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**Environmental, Health, & Safety Impact of Common  
Water Resistant Additive Technologies In Gypsum  
Wallboard Production**

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## **Summary**

The two major commercial methods for making gypsum board water resistant are through incorporation of hydrocarbon wax emulsions or polymethylhydrogensiloxane (PMHS) into the gypsum slurry during board manufacture. While the chemistry and water resistance (WR) mechanisms of these two additives are quite different, they accomplish the same basic task in gypsum board. Any effective WR additive must reduce the level of water absorbance from over 40% for non-WR board to the ASTM specifications of less than 10% for Gypsum Sheathing and less than 5% for Water Resistant Gypsum Backing Board. Currently the US market share by plant of wax emulsions and PMHS is about 55% and 45% respectively<sup>1</sup>.

While both additives enjoy significant utilization in the industry, their overall environmental impact and worker safety aspects are dramatically different. In order to better understand these differences, Henry has recently published a technical white paper covering the EH&S considerations of both additives<sup>2</sup>. In this paper the chemistries and applications of wax emulsion, siloxane, gypsum and their interactions in the gypsum wallboard manufacturing process are discussed. In order to better understand quantitatively the differences in volatile organic content (VOC) contribution, a new laboratory method for comparison of VOC emissions during a simulated wallboard drying schedule was created. This method requires a special oven apparatus that was designed and fabricated to simulate EPA's Method 25 for testing plant stack emissions. Panel air emissions of VOCs over a typical plant drying schedule were determined and the types and quantities of air pollutants were identified. Although panels made with both wax emulsions and siloxane generated VOCs during the kiln drying process, the contribution of VOC emissions levels from siloxane panels were substantially higher, by as much as a factor 100 times during peak emissions of the wax emulsion containing panels. In addition, the VOCs created by siloxane contained a number of Hazardous Air Pollutants (HAPS) that may be a concern. It was also observed from various literature sources that siloxane contributed significantly to emissions of particulate matter (PM) and more importantly PM fewer than 10 microns (PM10), while the use of wax emulsions does not contribute to PM emissions in the wallboard process. According to the EPA, PM10 poses a health concern because it can be inhaled into and accumulate in the respiratory system. Particles less than 2.5 micrometers in diameter (PM2.5) are referred to as "fine" particles and are believed to pose the greatest health risks. Because of their small size, fine particles can lodge deeply into the lungs where they are more vulnerable to injury. Roughly one out of every three people in the United States is at a higher risk of experiencing PM2.5 related health effects.

This paper concluded that in situations where government emissions permitting is a concern for a specific manufacturing plant, wax emulsion use as a WR agent is recommended over siloxanes. Plants attempting to switch from wax emulsions to siloxanes need to address the specific HAPS created during the drying process, total VOCs emitted in order to stay in compliance with local EPA standards, and make efforts to mitigate the increased PM emissions (especially PM10 and less) otherwise air permit modifications may be required.

## **WAX CHEMISTRY**

Wax emulsions provide WR due to their hydrophobicity and distribution in the wallboard matrix. There is little wax emulsion chemistry that takes place during the manufacturing of the wallboard, merely evaporation of water with incorporation and distribution of the wax throughout the wallboard.

Although there are many types of waxes including Animal waxes<sup>3,4</sup>, Plant waxes<sup>3,5</sup>, Mineral waxes<sup>6,7</sup>, and Synthetic waxes<sup>5</sup>, it is typical to blend these to achieve the target end properties of the application with

the lowest cost. Typical wax emulsions designed for incorporation into the gypsum slurry are composed of a blend of paraffin and other waxes, emulsifiers, and stabilizers. The latter materials enable stability of the wax emulsion for shipping and storage prior to addition to the gypsum slurry, as well as compatibility in the aqueous gypsum slurries. These emulsions upon addition to the gypsum wallboard slurry improve both WR and strength of the wallboard end product. Since paraffins are straight chained alkanes with no double bonds or easily reactive groups, they tend to be of very low reactivity and toxicity.

## **SILOXANE CHEMISTRY**

Using siloxanes is more complex and involves chemical reactions that occur during the wallboard manufacturing process. The simplest theory published to explain the mechanism involves two reactions. The first siloxane reaction in the gypsum slurry is hydration at the hydrogen site to generate a hydroxyl group on the siloxane with resulting hydrogen gas ( $H_2$ ) generation. The second siloxane reaction involves the cleavage of trimethylsilanol end groups to allow endwise polymerization to the WR methylsilicone network. Trimethylsilanol is volatile and moves from the board core to the board surface with the water liquid and vapor. The trimethylsilanol condenses to form spherical amorphous silica particles similar in appearance to fumed silica which deposits on the interior of kiln components such as glass windows and even the impellers of forced air fans.

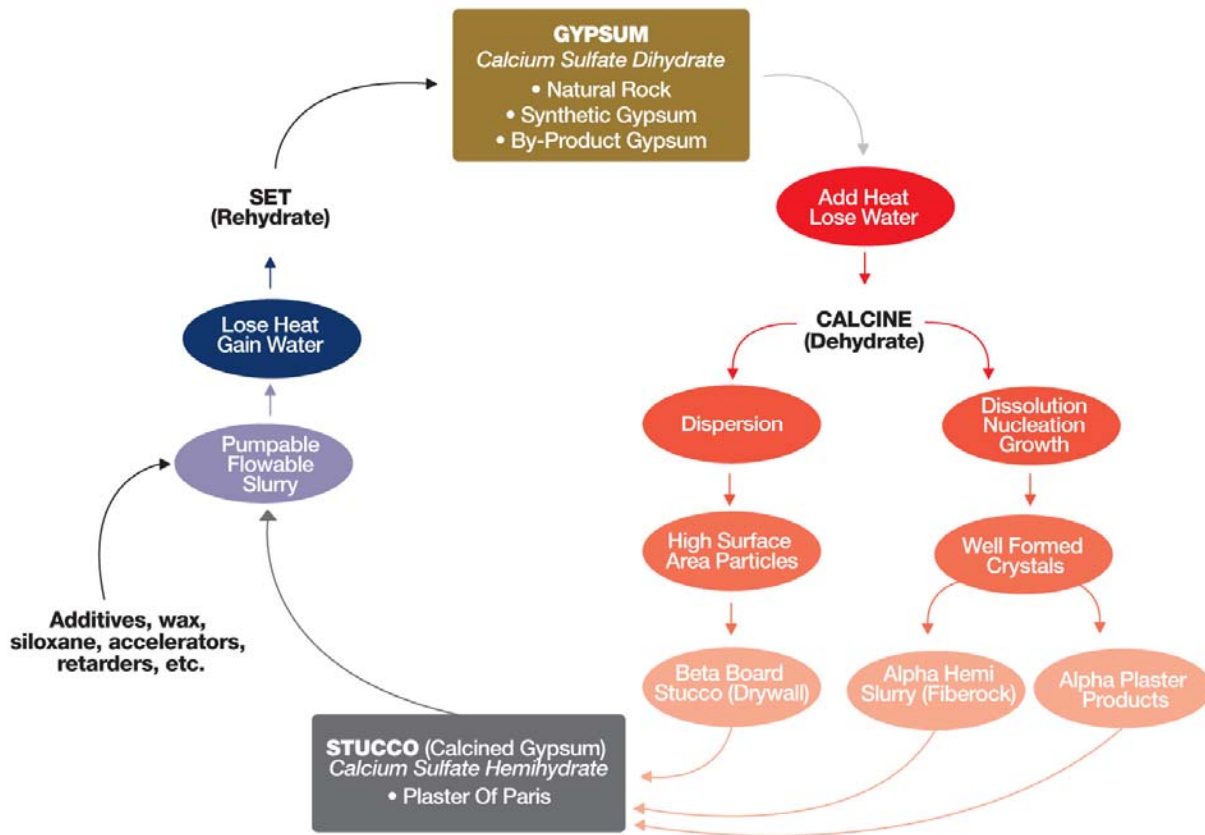
In an effort to compare these two techniques and understand the process requirements of using either chemistry, a test protocol was developed and laboratory test equipment built to measure the amount and identify of the VOCs generated during wallboard manufacturing using both products.

## **GYPSUM CHEMISTRY**

Gypsum is a calcium sulfate hydrate crystal with an average of two molecules of water per molecule of calcium sulfate ( $CaSO_4 \cdot 2H_2O$ ). One major source of gypsum is from mines of natural gypsum deposits. The second major source of gypsum is synthetic gypsum, usually from the sulfur scrubbing of coal powered electric generation. This gypsum is called flue gas desulfurization gypsum or FGD gypsum.

For wallboard applications, the gypsum is heated to calcine and remove some of the water of crystallization to generate calcium sulfate hemihydrate with an average of  $\frac{1}{2}$  molecule of water per molecule of calcium sulfate ( $CaSO_4 \cdot \frac{1}{2}H_2O$ ). This stucco is then mixed with other additives and water to give a flow able slurry that is applied between two sheets of paper or other surfacing materials. The stucco then rehydrates to form the starting gypsum dihydrate material and excess moisture is dried off in a kiln before final stacking and shipping. Figure 1 shows the industrial chemistry of this gypsum cycle.

Figure 1: Industrial Gypsum Chemistry Cycle



## WAX AND SILOXANE IN THE WALLBOARD MANUFACTURING PROCESS

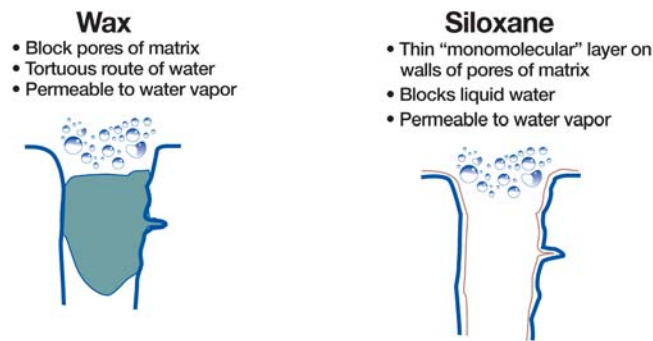
As shown in the gypsum cycle above, the WR additive is added to the stucco slurry at the pin mixer of the wallboard manufacturing line. While on the forming table and prior to the kiln, the hemihydrate stucco sets and stiffens back to the dihydrate form locking the additives in place and forming a strong, porous structure to the board.

When the drying temperature of the board core increases to the melt point of the wax fractions, the wax flows to increase coverage and locks into the gypsum or gypsum/paper matrix around the wax particle. The WR mechanism of the wax is to block pores in the matrix and protect the dried board from liquid water intrusion. All of the pores are not fully blocked however so gases including water vapor can still pass through the panel. WR from wax emulsions is due to microscopic particles of wax<sup>8</sup> which are uniformly dispersed throughout the board.

For siloxane, water repellency is achieved through a thin layer of siloxane adsorbed onto the gypsum crystals. It appears to coat the walls of the pores but does not occlude pore openings allowing water vapor to escape. The low affinity of water for siloxane on the gypsum matrix then slows liquid water ingress. If the siloxane reaction is too late in the process and little water is available for the remaining siloxane reactions due to drying, the board will exit the kiln with poor WR and will require storage in the warehouse until the siloxane has absorbed sufficient moisture from the air to complete the reaction and achieve the desired WR.

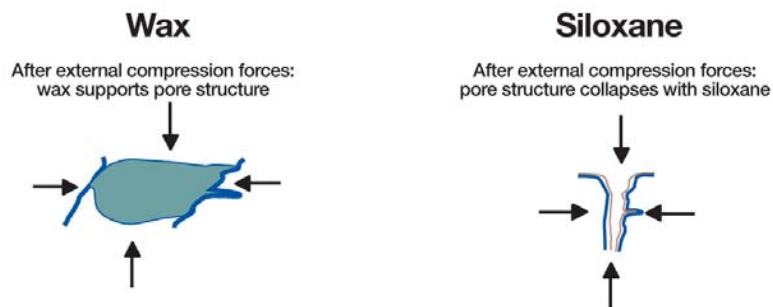
With regard to impurities in the starting gypsum, wax emulsions, are more forgiving toward lower purity gypsum. Generally, the more intricate the binding mechanism, the more susceptible to impurities and side reactions the water repellency process will be. This may explain why some stucco sources are not efficient with siloxane but work well with wax.

Figure 2: Longitudinal Section of Typical Gypsum Matrix Pore with Wax and Siloxane WR Additive



The pore blocking mechanism described above may also explain the increased strength often found with wax emulsion treated panels. The siloxane treated pore walls offer little resistance to load, while the wax particle reinforces the pore of the matrix and absorbs some of the load energy in ductile deformation as shown in Figure 3.

Figure 3: Compression Loading and Deformation of Gypsum Matrix Pore with Wax and Siloxane WR Additive



## **STORAGE AND DISPOSAL**

Wax emulsions are typically innocuous materials and many have been FDA approved for human contact or contact with food. As an emulsion of roughly half water, it is neither reactive nor flammable. As such, there are no unusual hazards with storage and disposal.

Siloxanes are typically stored in smaller containers than wax emulsions in wallboard plants for safety. Siloxane, catalysts, and water need to be segregated from each other to minimize reactions resulting in H<sub>2</sub> generation and potential explosion. Storage containers for siloxane should be stainless steel or plastic (as is common in 300 gallon totes) and sealed to keep out atmospheric moisture.

Blending of any spilled siloxane, use of secondary containers (containing rust, metal soaps, acids, bases, or other incompatible materials) or other accidental contamination can release high localized concentrations of H<sub>2</sub> and create an explosion risk. Although the auto ignition temperature for H<sub>2</sub> is 530°C, it can be ignited by sparks and has even been reported to be ignited by sunlight<sup>10</sup>.

The evolution of H<sub>2</sub> gas is not always easy to predict due to an induction time after which rapid evolution of gas occurs.

Based upon the potential to release H<sub>2</sub> and its OSHA characterization under SARA 311 and 312<sup>11</sup>, unused siloxane will not be accepted for disposal in municipal solid waste (MSW) incinerators that burn household and non-hazardous wastes. Discarding off-spec or unused chemical by pouring it into the drain or into a septic line is never recommended and could lead to permit violations and explosions or fires.

### **IMPACT ON WALLBOARD LIFE CYCLE**

Gypsum wallboards produced with siloxanes may be difficult to recycle both at the end of their life cycle and also in the board making process when scrap boards are generated. As these boards are ground up and put back through the board making process, they can result in high water absorbance variability often resulting in significantly higher dosage levels of siloxane to achieve the desired WR levels as well as disruption of the board core structure generating blisters and blows. As a result producers are sometimes more inclined to land fill waste boards rather than recycle them back into their process.

Water resistant wallboard produced with wax emulsions is readily recyclable both at end of life cycle as well as scrap boards. Wax emulsion that makes its way into the equipment, process, or recycle water does not disrupt subsequent board manufacture and actually can remain active in imparting WR properties to subsequent boards.

### **OCCUPATIONAL AND REGULATORY ISSUES**

#### **Polymethylhydrogensiloxanes (PMHS)**

Although PMHS is not a fire hazard in itself, it must be considered a reactive hazard due to generation of H<sub>2</sub> gas and a flammable hazard due to its flammability. MSDSs have classified this material as a hazardous waste (reactive), which limits its disposal to hazardous waste incineration or solidification. As a general rule, siloxanes should not be shipped by air. Problems can occur in the handling of this material if it is either spilled or transferred to another container. Assumptions in the MSDSs generally apply to siloxane that has not been spilled, transferred, or contaminated.

Another hazard is the potential generation of formaldehyde at temperatures in excess of 150°C in the presence of oxygen. The temperature of the drying air in most wallboard kilns is in excess of 150°C. Formaldehyde is a skin and respiratory sensitizer, eye and throat irritant, acute toxicant, and potential cancer hazard.

MSDSs also list siloxane as an acute health hazard and a fire hazard under SARA 311, 312 Hazard Class.

### Wax Emulsion

Wax emulsions typically consist of paraffin and other waxes, polyvinyl alcohol, and water. The amount can vary, but roughly 50% of this material is water. It is not reactive or flammable and would not be considered a hazardous waste upon disposal. Unlike the siloxanes, this material will not form explosive mixtures upon incineration or lead to increased VOC or PM emissions in stack gases.

## **IMPACT OF PMHS ON WALLBOARD PRODUCTION BASED ON TITLE V AIR EMISSION PERMITS**

US EPA Title V air permits for wallboard plants were examined for indications of the effects of siloxane use on air emissions of PM and VOC.

One negative by-product of the use of siloxanes is silicon dioxide (SiO<sub>2</sub>) which is produced during the drying of siloxane treated wallboard. Increasing PM and PM10 emissions alone may necessitate a modification of the facility's Title V permits. The EPA's national air quality standards for fine particles, also known as PM2.5 standards, are levels allowed in the outdoor air for PM2.5 microns in diameter or smaller. EPA issued PM2.5 standards in 1997 to protect human health and the environment. Studies have linked increased exposure to PM 2.5 to increases in premature death as well as a range of serious respiratory and cardiovascular effects. Siloxane use in wallboard plants significantly increases PM emission levels. These volatile siloxane by-products can also cause secondary damage to wallboard processing equipment, in particular kiln bearings and drive mechanicals as well as build-up on kiln windows and air re-circulating fan blades.

US wallboard producers typically must maintain Title V air permits granted by US EPA in conjunction with state programs. Even small increases in PM may trigger regulatory scrutiny including PSD (prevention of significant deterioration) review which can result in requirements to install emissions controls.

A consistent thread through these permits is that higher VOC and PM/PM10 emissions are observed with use of siloxanes as the WR additive for gypsum wallboards versus wax emulsion additives. These increases often resulted in production limitations on WR board on an annual basis.

## **MATERIALS & METHODS**

In order to investigate the relative VOC emissions during drying of panels made with wax emulsions or PMHS WR additives, laboratory panels were prepared and tested using a small scale drying oven discharging to a Total Hydrocarbon Detector. ARCADIS has developed an oven-testing procedure to evaluate total hydrocarbon (THC) emissions from gypsum boards. The THC results from the board oven testing procedure have historically compared well with stack results for similar products<sup>13</sup>. The THC analyzer breaks down organic constituents to determine THCs. It does not discriminate the type of organic compounds being decomposed, but aggregates all organic compounds based on the carbon content. By convention, the concentration reported by the THC analyzer is reported in terms of the gas used to span the analyzer. Propane was used in this case and the results are reported as "propane equivalents".

Initial third party testing was done at the ARCADIS's Research Triangle Park, North Carolina lab where total VOC and speciation of the individual compounds from the EPA TO-15 list using GC/MS were performed for two levels of wax dosage and two levels of PDMS dosage. The local ERG lab was used for

the speciation analysis.

A similar emissions test oven was set up at the Henry Company Kimberton, Pennsylvania Research & Development Center where additional VOC and TO-15 testing was done. A photo of the apparatus is shown in Figure 4.

Figure 4: Henry Company Emissions Oven Apparatus



#### Total VOC Comparison

Effective dosage rates of WR additives are dependent on differing chemistries of individual plant stucco slurries and can vary from plant to plant with the gypsum used for the stucco. Siloxane dosage rates of 8 pounds/MSF and 12 pounds/MSF were chosen for this study as the range of dosage commonly used commercially in wallboard plants to achieve target immersion properties of WR panels. Likewise, 50 pounds/MSF and 90 pounds/MSF dosages were chosen for wax to give similar water immersion protection as the siloxane dosages. Boards were prepared by experienced board makers, with the formulations shown in Table 1. It should be noted that siloxanes were used in conjunction with a common catalyst at industry standard levels.

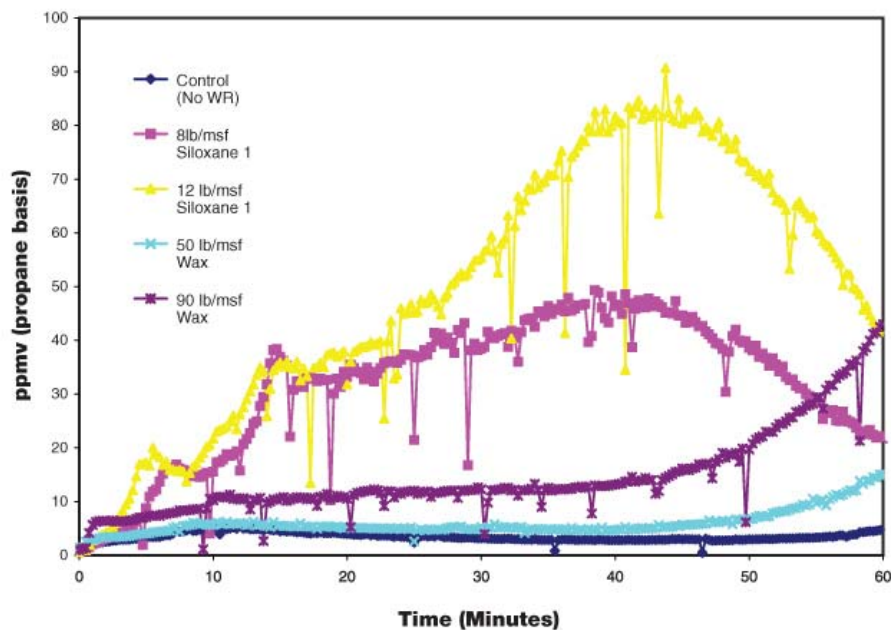
#### Table 1: FORMULATIONS OF THE PANELS AT ARCADIS

## FORMULATIONS OF PANELS FABRICATED AND TESTED AT ARCADIS

Code	Stucco Accel (g)	Water (g)	Stucco (g)	Additive	Additive (g)	Additive (lb/msf)	Catalyst	Catalyst (g)	Catalyst (lb/msf)	Acid Mod Starch (g)	Acid Mod Starch (lb/msf)	TEST
ARCADIS1	0.19	900	900	none	0.0	0.0	none	0.00	0.00	3.17	6.7 lb/msf	VOC
ARCADIS2	0.19	900	900	Wax	3.8	8.0	MgO	1.89	4.00	3.17	6.7 lb/msf	VOC
ARCADIS3	0.19	900	900	Siloxane 1	5.8	12.0	MgO	2.88	6.00	3.17	6.7 lb/msf	VOC
ARCADIS4	0.19	900	900	Wax	24.0	50.0	none	0.00	0.00	3.17	6.7 lb/msf	VOC
ARCADIS5	0.19	900	900	Wax	45.0	90.0	none	0.00	0.00	3.17	6.7 lb/msf	VOC
ARCADIS6	0.19	900	900	none	0.0	0.0	none	0.00	0.00	3.17	6.7 lb/msf	TO-15
ARCADIS7	0.19	900	900	Siloxane 1	3.8	8.0	MgO	1.89	4.00	3.17	6.7 lb/msf	TO-15
ARCADIS8	0.19	900	900	Siloxane 1	5.8	12.0	MgO	2.88	6.00	3.17	6.7 lb/msf	TO-15
ARCADIS9	0.19	900	900	Wax	24.0	50.0	none	0.00	0.00	3.17	6.7 lb/msf	TO-15
ARCADIS10	0.19	900	900	Wax	45.0	90.0	none	0.00	0.00	3.17	6.7 lb/msf	TO-15

The boards were then immediately cut to 10X13cm size and placed in an electric resistance heated oven where the emissions over the drying period were monitored by a total VOC Flame Ionization Detector (FID) using a hydrogen flame. VOC emission data were collected in real time during drying. The graphs of VOC emissions over the drying interval for the five types of test panels are shown in Figure 5.

Figure 5: VOC Drying Emissions from ARCADIS samples



### TO-15 Comparison

A second set of identical panels was prepared and emissions collected in vacuum cans for Gas Chromatography/Mass Spectrometer (GC-MS) speciation per EPA Method TO-15<sup>14</sup> by the ERG lab in Durham, North Carolina. This test lab has developed standards for EPA testing of hazardous air pollutants and combines their GC-MS method with SIM (Selective Ion Monitoring<sup>15</sup>) to improve accuracy and resolution of pollutant identification. Data were reported as a quantity in both a mass ( $\mu\text{g}/\text{m}^3$ ) and a volume (ppbv) basis for each of the 60 compounds on the EPA TO-15 Air Toxics list. Two additional testing laboratories, ALS and Air Toxics, Ltd. were used for additional studies.

## **RESULTS**

### **VOC Emissions**

Emissions of the panels were compared using the area under the VOC emissions curve (see previous Figure 5) over the 60 minute drying cycle. A simple trapezoidal rule was applied to the spreadsheet for the calculation. This gave a total VOC emission over the 60 minute drying period. These relative emissions (ppmv minutes) are compared in Table 2.

Table 2: Comparisons of Emissions of Test Panels

<b>Comparisons of ARCADIS Total Emissions of Test Panels during 60 Minute 232°C Drying</b>				
<b>Additive</b>	<b>Dosage (lb/msf)</b>	<b>Total VOC Over 60min</b>	<b>% Increase</b>	<b>Multiplier Increase</b>
Control	0	205	0%	1.0
Wax	50	354	72%	1.7
Wax	90	856	317%	4.2
Siloxane 1	8	1,892	821%	9.2
Siloxane 1	12	2,938	1,330%	14.3

All additives increased emissions over that of the control panel. The siloxane group emitted substantially more than the wax group. ARCADIS estimates of the VOC emissions for the 12 lbs/MSF siloxane, 90 lbs/MSF wax emulsion, and the control no WR additive systems were 152.1 tpy VOC, 22.4tpy VOC, and 5.3 tpy VOC respectively. These estimates show the increased risk of VOC EPA air quality violations with the use of siloxanes.

Models were developed for the data to allow comparisons of VOC emissions at the same point in the drying process.

Table 3: Comparative VOC Emissions of Various Additives and Dosages

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

Additive	Additive Dosage (lb/msf)	5 Minute Point (ppmv)	12 Minute Point (ppmv)	47 Minute Point (ppmv)	Full Trace Average (ppmv)
No Board	0	0.00	0.00	0.01	0.05
No Additive	0	9.76	14.12	8.48	10.87
Wax	50	6.30	9.01	8.31	10.62
Wax	90	11.46	15.85	19.27	19.03
Siloxane 1	8	24.11	44.85	114.27	57.45
Siloxane 1	12	40.07	56.30	143.64	78.10
Siloxane 2	12	51.56	74.58	264.75	87.40
Siloxane 3	12	69.00	89.82	182.22	112.30

TO-15 Speciation Results

The TO-15 GC-MS data sheets from the ARCADIS ERG testing were consolidated and sorted by the compounds in greatest abundance in the can sample. A summary is shown in Table 4, ranked from highest to lowest for the high siloxane dosage panel, of the 17 most abundant compounds in the board drying emissions to give a comparison of wax versus siloxane and the high and low dosages of each. A comparison of relative toxicity, based on the NIOSH Immediately Dangerous to Life or Health Conservation Level (IDLH) is shown in the first column. Other columns list relative safety comparisons based on NFPA and HMIS safety ratings as well as the required Department of Transportation (DOT) placards. PEL TWA is the OSHA Permissible Exposure Limits based on a Time Weighted Average for an 8 hour day over a 40 hour work week.

Table 4: Consolidated Results of Hazardous Compounds Identified per EPA TO-15 by ARCADIS/ERG

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

CAS#	Code → Sample →	7 Siloxane 1 (8lb/msf)	8A Siloxane 1 (12 lb/msf)	9 Wax (50 lb/msf)	10 Wax (90 lb/msf)	Safety NFPA	Safety HMIS <sup>1</sup>	Safety Toxicity <sup>2</sup> (ppmv)	Safety PEL TWA <sup>4</sup> (ppmv)	DOT Placard <sup>5</sup>
108-88-3	Toluene	476.0	1,240.0	1,390.0	2,130.0	2	2	500	200	Irritant, Flammable
74-87-3	Chloromethane	98.9	41.5	21.5	24.8	3	3	2,000	100	Toxic, Flammable
107-02-8	Acrolein	62.0	37.0	56.4	57.7	4	4	2	0.1	Poison, Inhalation Hazard, Flammable Liquid
111-65-9	n-Octane <sup>3</sup>	20.4	23.9	23.7	17.7	2	0	1,000 <sup>3</sup>	500	Flammable Liquid
87-68-3	Hexachloro-1,3-butadiene	0.8	6.8	ND <sup>*</sup>	ND <sup>*</sup>	3	3	na <sup>**</sup>	0.02	Poison, Toxic, Irritant, Carcinogen
115-07-1	Propylene	12.2	6.7	9.8	10.9	0	0	na <sup>**</sup>	na	Flammable Gas
67-66-3	Chloroform	3.8	5.0	4.1	3.9	2	2	500	50	Irritant, Carcinogen
75-05-8	Acetonitrile	1.8	2.9	44.9	17.9	2	2	500	40	Flammable Liquid
95-63-6	1,2,4-Trimethylbenzene	8.3	1.6	3.5	2.0	2	1	na <sup>**</sup>	none	Combustible Liquid
108-38-3	m-Xylene	8.6	1.4	3.1	4.9	2	2	900	100	Irritant, Flammable Liquid, Reproduction Hazard
106-42-3	p-Xylene	8.6	1.4	3.1	4.9	2	2	900	100	Irritant, Flammable Liquid, Reproduction Hazard
75-15-0	Carbon Disulfide	2.0	1.3	2.1	2.0	2	2	500	20	Flammable Liquid
74-86-2	Acetylene	1.7	1.0	1.4	1.6	1	1	na <sup>**</sup>	none	Flammable Gas
71-43-2	Benzene	1.3	0.9	1.7	2.3	2	3	500	1	Toxic, Carcinogen, Flammable
100-41-4	Ethylbenzene <sup>3</sup>	2.7	0.7	1.2	3.0	3	2	800 <sup>3</sup>	100	Flammable Liquid, Irritant, Carcinogen
108-67-8	1,3,5-Trimethylbenzene	1.9	0.6	1.1	1.1	2	2	na <sup>**</sup>	none	Combustible Liquid, Irritant
95-47-6	O-Xylene	2.3	0.5	1.2	2.0	2	2	900	100	Irritant, Flammable Liquid, Reproduction Hazard
78-93-3	Methyl Ethyl Ketone	24.1	ND	23.5	24.3	1	2	3,000	200	Flammable Liquid

<sup>1</sup>Hazardous Material Identification System (HMIS): 0=Least, 1=Slight, 2=Moderate, 3=High, 4=Extreme

<sup>2</sup>National Institute for Occupational Safety and Health (NIOSH) Immediately Dangerous to Life or Health Concentrations (IDLH)

<sup>3</sup>Ethylbenzene and n-Octane IDHL toxicity values are based on 10% of the lower explosive limit

<sup>4</sup>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

<sup>5</sup>DOT Placard Information from MSDS

\*None Detected (ND)

\*\*Not Available (na)

One would expect a greater number and amount of aromatics to be generated from the wax and a greater amount of chlorinated compounds from the siloxane, based on their chemical composition of the raw materials used in their manufacture.

Hexachloro-1, 3 butadiene (HCBD) was the clearest distinction between the wax and siloxane emissions of the EPA TO-15 list. HCBD was only found in the boards made with siloxane, and showed increased emissions as the level of siloxane was increased. None of the other compounds analyzed showed a complete lack in one type of board, while presence in both of the other type of board. As shown in Table 2, HCBD has the highest risk factors of the compounds in the table for both the Hazardous Material Identification System (HMIS) and the National Fire Protection Association (NFPA) systems.

Overall, compared to the wax panel and the control panel, the siloxane samples generated a massive amount of VOC, which were predominately siloxane products as indentified by Air Toxics Ltd. TO-15 results from samples made and collected from the Henry Emissions Oven. This clarifies that the large peaks on the VOC traces over the 60 minute drying period are predominately siloxane-based materials.

Substantially more VOCs are generated than are measured using the EPA TO-15 protocol for hazardous air pollutants. Formaldehyde, for example, and similarly methanol, methane and other alcohols, aldehydes and alkanes, etc. would be measured by the flame ionization detector for total VOC, but not by the TO-15 method. Wallboard plants may need to re-look at levels in permits based on this testing and limitations or restrictions of specific HAPS.

**CONCLUSIONS AND RECOMMENDATIONS**

With average siloxane VOC emissions of greater than 10 times that of the wax, to achieve the reduced emissions of wax, the siloxane dosage would need to be reduced from the 8 to 12 lbs/MSF to around 1 lb/MSF, which would likely be ineffective. Increased VOC emissions will impact plant EPA air emissions permitting. Based on these results, plants switching from wax to PMHS may face EPA penalties or re-

permitting requirements. Based on the data from this new analytical method, plants already running siloxanes may need to re-evaluate previous air permit modifications and resulting production limitations as well as concerns regarding specific HAPS.

If a plant switches from wax to PMHS and still wants to generate saleable WR product, plant stack emissions will increase and may result in EPA penalties, the cost of re-permitting, and/or emissions mitigation costs. PMHS generates a toxic air pollutant that wax does not. This particular compound, HCBd, is one of the more toxic chemical compounds on the EPA TO-15 list. Title V EPA documents of plants switching to siloxane indicate a significant increase in PM as well. Siloxane use in wallboard plants generates significant quantities of PM10 and specifically PM2.5 which is under severe scrutiny.

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