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

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About the Authors

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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

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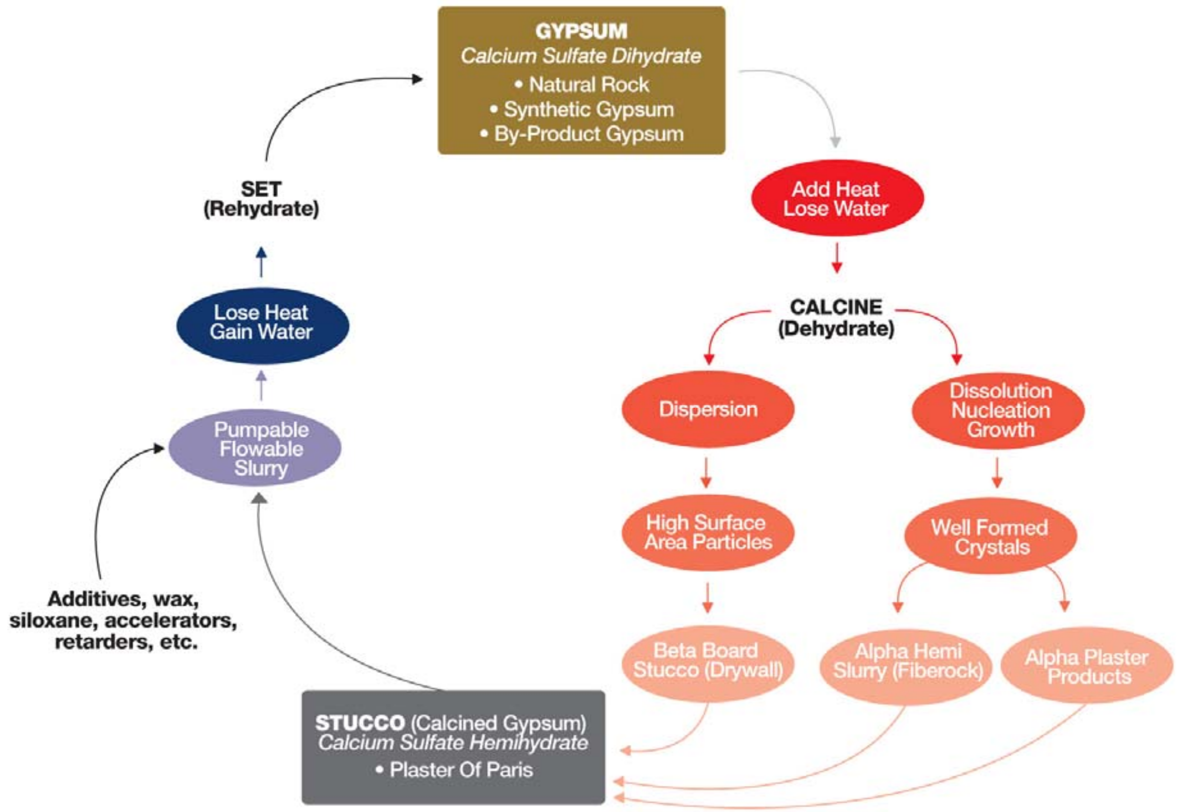
Gypsum Chemistry

- Industrial Gypsum Chemistry Cycle



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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

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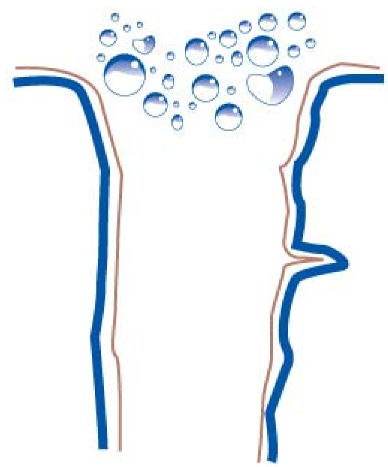
Wax and Siloxane WR Mechanisms

Wax

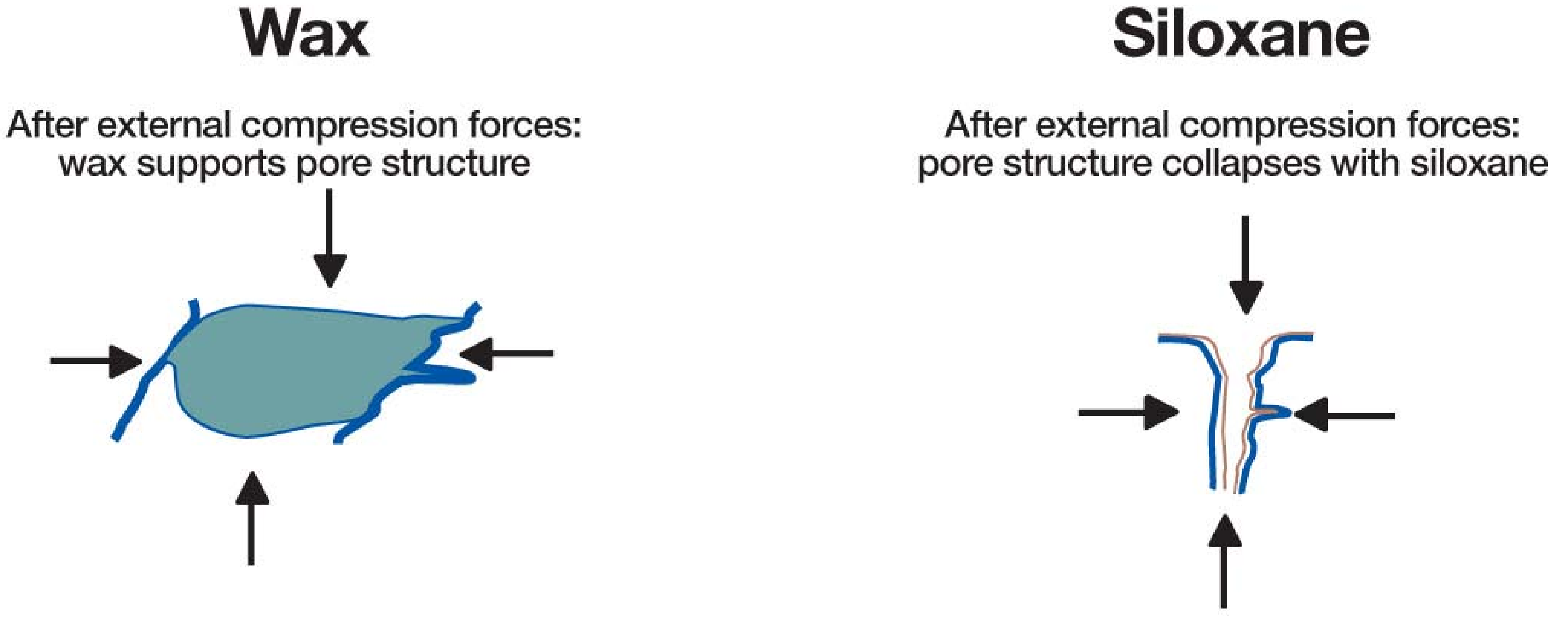
- Block pores of matrix
- Tortuous route of water
- Permeable to water vapor

Siloxane

- Thin "monomolecular" layer on walls of pores of matrix
- Blocks liquid water
- Permeable to water vapor



Wax and Siloxane WR Mechanisms (cont…)



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 H_2) 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 H_2
- 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 H_2 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 siloconate, 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

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

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New VOC Testing Method

- Board Drying Oven

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Results of VOC Testing

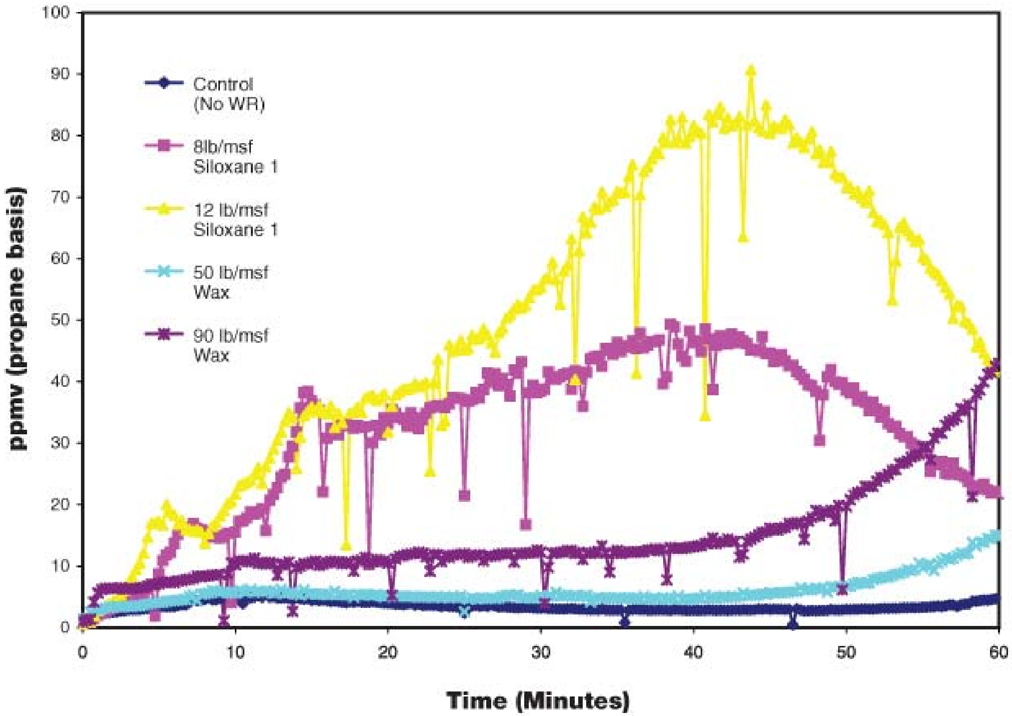
Comparisons of ARCADIS Total Emissions of Test Panels during 60 Minute 232°C Drying

Additive	Dosage (lb/msf)	Total VOC Over 60min	% Increase	Multiplier Increase
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

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

VOC Drying Emissions Over 60 Minute 232°C Drying



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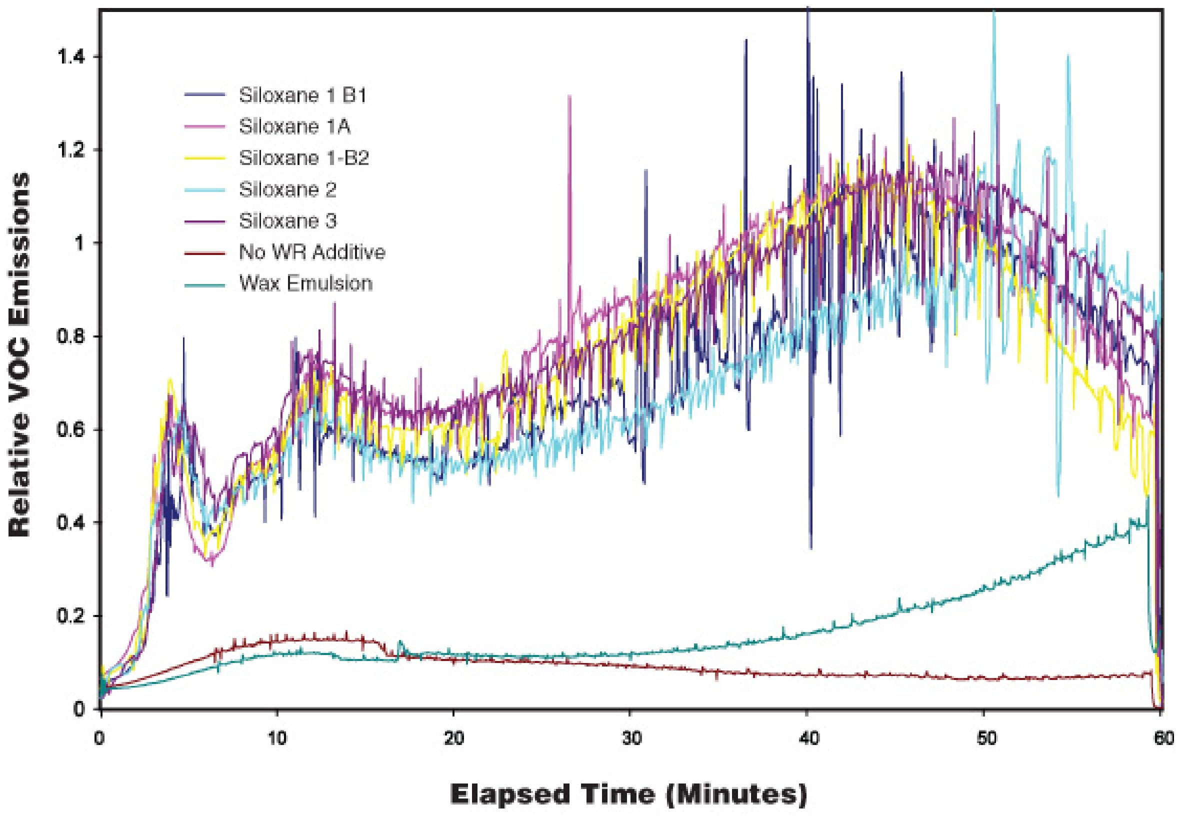
Results of VOC Testing

Henry Oven Data

VOC Drying Emissions Over 60 Minute 232°C Drying



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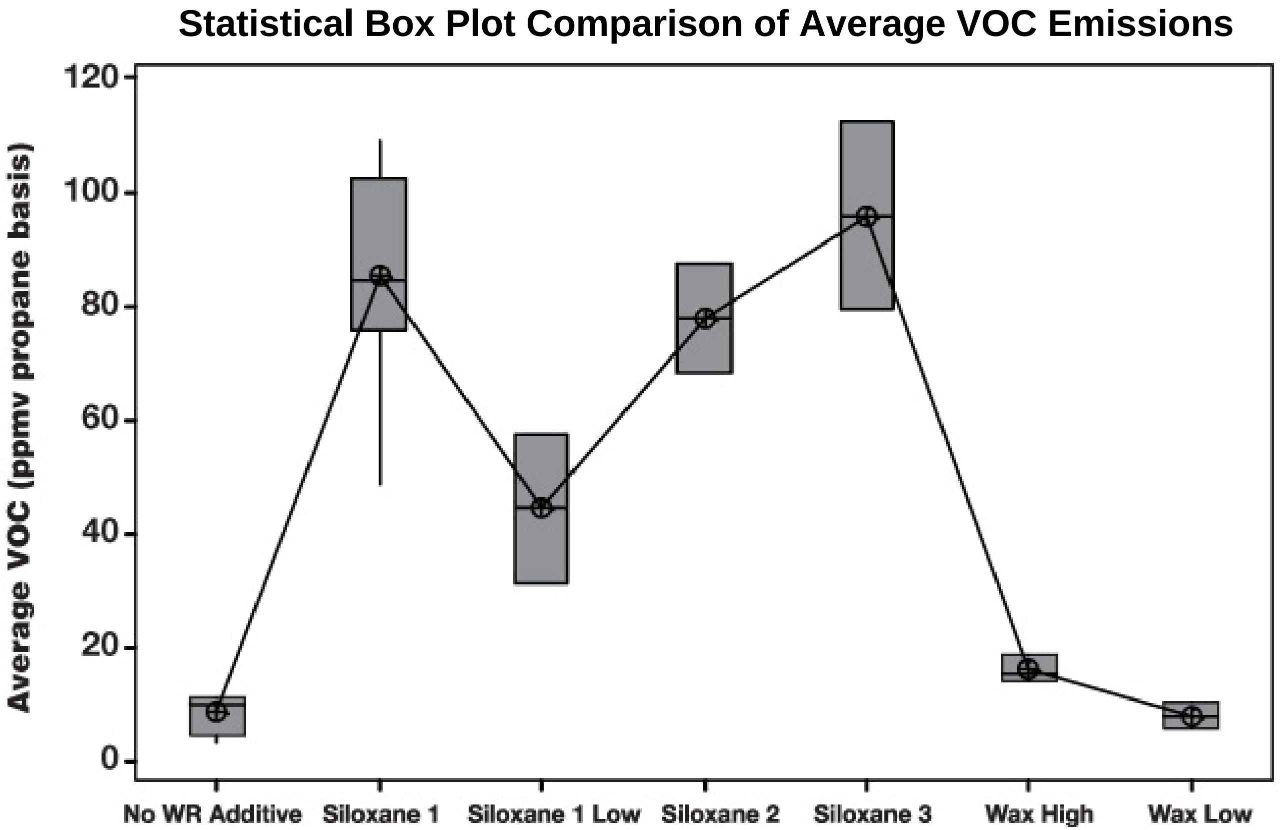
Results of VOC Testing

Reproducible Results



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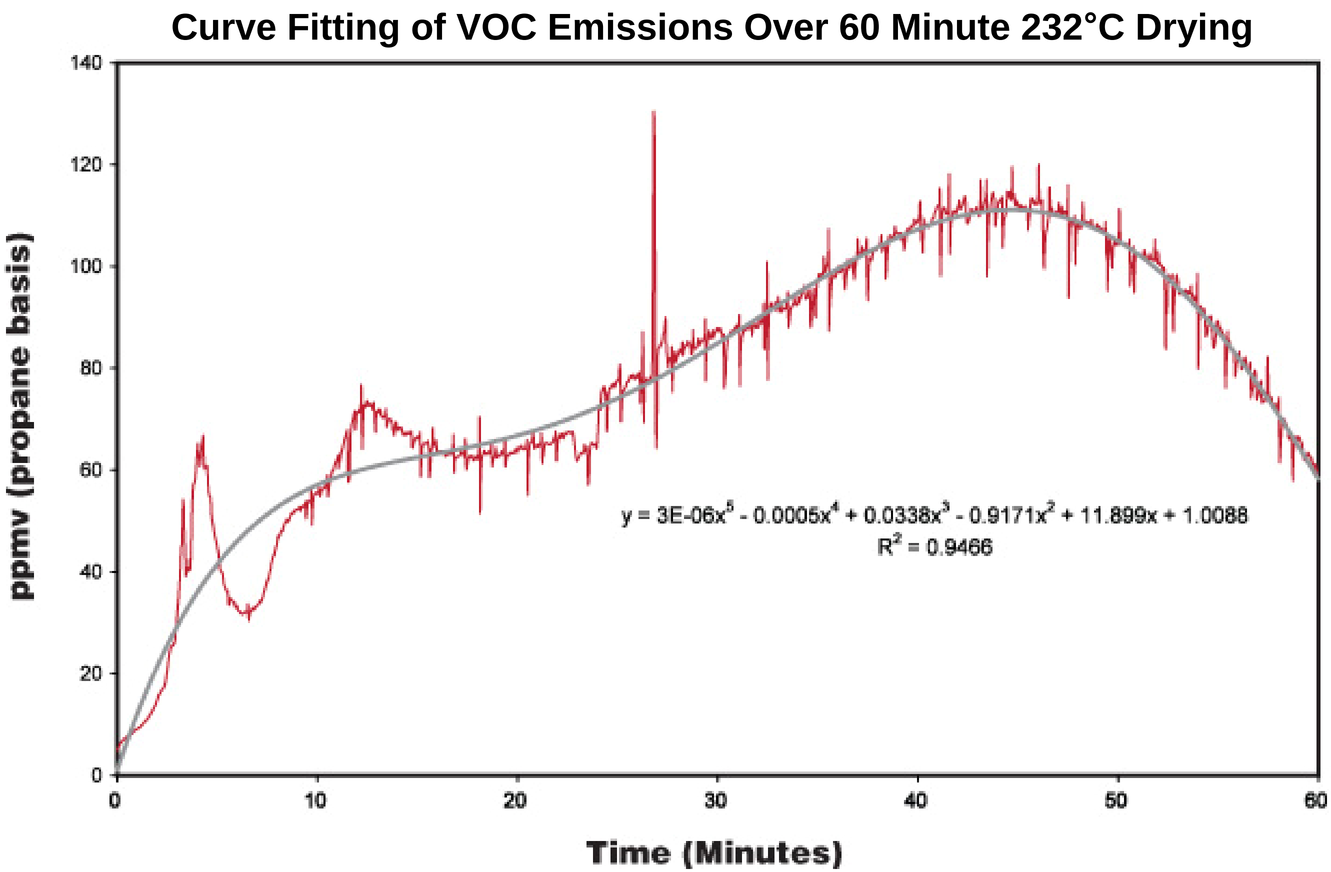
Results of VOC Testing

Curve Fit Data



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

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Results of VOC Testing

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[1]	Safety Toxicity[2] (ppmv)	Safety PEL TWA[4] (ppmv)	DOT Placard[5]
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[3]	20.4	23.9	23.7	17.7	2	0	1,000[3]	500	Flammable Liquid
87-68-3	Hexachloro-1,3-butadiene	0.8	6.8	ND*	ND*	3	3	na**	0.02	Poison, Toxic, Irritant, Carcinogen
115-07-1	Propylene	12.2	6.7	9.8	10.9	0	0	na**	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**	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**	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[3]	2.7	0.7	1.2	3.0	3	2	800[3]	100	Flammable Liquid,Irritant, Carcinogen
108-67-8	1,3,5-Trimethylbenzene	1.9	0.6	1.1	1.1	2	2	na**	none	Combustible Liquid, Irritant
95-47-6	0-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

[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 IDHL 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

ALS Laboratory TO-15 Chemical Compound Speciation Results (ppbv) from Henry Company Emissions Oven Panel Samples with Wax and Three Siloxanes

CAS#	Collection Time (Minutes) Sample Code	60 ALS2 Control Control Board	60 ALS3W Wax	60 ALS4 BSF Siloxane 1	7 ALS5 BS7 Siloxane 1 1st peak	13 ALS5 BS8 Siloxane 1 2nd peak	40 ALS5 BS9 Siloxane 1 3rd Peak	60 ALS5 OM Siloxane2	60 ALS5 MO Siloxane3	PEL TWA[1] ppmv	other
1066-40-6	trimethylsilanol	ND	ND	5479	2145	3854	6188	4096	5399	na	
002370-88-9	2,4,6,8 tetracyclotetrasiloxane	ND	ND	2064	1972	1272	1854	254	1542	na	
???-??-?	unknown siloxane	ND	ND	1533	988	782	1461	302	1157	na	
87-68-3	hexachloro-1,3-butadiene	ND	ND	ND	ND	ND	ND	ND	ND	none	Poison, Toxic, Irritant, Carcinogen
107-02-8	acrolein-2-propanal	36.0	ND	126.0	97.0	210.0	196.0	ND	280.0	0.1	Poison, Inhalation Hazard, Flammable Liquid
108-88-3	toluene	17.0	67**	220**	220**	220**	140**	12.0	11.0	200	Irritant, Flammable
74-87-3	chloromethane	6.8	9.5	19.0	15.0	90**	390**	29**	690**	100	Toxic, Flammable
142-82-5	heptane	ND	1.2	ND	3.7	1.3	6.5	1.0	9.1	500	n-heptane, $CH_3(CH_2)5CH_3$
110-54-3	hexane	ND	1.5	ND	2.0	1.3	ND	1.1	ND	500	hexyl hydride, normal-hexane, $CH_3(CH_2)4CH_3$
67-66-3	chloroform	1.2	ND	1.1	ND	1.0	2.9	ND	5.7	50	Irritant, Carcinogen
75-15-0	carbon disulfide	2.8	1.8	1.5	20.0	2.9	11.0	4.6	18.0	20	Flammable Liquid
95-63-6	1,2,4-trimethylbenzene	36**	23.0	44**	8.1	11.0	9.5	9.7	14.0	none	Combustible Liquid
108-67-8	1,3,5-trimethylbenzene	10.0	6.3	ND	ND	ND	ND	2.9	ND	none	Combustible Liquid, Irritant
67-64-1	acetone	150**	110**	78**	81**	99**	460**	90**	700**	1000	dimethyl ketone, ketone propane, 2-propanone, $(CH_3)_2CO$
67-63-0	2-propanol	12.0	13.0	4.7	14.0	9.6	32**	8.4	48**	400	isopropyl alcohol, dimethyl carbinol, IPA, Isopropanol, sec-Propyl alcohol, rubbing alcohol, $(CH_3)2CHOH$
78-93-3	methyl ethyl ketone	39**	29**	ND	ND	ND	ND	ND	ND	200	Flammable Liquid, 2-butanone
115-07-1	propylene-propene	ND	ND	ND	ND	ND	ND	ND	59.0	na	Flammable Gas
100-42-5	styrene	ND	ND	ND	ND	ND	ND	ND	1.3	100	ethenyl benzene, phenylethylene, styrene monomer styrol, vinyl benzene, $C_6H_5CH=CH_2$
71-43-2	benzene	ND	ND	ND	ND	ND	4.2	ND	5.7	1	Toxic, Carcinogen, Flammable
79-01-6	trichloroethene	0.8	0.4	ND	ND	ND	ND	ND	ND	100	ethylene trichloride, TCE, trichloroethene, trilene, $ClCH=CCl_2$
98-82-8	cumene	2.2	ND	ND	ND	ND	ND	ND	ND	50	cumol, isopropyl benzene, 2-phenyl propane, $C_6H_5CH(CH_3)_2$
108-10-1	4-methyl-2-pentanone	2.2	1.4	ND	1.6	ND	ND	1.2	ND	100	hexone, isobutyl methyl ketone, methyl isobutyl ketone, MIBK
110-82-7	cyclohexane	ND	3.1	ND	ND	ND	ND	ND	ND	300	benzene hexahydride, hexahydrobenzene, hexamethylene, hexanaphthene, C_6H_{12}
74-83-9	bromomethane	ND	ND	ND	ND	1.1	5.3	ND	8.1	20	methyl bromide, monobromomethane, Ch_3Br
75-09-2	methylene chloride	ND	ND	ND	ND	ND	2.1	ND	ND	25	methylene dichloride, dichloromethane, CH_2Cl_2
108-38-3 106-42-3	m,p-xylene	23.0	10.0	17.0	9.9	16.0	7.4	8.6	10.0	100	Irritant, Flammable Liquid, Reproduction Hazard
622-96-8	4-ethyltoluene	8.9	5.5	9.4	2.5	2.9	1.8	2.6	3.6	na	p-ethyl toluene, 4-methyl ethyl benzene, 1-ethyl-4-methyl benzene
95-47-6	0-xylene	7.3	3.7	6.1	3.6	4.5	2.5	3.0	3.5	100	Irritant, Flammable Liquid, Reproduction Hazard
591-78-6	2-hexanone	7.7	7.2	5.1	3.0	4.3	2.8	3.3	4.0	100	butyl methyl ketone, MBK, methyl butyl ketone, methyl n-butyl ketone, $CH_3CO(CH_2)3Ch_3$
100-41-4	ethylbenzene	3.9	1.8	3.2	3.0	3.5	1.8	2.3	2.5	100	Flammable Liquid, Irritant, Carcinogen

[1]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 work week
**Value above quantitation range
nd=None detected, NA=None 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

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