports pore structure

**Siloxane**
After external compression forces: pore structure collapses with siloxane
Storage and Disposal

Waxes

- Waxes are innocuous materials and many have been approved by the FDA for direct food contact
- Paraffin is comprised of long chain aliphatic hydrocarbons of very low reactivity and toxicity
- Wax emulsions are roughly 50% water and are not reactive, flammable, or hazardous in storage or handling
- Wax containing gypsum board is readily recyclable both at end of life cycle and scrap production
Storage and Disposal

**Siloxanes**

- Siloxanes are reactive (generate H₂) and need to be stored in smaller vessels and segregated from catalysts and water.
- Air gaps are often recommended to prevent build up of potentially explosive concentrations of H₂.
- Disposal of any spilled or waste siloxane requires proper packaging and disposal in approved hazardous waste disposal facility.
Storage and Disposal

Siloxanes (cont…)

• Siloxanes are classified as hazardous wastes (reactive), acute health hazards, and fire hazards (explosion potential)

• Siloxane containing gypsum board is typically difficult to recycle both at end of life cycle and scrap production
Occupational and Regulatory Issues – Waxes

- Wax emulsions typically consist of paraffin wax, some specialty waxes, polyvinyl alcohol and water and as such are not reactive, flammable, or hazardous to store or handle
Occupational and Regulatory Issues – Siloxanes

- Siloxanes pose a reactive hazard and can generate H₂ in explosive concentrations
- Siloxanes can generate formaldehyde at temperatures above 150°C in the kiln
- Siloxanes are listed as acute health hazards, fire hazards, and toxic wastes on MSDSs
- Siloxanes are listed as hazardous in 29 CFR 1910.1200 which requires a comprehensive hazard communication program and comprehensive MSDS
Occupational and Regulatory Issues – Siloxanes (cont…)

- Siloxanes can also contain volatile processing aids such as heptane or other VOCs.
- Siloxanes often require the use of a catalyst either amine, alkaline, metallic based, or siliconate, all of which have some toxicity character and or hazardous handling requirements.
Impact on Title V Air Permits

Waxes

- Wax emulsions are negligible contributors to VOCs and PM based on review of many US EPA issued air permits
Impact on Title V Air Permits

Siloxanes

- Siloxanes dramatically increase VOC and PM (especially PM10 and PM2.5) emissions when manufacturing gypsum board
- Increased VOC and PM can impose production limitations on some plants (preserve minor source status for PSD) and often require application for permit modification
- Air permits show >5X increase in PM when using siloxane as WR additive
Impact on Title V Air Permits

Siloxanes (con’t…)

- VOCs from siloxane also >5X increase per air permits
- Raises the question, what are these VOCs?
- Henry wanted to understand this better since we were interested in this technology
New VOC Testing Method

• New oven built by ARCADIS to simulate stack VOC emissions
• Total Hydrocarbon (THC) VOC testing has been shown to compare well with stack emissions
• Oven – gas tight, PTFE gasketing, electrical resistance heating, precision mass flow controlled zero grade air, PID temperature controlled oven
• Measurements – THC FID analyzer calibrated to propane equivalents and GC/MS for speciation of VOCs
New VOC Testing Method

• 3 separate analyses by different air quality labs for speciation of the VOCs
• Gypsum boards prepared by experienced board makers
• Boards set until 2X VICAT then 10 X 13cm samples cut from the center of the board and placed in oven at 232°C for 60 min
• Board compositions included controls, wax emulsion, and siloxanes with appropriate catalyst
• VOC emissions data collected in real time during drying
## New VOC Testing Method

### Formulations of Panels Fabricated and Tested at Arcadis

<table>
<thead>
<tr>
<th>Code</th>
<th>Stucco Accel (g)</th>
<th>Water (g)</th>
<th>Stucco (g)</th>
<th>Additive</th>
<th>Additive (g)</th>
<th>Additive (lb/msf)</th>
<th>Catalyst (g)</th>
<th>Catalyst (lb/msf)</th>
<th>Acid Mod Starch (g)</th>
<th>Acid Mod Starch (lb/msf)</th>
<th>TEST</th>
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<tr>
<td>ARCADIS1</td>
<td>0.19</td>
<td>900</td>
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<td>MgO</td>
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<td>6.7 lb/msf</td>
<td>VOC</td>
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<td>Siloxane 1</td>
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<td>MgO</td>
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<td>none</td>
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<td>0.00</td>
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<td>MgO</td>
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<td>0.00</td>
<td>0.00</td>
<td>3.17</td>
<td>TO-15</td>
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New VOC Testing Method

- Board Drying Oven
Results of VOC Testing

Comparisons of ARCADIS Total Emissions of Test Panels during 60 Minute 232°C Drying

<table>
<thead>
<tr>
<th>Additive</th>
<th>Dosage (lb/msf)</th>
<th>Total VOC Over 60min</th>
<th>% Increase</th>
<th>Multiplier Increase</th>
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<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>205</td>
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<td>Wax</td>
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<td>354</td>
<td>72%</td>
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<td>Wax</td>
<td>90</td>
<td>856</td>
<td>317%</td>
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<td>Siloxane 1</td>
<td>8</td>
<td>1,692</td>
<td>621%</td>
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<td>Siloxane 1</td>
<td>12</td>
<td>2,538</td>
<td>1,330%</td>
<td>14.3</td>
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</table>

Comparative VOC Emissions of Panels with Various Additives and Dosages at Specific Points in the 232°C Drying Process

<table>
<thead>
<tr>
<th>Additive</th>
<th>Additive Dosage (lb/msf)</th>
<th>5 Minute Point (ppmv)</th>
<th>12 Minute Point (ppmv)</th>
<th>47 Minute Point (ppmv)</th>
<th>Full Trace Average (ppmv)</th>
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<tr>
<td>No Board</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.05</td>
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<td>No Additive</td>
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<td>9.76</td>
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<td>6.30</td>
<td>9.01</td>
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<tr>
<td>Wax</td>
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<td>11.46</td>
<td>15.86</td>
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<td>24.11</td>
<td>44.85</td>
<td>114.27</td>
<td>57.45</td>
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<td>Siloxane 1</td>
<td>12</td>
<td>40.07</td>
<td>56.30</td>
<td>143.64</td>
<td>78.10</td>
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<td>Siloxane 2</td>
<td>12</td>
<td>51.56</td>
<td>74.68</td>
<td>264.75</td>
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<td>Siloxane 3</td>
<td>12</td>
<td>69.00</td>
<td>89.82</td>
<td>162.22</td>
<td>112.30</td>
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</table>

VOC Drying Emissions Over 60 Minute 232°C Drying

Graph showing VOC emissions over time with various additives and dosages.
Results of VOC Testing

*Henry Oven Data*

VOC Drying Emissions Over 60 Minute 232°C Drying
Results of VOC Testing

Reproducible Results

Statistical Box Plot Comparison of Average VOC Emissions

Average VOC (ppmv propane basis)
Results of VOC Testing

Curve Fit Data

Curve Fitting of VOC Emissions Over 60 Minute 232°C Drying

\[ y = 3E-06x^5 - 0.0005x^4 + 0.0338x^3 - 0.9171x^2 + 11.899x + 1.0088 \]

\[ R^2 = 0.9466 \]
Results of VOC Testing

- GC/MS Speciation of VOCs
- Gas stream collected during drying in six liter vacuum sampling canisters
- VOCs analyzed per EPA Method TO-15 by ERG lab in Research Triangle Park, NC
Results of VOC Testing

- Test lab utilized standards developed for EPA testing of hazardous air pollutants through combined GC/MS and Selective Ion Monitoring (SIM) to improve sensitivity
- VOC data reported in both mass (ug/m3) and volume (ppbv) for the 60 compounds on the EPA TO-15 list
- To confirm these results, additional studies were done at ALS and Air Toxics, Ltd. testing laboratories
# Results of VOC Testing

## Consolidated Results of VOCs Identified per EPA TO-15 by ARCADIS-ERG (ppbv)

<table>
<thead>
<tr>
<th>CAS#</th>
<th>Code</th>
<th>Sample</th>
<th>7 Siloxane (8 lb/mst)</th>
<th>8A Siloxane (12 lb/mst)</th>
<th>9 Wax (50 lb/mst)</th>
<th>10 Wax (60 lb/mst)</th>
<th>Safety NFPA</th>
<th>Safety HMIS</th>
<th>Safety Toxicity (ppmv)</th>
<th>Safety PEL TWA (ppmv)</th>
<th>DOT Placard</th>
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<tbody>
<tr>
<td>108-88-3</td>
<td>Toluene</td>
<td>475.0</td>
<td>1,240.0</td>
<td>1,390.0</td>
<td>2,130.0</td>
<td>2</td>
<td>2</td>
<td>500</td>
<td>200</td>
<td>Irritant, Flammable</td>
<td></td>
</tr>
<tr>
<td>74-87-3</td>
<td>Chloroform</td>
<td>96.9</td>
<td>41.5</td>
<td>21.5</td>
<td>24.8</td>
<td>3</td>
<td>3</td>
<td>2,000</td>
<td>100</td>
<td>Toxic, Flammable</td>
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<td>107-02-8</td>
<td>Acetone</td>
<td>62.0</td>
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<td>4</td>
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<td>111-65-9</td>
<td>n-Octane</td>
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<td>500</td>
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<td>87-68-3</td>
<td>Hexachloro-1,3-butadiene</td>
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<td>Na</td>
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<td>5.0</td>
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<td>2</td>
<td>500</td>
<td>50</td>
<td>Irritant, Carcinogen</td>
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<td>75-05-8</td>
<td>Acetonitrile</td>
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<td>2.9</td>
<td>44.9</td>
<td>17.9</td>
<td>2</td>
<td>2</td>
<td>500</td>
<td>40</td>
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<tr>
<td>95-63-6</td>
<td>1,2,4-Trimethylbenzene</td>
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<td>1.6</td>
<td>3.5</td>
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<td>2</td>
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<td>Na**</td>
<td>None</td>
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<tr>
<td>108-38-3</td>
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<td>1.1</td>
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<td>2</td>
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<td>3,000</td>
<td>200</td>
<td>Flammable Liquid</td>
<td></td>
</tr>
</tbody>
</table>

**1** Hazardous Material Identification System (HMIS): 0-Least, 1-Slight, 2-Moderate, 3-High, 4-Extreme

**2** National Institute for Occupational Safety and Health (NIOSH) Immediately Dangerous to Life or Health Concentrations (IDLH)

**3** Ethylbenzene and n-Octane IDLH toxicity values are based on 10% of the lower explosive limit

**4** OSHA Permissible Exposure Limits (PEL), Time Weighted Average (TWA), from NIOSH Pocket Guide to Chemical Hazards, for up to 10 hr workday during 40 hr

**5** DOT Placard Information from MSDS

*None Detected (ND)*

*Not Available (Na)*
## Results of VOC Testing

<table>
<thead>
<tr>
<th>CAS#</th>
<th>Collection Time (Minutes)</th>
<th>Sample Code</th>
<th>60 ALS2 Control</th>
<th>60 ALS8W Wax</th>
<th>60 ALS8S1 Silicone 1</th>
<th>7 ALS8S1 Silicone 1 1st peak</th>
<th>13 ALS8S1 Silicone 1 2nd peak</th>
<th>40 ALS8S1 Silicone 1 3rd peak</th>
<th>60 ALS8S1 Silicone 2</th>
<th>80 ALS8S1 Silicone 2</th>
<th>REL Turnbull ppm</th>
<th>ppm</th>
<th>Other</th>
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<tbody>
<tr>
<td>100-46-0</td>
<td>1,3-dimethylacetone</td>
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</tr>
</tbody>
</table>

Note: ND - Not detected, NA - Not available
Results of VOC Testing

- VOC Summary
  - Largest portion of VOCs from siloxane systems are siloxane fragments
  - Emission are due to reactions and subsequent volatilization of material during the curing process
  - Several HAPs from siloxane use, most notably that from HCBD
  - Siloxane VOC emissions are much greater than wax VOC emissions
  - Wax emulsion VOC emissions may contain some processing/purification materials from the wax manufacturing process
  - Total board emissions may also include VOC from additional board components such as facers
Conclusions

• Siloxane produces VOC emissions with an average 10X greater than wax and up to 100X during peak emissions
• Siloxane dose would need to be reduced to ~1lb/MSF to equal the emissions of wax
• Siloxane generates one of the more toxic air pollutants (HCBD) on the TO-15 list
• Siloxane use in gypsum board plants generates significant PM, especially PM10 and PM2.5
Conclusions (cont…)

• Increased emissions will impact EPA air permitting

• Wax emulsions are the simplest, safest, most robust, and the most environmentally friendly option

• Gypsum board producers striving to be environmentally responsible and minimize adverse impacts from their process may select wax emulsions in the future

• Gypsum board end-users likely to prefer a more environmentally friendly option
EH&S Impact of Common Water Resistant Additive Technologies in Gypsum Board

Mark R. Adams
Henry Company