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Environmental, Health and Safety Considerations for Common Moisture Resistant Additive Technologies in Gypsum Wallboard Production

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ABSTRACT

Currently, the two major commercial methods to make gypsum wallboard water resistant (WR) are by incorporating hydrocarbon wax or polymethylhydrogensiloxane (PMHS or siloxane) into the gypsum slurry during board manufacture. In this paper, the chemistries and applications of wax, siloxane, gypsum and their interactions in the gypsum wallboard manufacturing process are discussed. A new laboratory method for comparisons of Volatile Organic Compound (VOC) emissions during a simulated wallboard drying schedule is also presented with data for a variety of siloxanes and wax emulsion. In addition, regulatory burdens associated with storage, handling and disposing unused siloxane is considered.

An emissions testing oven was designed and fabricated that replicated United States Environmental Protection Agency (EPA) Method 25 testing of plant stack emissions. Panel air emissions of VOCs over a typical plant drying schedule were determined and the types of air pollutants were identified at a third-party test site in Research Triangle Park, North Carolina. Second and third blocks of testing were done at the Henry Research & Development Center in Kimberton, Pennsylvania with samples sent to additional third parties for analysis of the air pollutants collected, in particular siloxane-related compounds.

Although panels made with wax or siloxane generated VOCs during the kiln drying process, the contribution of VOC emission levels from siloxane panels were substantially higher by as much as a factor ten times that of the wax-containing panels. The higher emissions are thought to be due to reactions and subsequent volatilization that occurs as the siloxane raw material is converted to the WR silicone form during the gypsum wallboard manufacturing process. Based on reviews of Title V EPA documents of wallboard manufacturers, emissions of particulate matter (PM) and PM under ten microns (PM 10) are also significantly increased when using siloxane (specifically particles at 2.5 microns and smaller, which are defined by the EPA as "fine particles").

If government emissions permitting, and storage and disposal requirements are a concern for a manufacturing plant, wax emulsion use as a WR agent is recommended over siloxanes. Plants switching from wax emulsions to siloxane may need to decrease VOCs from other plant sources to stay in compliance with local EPA standards. In addition, mitigating any increased PM emissions to avoid air permit modifications and devoting resources to properly handle and dispose of unused siloxanes may be necessary.

INTRODUCTION

Currently, the two major commercial methods to make gypsum wallboard WR are by incorporating hydrocarbon wax or polymethylhydrogensiloxane (PMHS or siloxane) into the gypsum slurry during board manufacture. In this paper, the chemistries and applications of wax, siloxane, gypsum and their interactions in the gypsum wallboard manufacturing process are discussed.

While the chemistry and WR mechanisms of these two materials are different, they accomplish the same task. Wax is non-reactive and considered to have a bulk, pore blocking effect in the gypsum matrix which controls water mobility. Siloxane is a complex, reactive mechanism thought to create a thin, low surface tension layer that interacts with the water surface tension in the matrix to protect the board from moisture. Currently, the US market share by plant of wax emulsions and siloxane is about 55% and 45% respectively¹. This paper compares the chemistries of each method as they relate to Environmental, Health and Safety considerations including operational issues, product performance, regulatory, as well as disposal and recycling. A new laboratory method for comparison of VOC emissions during a simulated wallboard drying schedule is also presented with data for a variety of siloxanes and wax emulsion.

BACKGROUND

Modern gypsum board has as its predecessor a product called "Sackett Board," a composite material made of layers of thin plaster placed between four plies of wool felt paper². This board was patented in 1894 by Augustine Sackett, the man generally considered to be the grandfather of the gypsum board manufacturing industry. WR board came into being around 1934 with US patent #1,975,787 issued to American Cyanamid for metallic resonates added to the gypsum slurry to impart WR in the finished board. Since that time, a number of techniques to impart WR have been used. Typical additives include: metallic soaps, vegetable oils, fatty acids, wax emulsions, styrene butadiene emulsions, vinyl acetate emulsions, asphaltic emulsions, silicone compounds, siliconized waxes, polysiloxanes, polyurethanes and polyvinyl alcohol.

There are two primary methods that are used to impart WR to gypsum wallboards during modern wallboard manufacture – the incorporation of wax blends or siloxane into the gypsum slurry. Typical wax emulsions for incorporation into the gypsum slurry are composed of a blend of hydrocarbon waxes, emulsifiers and stabilizers. The latter materials give stability to the wax emulsion prior to addition to the gypsum slurry and in the application. Waxes provide WR due to their hydrophobicity and distribution in the wallboard matrix. There is little wax chemistry that takes place during the manufacturing of the wallboard, merely evaporation of water with incorporation and distribution of the wax throughout the wallboard.

The siloxane method is more complex, with chemical reactions that occur during the wallboard manufacturing process. There are a number of theories that have been published to attempt to explain the mechanism. The simplest involves two reactions. The first siloxane reaction in the stucco slurry is hydration by water at the hydrogen site to generate a hydroxyl group on the siloxane with resulting hydrogen gas (H₂) generation. The second siloxane reaction involves the cleavage of trimethylsilanol end groups to allow endwise polymerization to the water resistant methylsilicone network.

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

WAX CHEMISTRY

Waxes have been used extensively since early history in many areas including art, lubrication, the protection of surfaces, cosmetics and pharmaceuticals. Waxes can be broadly categorized as follows:

- Animal waxes^{3,4} (Beeswax, Shellac insect wax, Chinese insect wax, wool wax, etc.)
- Plant waxes^{3,5} (Carnauba leaf wax, Candelilla stem wax, Jojoba seed oil wax, Ouricouri palm wax, etc.)
- Mineral waxes^{6,7} (Ozocerite fossil wax, Montan lignite wax, petroleum waxes such as paraffins)
- Synthetic waxes⁵ (Fisher-Tropsch paraffins, polyethylene waxes, polypropylene waxes)

Waxes are typically blended to achieve the target end properties of the application. Natural product waxes such as animal and plant waxes can vary tremendously within each group based on species, food source and even weather during the growing season. Mineral waxes tend to be somewhat less variable within each group, but may still vary based on the petroleum, lignite, or peat source. Synthetic waxes tend to be the least variable. Since they can be produced in large quantities at relatively low prices compared to natural waxes, synthetic waxes have displaced waxes such as carnauba and Montan waxes in some areas⁵.

Chemically, waxes are esters of long chain aliphatic alcohols and acids in the 16 to 36 carbon range – most commonly in the 22 to 36 carbon range. Natural waxes may contain a myriad of other organic moieties such as glycerides, long chain carbonyls, dicarboxylic and aromatic acids, terpenes, other resin and resin acids.

Crude Montan wax (>60% wax) may contain a variety of alcohols, acids, ketones, and sterols that may provide active sites for specialized reaction and derivitization. Montan wax components are typically straight chains in the 16 to 34 carbon range, predominately in the 26 to 30 carbon range⁵. Extraction and purification of Montan wax are typically through solvent extraction (ethanol, toluene, etc.).

Petroleum waxes such as paraffin and microcrystalline waxes are generated from cracking of crude oil and are co-products separated from lubricating oils. Paraffin waxes are predominately straight chain alkanes (a.k.a. paraffinic series in traditional organic chemistry) in the 18 to 45 carbon range. As straight chained alkanes with no double bonds or easily reactive groups, paraffins tend to be of low reactivity. As with Montan waxes, paraffins are typically purified by solvent extraction (toluene, MEK, etc). Microcrystalline waxes tend to be more branched and susceptible to reaction with heat or oxygen.

Waxes have been used extensively in textile and paper applications, including sizing and platen, or mold release. In the construction panel industry, molten Petrolatum wax was used in fiberboard panels made using a wet forming process. For gypsum wallboard applications, waxes are typically emulsified to improve handling and compatibility with aqueous gypsum based slurries. As mentioned previously, mixtures of waxes tend to be used to tailor the wax formulation to the target application. One commonly used example in gypsum wallboard manufacture is a combination of a paraffin and a Montan wax⁸. The molten waxes are mixed with hot water and alkali to saponify the Montan components to form a soap. After high shear mixing and rapid cooling, the wax droplets solidify and form a finely divided dispersion, similar to those formed from polar polyolefinic wax emulsions⁵. These emulsions can then be transported to the wallboard manufacturer's site for addition to the gypsum wallboard slurry to improve WR and strength of the end wallboard product.

SILOXANE CHEMISTRY

For “waterproofing” of masonry and gypsum-based substrates, a variety of silanes, siloxanes and siliconates have been used historically. For gypsum wallboard slurry, the lower molecular weight silanes tend to be more mobile in the gypsum slurry and during drying of the gypsum board. This poses retention problems during setting and drying. As a result, they require relatively higher dosages to achieve acceptable performance. Siliconates by nature tend to be alkaline and that alkaline nature also tends to retard the setting reactions of stucco hemihydrate calcium sulfate into gypsum dihydrate calcium sulfate in the gypsum board manufacturing process. Carrier solvents occasionally used for silanes and siloxanes should be avoided in wallboard manufacturing due to the volatile emissions at the board mixer where operators are exposed and in the kiln due to VOC stack emissions.

Siloxanes have more typically been used for wallboard applications. Both polymethylsiloxanes and polymethylhydrogensiloxanes can be used, however, the former chemistry tends to have higher dollar value in other applications as well as liberate methanol from reactions in the wallboard slurry. (Polymethylsiloxanes contain methyl groups attached to the backbone, some of which are lost in the polymerization reactions in the wallboard manufacturing process.) To minimize methanol VOC emissions and for better cost/performance, polymethylhydrogensiloxane has been used in the United States. However, polymethylhydrogensiloxanes preferentially lose hydrogen groups attached to the backbone to generate H_2 , which is an explosion hazard at concentrations above four percent. The other methyl groups on the backbone tend to repel water from whatever substrate the siloxane is attached or deposited.

The first siloxane reaction in the gypsum slurry is hydration at a hydrogen site to generate a hydroxyl group on the siloxane with H_2 generation. This effect is easily seen in bench made panels as the H_2 forces water out of the wet panel core through the paper. In some cases, this reaction can be sufficiently forceful to damage the paper bond to the gypsum core. The second siloxane reaction involves the cleavage of trimethylsilanol end groups to allow endwise polymerization to the WR methylsilicone network. Trimethylsilanol is volatile and most likely moves from the board core to the board surface with the water liquid and vapor. The trimethylsilanol condenses on the interior of the kiln components, such as glass windows and the impellers of forced air fans. The trimethylsilanol also forms spherical amorphous silica particles (similar in appearance to fumed silica), which are released to the environment through the kiln exhaust stack as particulate matter (PM). In these types of reactions, most likely methanol, methanal (formaldehyde), methane or other reaction products are also generated and emitted through the kiln stack as VOCs. It has been observed that crystalline silica is also present in dryer dust samples obtained from kilns where siloxane has been utilized to impart WR. It is unclear at this time the relative amount of this crystalline silica that potentially originates from the starting gypsum versus that from the siloxane used in the wallboard manufacturing process.

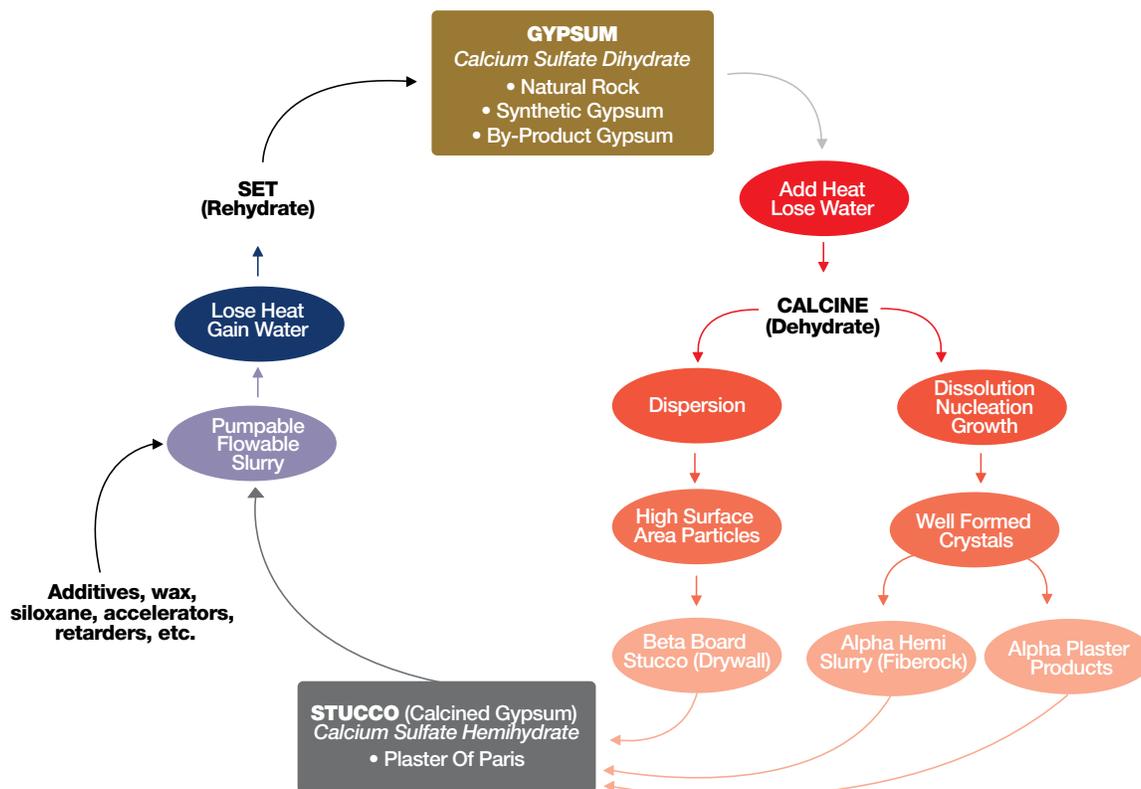
GYPSUM CHEMISTRY

Gypsum is a calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) crystal with an average of two molecules of water (H_2O) per molecule of calcium sulfate (CaSO_4). One major source of gypsum originates from mines of calcium carbonate (CaCO_3) remains that originate from ancient sea life that over time, pressure and sulfur addition were oxidized to calcium sulfate (natural rock gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The second major source of gypsum is synthetic gypsum or byproduct gypsum from a variety of manufacturing processes including sulfuric, citric, or phosphoric acid production or from power plant stack scrubbing. The most commonly used synthetic source of gypsum in the United States is from the sulfur scrubbing of coal powered electric generation, where ground limestone (CaCO_3) is injected into power plant stack discharge gases to capture sulfur and form calcium sulfite (CaSO_3), which is later oxidized and re-crystallized to form CaSO_4 . This gypsum is called flue gas desulphurization gypsum or FGD gypsum. For wallboard manufacture, natural rock requires cost and energy to mine and grind, while FGD gypsum, although already in a finer particle size, requires cost and energy to dry. Natural rock

gypsums may have a variety of other minerals and salts as contaminants that can interfere with the reactions occurring in the wallboard manufacturing process. FGD gypsum may also contain contamination from the limestone or crystal modifiers added in the scrubbing process that are used to generate larger gypsum crystals that make dewatering easier and allow better reclamation of process water. These crystal modifiers can also interfere with the wallboard manufacturing reactions and in some cases may adversely affect set, or the conversion of the stucco slurry back to gypsum.

For wallboard, the gypsum is heated to calcine and remove some of the water of crystallization to generate calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) with an average of $\frac{1}{2}$ molecule of water ($\frac{1}{2}\text{H}_2\text{O}$) per molecule of CaSO_4 . This stucco is then mixed with other additives and water to give a flowable, pumpable 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 in Figure 1, the WR additive is added to the stucco slurry at the mixer of the wallboard manufacturing line. The siloxane or wax emulsion is typically added to the water stream where turbulent flow and static mixing elements disperse them prior to the board mixer. Liquid and dry powder streams are continuously fed to the mixer where residence time is seconds. Before discharge between two continuously moving sheets of paper or other facing materials, all additives need to be uniformly dispersed into the slurry and foam. Maintaining the uniformity of the additives as laid down at the former assures uniform water protection throughout the core. In some cases, migration of other additives is intentional to improve properties at the facing-core interface or the end of the panels.

While on the forming table and prior to the kiln, the hemihydrate stucco chemically sets and stiffens back to the dihydrate form to lock the additives in place and form a strong porous structure to the board. This setting or crystallization process requires dissolution of the hemihydrate and then nucleation and crystal growth to form the crystalline gypsum board structure. If the WR additive becomes available in the slurry too soon, it may interfere with the setting process of the hemihydrate stucco and coat or block the growth of the dihydrate gypsum crystallites that give the board its strength.

For the wax emulsion slurry to have the greatest beneficial effect, the emulsion must maintain integrity until the stucco is set. As water is removed during drying and the surface tension in the board core matrix changes, the wax emulsion is broken and allows the wax particle to become available. (During wax emulsion manufacture, the wax components are heated above their melting points and an emulsion is made of the liquid wax at high temperature. The emulsion is then cooled below the wax fractions melt points to yield solid wax particles dispersed in water). As the drying temperature of the board core increases to the melt point of the wax fractions, the wax melts and flows to increase coverage and locks into the gypsum or gypsum/paper matrix. The WR mechanism of the wax blocks pores in the matrix and protects 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 thought to not be due to a layer of liquid wax but due to microscopic particles of wax⁹ which are uniformly dispersed throughout the board.

For siloxane, the greatest beneficial effect is achieved when the siloxane forms an inverted emulsion in the stucco slurry with hydrated siloxane tails on the outside and hydrophobic siloxane chains to the inside. The siloxane micelles are then locked in place by the setting stucco. As the methylhydrogensiloxane (MHS) is exposed to water, hydrogen groups are lost and replaced with a hydroxyl group with subsequent generation of H_2 . As the board dries in the kiln and the surface tension changes, the micelles are disrupted and the siloxane is allowed to “flow” and coat the pore interior of the board matrix. Because this is an ongoing chemical reaction, the high kiln temperatures also promote volatilization of some of the siloxane reaction products which subsequently produce kiln stack VOCs and PM and may reduce the efficiency of the siloxane additive dosage. Water repellency is achieved through a thin layer of silicone adsorbed onto the gypsum crystals. TEM-EDX confirms a thin layer of siloxane is adsorbed to the gypsum surface¹⁰. This includes the outer surfaces and the surfaces associated with pores. The siloxane appears to coat the walls of the pores but does not occlude pore openings. The low affinity of water for the silicone on the gypsum matrix then restricts liquid water ingress, but allows water vapor movement. Current theory suggests that the silicone-oxygen atomic bond is of sufficient size to allow water vapor to pass through.¹¹ It is not likely that all of the internal pores are coated since a cup of board slurry with siloxane additive will show water being pushed to the top of the slurry during initial hydration by the H_2 pressure of the reacting siloxane. However, after a couple of hours at room temperature, the stucco has reabsorbed the water that was expressed from the stucco.

For water repellency to be effective, the Si-OH oligomer must compete with the effect of drying for rehydrating water. A catalyst is typically required to achieve the targeted reaction rate. If the reaction is too late in the process and insufficient water is available for the remaining siloxane reactions due to drying, the board will exit the kiln with poor WR and will either need to be recycled back into the process or stored in the warehouse until the siloxane has absorbed sufficient moisture from the air to complete the siloxane to silicone reaction and achieve the desired WR.

With regard to the impurities in the starting gypsum mentioned above, wax moieties tend to be 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.

The desired effect of WR treatment is to lower the two-hour water uptake of the gypsum board from over 40 percent to the ASTM C-1396/C1396M-06A specifications of less than ten percent for Gypsum Sheathing and less than five percent for WR Gypsum Backing Board¹². Strength of the panel should be maintained as well as the integrity of coatings or surface treatments on the panel. Figure 2 illustrates the concept of the difference in mechanism of siloxane and wax in the dry wallboard panel as described above.

To minimize the dosage required of WR additives, some wallboard processes use potassium sulfate (K_2SO_4) as a stucco set accelerator. The potassium sulfate modifies the gypsum crystal growth to larger geometry crystals of lower surface area, requiring less WR additive, but unfortunately, resulting in lower panel strength as well. In the wax additive case, the strength is often maintained or improved. The pore blocking mechanism described above may also explain the increased strength often found with wax 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 2. Longitudinal Section of Typical Gypsum Matrix Pore Having Wax (Left) or Siloxane (Right) Water Resistance Additive

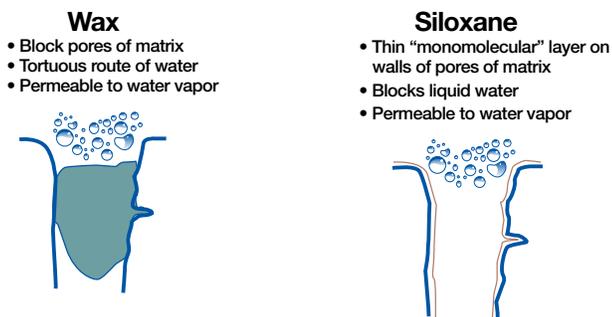
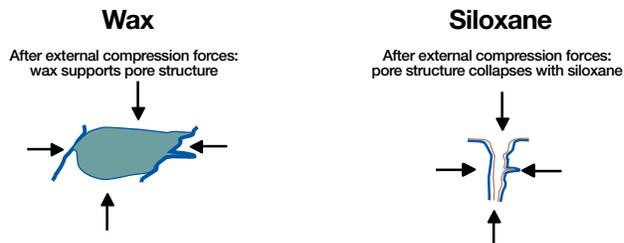


Figure 3. Compressive Loading and Deformation of Gypsum Matrix Pore Having Wax (Left) or Siloxane (Right) Water Resistance Additive



STORAGE AND DISPOSAL

Waxes are typically innocuous materials and many have been United States Food and Drug Administration (FDA) approved for human contact or contact with food. As mentioned earlier, the paraffinic component is typically comprised of long chain aliphatic hydrocarbons of low reactivity. As an emulsion of roughly half water, it is neither reactive nor flammable. As such, there is no unusual hazard with storage and disposal. Many commercial wax emulsions for wallboard either have a slightly alkaline nature or have biocides to minimize decomposition over time. The mild alkalinity may be a hazard to mucous membranes such as eyes, mouth, etc. and safety glasses should be used by personnel handling them. Since these are typically required of all workers on a gypsum wallboard manufacturing line, there are no additional precautions required. Wax tanks and lines may be fiberglass, steel or plastic. Wax tanks and lines that have become contaminated with bacteria should be flushed with chlorine water, as is common for tank cleaning in the paint and coatings industry.

Siloxanes are typically stored in smaller containers than wax emulsions in wallboard plants due to their overall lower usage rates and for safety. Siloxane, catalysts and water need to be segregated from each other to minimize reactions resulting in H₂ generation. For example, a five gallon bucket with four percent siloxane in water will dramatically bulge, distending the lid over one inch if left sealed for one month. The catalyst and siloxane are stored as separate materials until they are added simultaneously from two separate containers. Plant washdown waters should be kept from backing up into siloxane lines or tanks. An air gap somewhere in the system and/or a smaller day tank near the board mixer is recommended. Storage containers for siloxane should be stainless steel or plastic (as is common in 300 gallon totes) and sealed to keep out atmospheric moisture. Tanks and totes should be occasionally “burped” to relieve any pressure from H₂ generation.

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 H₂ and create an explosion risk. Although the auto ignition temperature for H₂ is 530°C, it can be ignited by sparks and has even been reported to ignite via sunlight¹³. Once ignition has started via H₂ gas combustion, the remainder of the material can become susceptible to decomposition, further exacerbating the flammability/explosion hazards. A variety of amines, metal salts and alkaline materials may also react as catalysts with the siloxane to generate H₂. The difficulty of predicting the effects of these materials or mixtures of them increases the hazard uncertainty in the disposal of unused siloxanes. The evolution of H₂ sometimes occurs with an induction time, after which a rapid evolution of gas occurs. As a result, the evolution of H₂ gas is not always easy to predict.

Based upon the potential to release H₂, the reported release of formaldehyde at temperatures in excess of 150°C and its OSHA characterization under SARA 311 and 312¹⁴, unused siloxane is unlikely to be accepted for disposal in many municipal solid waste (MSW) incinerators that burn household and non-hazardous wastes and may be required to be disposed of at permitted hazardous waste facilities. The potential release of H₂ and the accumulation of explosive mixtures of this material create risks if disposed in an MSW landfill. 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.

Disposal of waste siloxane is not usually as controlled as the storage of valuable virgin siloxane, so particularly detailed Standard Operating Procedures should be required for their disposal. Disposal may include the packaging, commingling, and destruction/treatment of the waste and/or unused siloxane. As a general rule, solid wastes are easier to dispose of than liquid wastes.

Gypsum wallboards produced with siloxanes may be difficult to recycle both at end of life cycle and also in the board making process when scrap boards are generated. When these boards are ground up and put back through the board making process, they can result in high soap variability process interactions generating blisters or blows, and/or the need to run at slower line speeds. As a result, producers are more inclined to land fill waste boards rather than recycle them back into their process. It has also been observed that introducing siloxanes into some wallboard manufacturing lines can detrimentally impact operation of the line for long periods of time as the material coats process surfaces. In addition, it can contaminate process water, resulting in uncontrolled introduction to the process throughout operation, even when manufacturing non-WR boards.

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

Material Safety Data Sheets (MSDS) sheets for siloxane additives will differ in their detail and overall quality, depending on the company that prepared them. In cases where there are additional ingredients or where 100% of the ingredients cannot be accounted for, it becomes difficult to accurately determine the appropriate waste disposal options and exposure and hazards. In many cases where the MSDS does not account for 100% of the material, the manufacturer may do this purposely to protect proprietary ingredients. In such cases, only permitted hazardous waste facilities may be willing to accept such material.

OCCUPATIONAL AND REGULATORY ISSUES

A variety of MSDS¹⁵⁻¹⁹ were used to estimate health and safety concerns with polymethylhydrogensiloxane and wax WR additives as supplied by their manufacturer.

Polymethylhydrogensiloxanes (PMHS or siloxane)

The flash point of this material¹⁵ is above the 60°C required for characterization as hazardous by virtue of the characteristic for flammability. Although siloxane is not a fire hazard in itself, it must be considered a reactive hazard due to generation of H₂ gas and a flammable hazard due to its flammability. Hazard results from the release of H₂ gas upon contact with acids, bases, oxidizing substances, catalysts and rust and the possibility of H₂ associated fires once the material is spilled or comes into contact with extinguishing media.

The MSDS claim no adverse effects from ingestion or inhalation under normal use, but mild skin and eye irritation can occur. There is no carcinogenicity associated with this product in the as-supplied form.

MSDS have classified this material as a hazardous waste (reactive), which limits its disposal to hazardous waste and triggers various requirements and limits on onsite handling, storage and accumulation. 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 and assumptions in the MSDS generally apply to siloxane that has not been spilled or transferred. The MSDS are not sufficiently explicit, but spills, recoveries, and transfers of this material introduce the possibility of commingling the as-received material with water, acids, bases, catalysts, and other reagents that would exacerbate the release of H₂ within the relatively confined space of the receiving container. Furthermore, any spill cleanup or transfer to secondary containers runs the risk that workers will not use a ventilated receiving container and produce an explosive mixture of H₂. The MSDS suggest keeping the container closed, but with weekly venting to avoid swelling, possible rupture and buildup of H₂ gas. Some vendors supply containers with one-way venting. The closed container is meant to exclude catalysts and most importantly water or water vapor that could lead to the generation of H₂. Some MSDS mention the use of inert gas purging and grounding.

Another hazard is the potential generation of formaldehyde at temperatures in excess of 150°C and in the presence of oxygen. Although the temperature of the drying air in most wallboard kilns is in excess of 150°C, due to evaporative cooling, the board temperature is typically below 100°C. To be exposed to the higher air temperature, the siloxane material would need to be mobile in the panel and transported to the surface through surfacing paper or scrim. However, decomposition products of the siloxane reactions in the board are more mobile and may be present in the kiln drying air to generate formaldehyde. Formaldehyde is a skin and respiratory sensitizer, eye and throat irritant, acute health hazard, and potential cancer hazard.

One MSDS lists siloxane as an acute health hazard and a fire hazard under Superfund Amendments and Reauthorization Act (SARA) 311, 312 Hazard Class. A brief description of the five hazardous characteristics (Occupational Safety & Health Administration/ OSHA Hazardous Communication Standard, 29CFR1910.1200¹⁴) is as follows:

1. *Acute health hazard:* Includes corrosive, highly toxic, irritant, sensitizer, toxic and other hazardous chemicals which cause an adverse effect to a target organ and manifests itself within a short period of time following a one-time, high exposure to the substance;
2. *Chronic health hazard:* Includes carcinogens and other hazardous chemicals which cause an adverse effect to the target organ and manifests itself after a long period of time following or during repeated contacts with the substance;
3. *Fire hazard:* Includes combustibles, flammables, oxidizers and pyrophorics;
4. *Reactive hazard:* Includes organic peroxides, unstable reactives and water reactives;
5. *Sudden release of pressure hazards:* Includes compressed gas and explosives.

Components on the MSDS are listed as hazardous in 29 CFR 1910.1200²⁰. The hazard character appears to originate from its meeting the reactive and flammable characteristics. It is important to note that the characterization of this material as hazardous under 29 Code of Federal Regulations (CFR) is not the same as the classification of hazardous under 40 CFR. The purpose under 29 CFR 1910.1200 is to ensure that the hazards of all chemicals produced or imported are evaluated and that information concerning their hazards is transmitted to employers and employees. This communication is accomplished by means of a comprehensive hazard communication program which includes, among other vehicles, a comprehensive MSDS. This standard is different from 40 CFR, which defines a solid waste and if the material meets the definition of a solid waste, it is then evaluated to determine if it is a hazardous waste. 29 CFR 1910.1200 is initiated upon first use of the chemical in the workplace; 40 CFR is not initiated until the material is treated in a manner consistent with disposal. Hence, the two criteria must be evaluated separately.

One siloxane MSDS lists heptane¹⁷ as a component in small amounts. Heptane would be volatile under the conditions present in the drying kiln and a contributor to VOC. Similar organic carriers that may be present in other siloxanes would also be contributors to VOC.

Catalysts for Siloxanes

Amine catalysts can cause serious eye damage and skin and respiratory tract burns. As a result, spills present significant challenges with respect to worker exposure. Response requires full protective gear and respirators (where ventilation is inadequate). The material should be classified as hazardous based on corrosivity. Disposal in a non-hazardous incinerator will be problematic due to its hazard classification resulting from corrosivity (which would first need to be neutralized), and the products of combustion (ammonia, NO_x and aldehydes). Fuel that increases a combustion facility's NO_x output is typically avoided unless it can be successfully blended. MSW incinerators also avoid liquids, as they are often difficult to contain and feed unless in adequate secondary containers and do not create flash fire hazards. Since the material is a liquid and could create a fire/explosion hazard during normal incinerator operations, most MSW incinerators would tend to avoid this product. These types of amines

are also rather toxic to aquatic organisms and would further limit disposal options as they would likely fail the typical acute and/or chronic toxicity using fish bioassays.

Alkaline catalysts have corrosion hazards as well as potential harm to mucous membranes as described above. The alkaline catalysts also have the disadvantage of stucco set retardation during the manufacturing process.

Metal catalysts such as tin, zinc, magnesium, etc. compounds may also in some cases present toxicity problems with disposal. However, compounds in this class can be judiciously chosen to present minimal risk while providing good control of the siloxane reactions and are most commonly used with siloxanes in the US.

Siliconates¹⁹ are more often used as water repellent treatments for masonry than for gypsum wallboard panels due to their corrosion and risk from high pH. When used in wallboard, it is often in combination with siloxanes. This material can cause extensive and often irreversible damage to eyes, respiratory tract and stomach owing mostly to its corrosivity. As discussed with other materials, these siliconates may be classified as hazardous based on the characteristic of corrosivity.

Wax Emulsion

Wax emulsions typically consist of paraffin wax 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, except for possibly the pH which can be in the 10 to 12 range. However, pH can be adjusted prior to disposal to remove this characteristic. Unlike the siloxanes, this material will not form explosive mixtures upon incineration or lead to increased silicon dioxide (SiO₂) particulate emissions in stack gases.

IMPACT OF SILOXANE ON WALLBOARD PRODUCTION BASED ON TITLE V AIR EMISSION PERMITS

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

One negative by-product of the use of siloxanes is silicon dioxide (SiO₂). This material is not particularly detrimental in the workplace, unless it is in the crystalline form, nor does it pose a fire/explosion risk. It is emitted during the drying of siloxane wallboard, increasing PM emissions and may, in many cases, necessitate a modification of the facility's Title V permits. Particles less than 2.5 μm in diameter (PM 2.5) are referred to as "fine" particles and are believed to pose the greatest health risks. Siloxane use in wallboard plants generates significant quantities of PM 10 and especially PM 2.5. The 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.

Other material in the kiln stack emissions may include hydrocarbon fractions (hexanes, pentanes and normal alkanes) and formaldehyde. The combustion chemistry that gives rise to formaldehyde is not as obvious as the remaining products, but does exist. The air temperatures in the kiln are much lower than those used in combustion. It is at these temperatures that products of incomplete combustion and reaction products of thermal rearrangements are most likely to occur.

US wallboard producers typically must maintain Title V air permits granted by US EPA in conjunction with state programs. The nature of the increased particulates associated with the use of siloxanes is likely due to silicon dioxide (SiO₂) generation as described earlier.

Data provided by one Midwestern US gypsum board plant permit indicated little change in PM when running wax emulsion as the WR agent as opposed to normal wallboard.

A Southeastern US gypsum board plant permit gave an estimate of the increase of PM with siloxane as the WR agent as 0.0144 pounds per one pound of siloxane processed or 1.44% (likely predominately as silicon dioxide). This permit placed an upper limit on the quantity of siloxane that could be used per year. It appears the objective of this facility, as with the Midwestern plant, was to preserve its minor source status for PSD. The discussions in this permit also shed some light on a comparison of PM emissions from both normal wallboard production and from wallboard production using siloxanes. Emissions from the Southeastern plant kilns associated with normal wallboard production were 6.65 pounds/hour PM, while emissions from kilns associated with production using siloxanes were 31.55 pounds/hour PM. Based on the metrics reported from the Midwestern plant, the PM associated with wax emulsions was negligible. From this plant data, there is a substantial increase in PM emissions when running siloxane. Just as with the Midwestern plant, there appears to be an upper limit on production - the amount that will no longer preserve the plant's minor source status for PSD. It is unlikely that plants would be willing to take on a change from minor source to major source status for PSD.

One Northeastern US gypsum wallboard plant permit in 2008 describes changes in emissions when going from normal to a mold-resistant product, which is presumed to have a biocide as well as siloxane WR agent. The total PM 10 limit was 5.134 tons/year during the production of normal wallboard, but 22.4 tons/year during the production of mold-resistant wallboard. Similarly, the VOC limit was 5.20 tons/year during the production of normal wallboard, but 26.84 tons/year during the production of mold-resistant wallboard. The 2008 permit modification reports a facility-wide PM 10 allowance of 125 tons/year and a VOC allowance of 44 tons/year.

A consistent thread through these permits is that significantly higher VOC and PM/PM 10 emissions are associated with the use of siloxanes as the WR additive for gypsum wallboards versus wax emulsion additives.

MATERIALS & METHODS

In order to investigate the relative VOC emissions during drying of panels made with wax or siloxane WR additives, laboratory panels were prepared and tested using a small scale drying oven discharging emissions gasses to a total hydrocarbon flame detector.

The Durham, North Carolina ARCADIS office was approached for third party emissions testing. ARCADIS is an international company providing consultancy, design, engineering and management services in the fields of infrastructure, water, environment and buildings. In its Environment Division, ARCADIS is a global leader in environmental consultancy with services ranging from environmental assessments and climate change mitigation to noise abatement, solid waste disposal, soil and ground water cleanup, and land remediation. The Durham, N.C. ARCADIS office also provides onsite testing of stack air emissions as well as engineering and design of related equipment. ARCADIS works closely with and provides services for the local US EPA research facility in Research Triangle Park, N.C. ARCADIS has substantial expertise in the testing and analysis of air emissions from drywall manufacturing facilities.

ARCADIS has developed an oven-testing process to evaluate total hydrocarbon (THC) emissions from gypsum boards. The THC VOC results from the board oven-testing procedure have historically compared well with stack results for similar products²¹.

The Henry Company High Temperature Test Oven developed by ARCADIS is a gas-tight oven with polytetrafluoroethylene (PTFE) gasketing and electrical resistance heating. Zero grade air is delivered to the oven through an Aalborg high precision mass flow controller from a high pressure cylinder. Air enters a vertical pre-heater section that warms the air to the set oven temperature. The oven and pre-heater temperatures are controlled by proportional integral derivative (PID) controllers in an adjacent power control box. Air passes through the oven chamber and exhausts from the horizontal center of the chamber opposite the feed inlet. This configuration is expected to result in nearly isothermal air temperatures throughout the oven; production drying of board at gypsum wallboard plants is a complicated air temperature profile through the kiln as a result of contacting pattern and adiabatic drying within the kiln. Gases are transported through stainless steel lines to a THC analyzer or through PTFE tubing to an evacuated SUMMA canister for gas chromatography/mass spectrometry (GC/MS) as per EPA TO-15 analysis²². Transport lines are heat traced to prevent condensation.

Gas exhausted from the oven was analyzed by a VIG Industries THC Flame Ionization Detector (FID) fired on ultra high purity (UHP) carrier grade hydrogen with zero grade air. This analyzer was heated to prevent liquid condensation inside the analyzer. Oven exhaust gas was fed wet to the analyzer, with no moisture being condensed prior to analysis, and with an atmospheric dump prior to the analyzer to allow the analyzer to sample the same amount of gas under all conditions. THC analysis was performed on a wet gas to prevent bias caused by organics condensing into the water phase. Zero and span calibrations were performed with propane prior to and after each test. The output of the analyzer was logged to a local computer every two seconds.

The THC analyzer breaks down organic constituents to determine THC's. 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; in this procedure propane is used. Units can be adjusted to another standard based on the carbon

content of the desired compound. Although there is no identification or supposition that the organics are propane, the concentration reported by the analyzer is based on all the carbon detected as propane equivalents.

Initial third-party testing was performed at ARCADIS' Durham, North Carolina lab where total VOC and speciation using GC/MS were conducted focusing on TO-15 compounds for two levels of wax dosage and two levels of PHMS dosage. The local ERG lab was used for the speciation analysis.

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

Figure 4. Henry Company Emissions Test Oven Apparatus



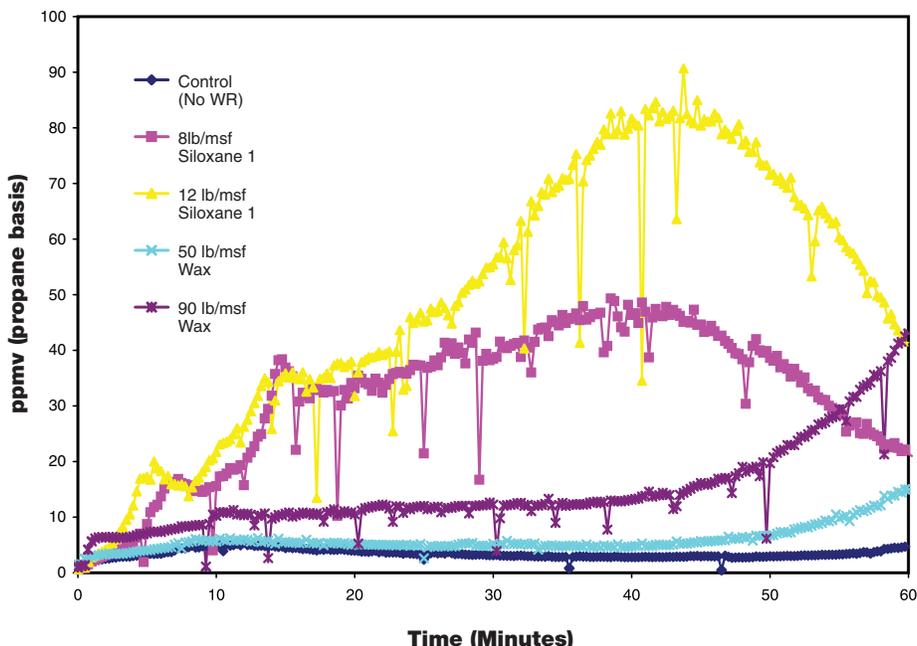
Total VOC Comparison

Effective dosage rates of WR additives are dependent on differing chemistries of individual plant stucco slurries and in particular can vary from plant to plant with the gypsum used for the stucco. Siloxane dosage rates of eight pounds/msf and 12 pounds/msf were chosen for this study as they are representative of the range of dosages commonly used 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, using the formulation sheet shown in Appendix A. At twice the vicat set (ASTM C472 10.2.2 used to measure the slurry thickening rate), four inch by five inch samples were cut from the center of each test board for test oven drying.

The boards were then immediately placed in an electric resistance heated oven and the emissions over the drying period were monitored by a total VOC FID using a hydrogen flame. Nine minutes after the stucco and water were first mixed, the panels were placed in the 232°C drying oven (see Appendix B for the physical layout of the oven at ARCADIS) with airflow of 1.5 liters/minute along the panel. Panels were removed from the oven at 69 minutes elapsed time (60 minutes of drying). VOC emission data were collected in real time during drying, displayed and recorded on an integrated computer. The graphs of VOC emissions over the drying interval for the five types of test panels are shown in Figure 5 and demonstrate the typical shapes of the VOC emission curves for siloxane, wax and a control gypsum board.

Figure 5. VOC Drying Emissions Over 60 Minute 232°C Drying of ARCADIS Panels



A second set or block of identical panels was prepared and emissions collected in vacuum cans for Gas Chromatography/Mass Spectrometer (GC/MS) speciation. In addition, a side stream was taken from that block for the determination of relative VOC emissions. Vacuum can collection gas did not go through the FID detector, so any detector buildup should not have affected TO-15 speciation results. Figure 6 shows the good repeatability of the trends between the VOC/speciation can and VOC blocks of data, with the VOC/speciation block from the can testing on the left and the VOC testing on the right.

TO-15 Comparison

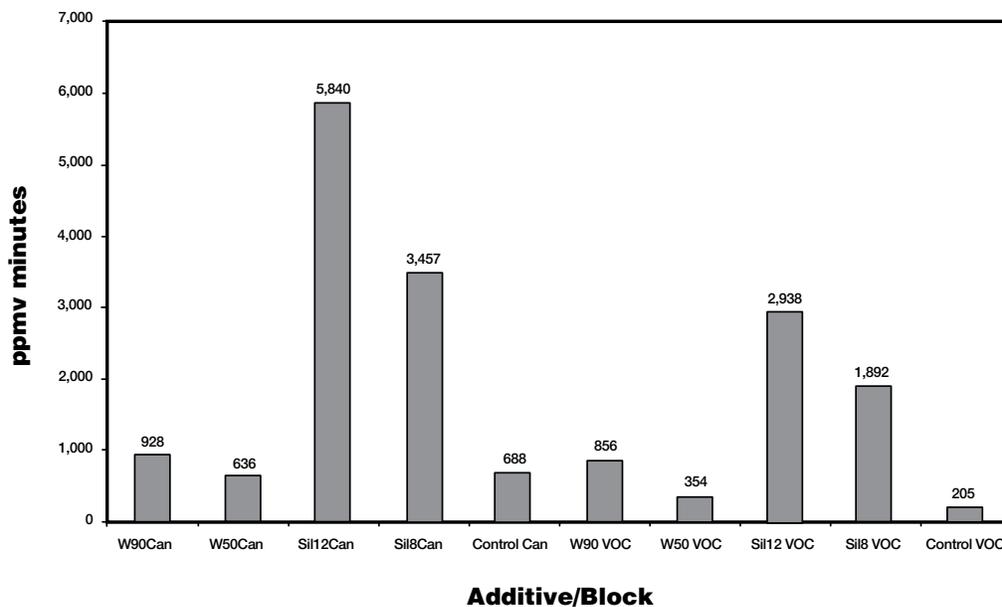
A gas stream from the emissions oven was collected during drying in six liter vacuum sampling canisters for later testing per EPA Method TO-15²². This testing was performed by the ERG lab in Research Triangle Park, North Carolina. This stream was collected in vacuum cylinders at a starting vacuum of approximately 28" Hg. Since the orifice used on the can appeared to let gas enter too rapidly, at approximately 43 to 46 minutes into the 60 minute drying schedule, a valve to the vacuum can was switched on and off in one minute cycles so that gases emitted toward the end of the drying cycle would

not be missed. Cans were typically left with a four-inch to six-inch vacuum to allow later incorporation of dry nitrogen to release analytes for GC/MS testing, as well as minimize condensation in each can.

The cans were hand delivered for GC/MS testing to the ERG lab in Research Triangle Park, North Carolina. This test lab has developed standards for EPA testing of hazardous air pollutants and combines their GC/MS method with Selective Ion Monitoring²³ (SIM) to improve sensitivity/reporting limits 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 list.

To confirm the results from ARCADIS, VOC studies were done at the Henry Company Research & Development Center. Multiple runs of Siloxane 1 were done as well as other polymethylhydrogensiloxanes. Two additional testing laboratories, ALS and Air Toxics, Ltd. were used for the additional studies.

Figure 6. Comparison of Can Block with VOC Block of ARCADIS VOC 60 Minute Total Emissions Data Can Block of Data on Left Side of Graph and VOC Block of Data on Right Side of Graph



RESULTS AND DISCUSSION

VOC Emissions

Emissions of the additive panels were compared using the area under the VOC emissions curve (see Figure 5) during the 60 minute drying cycle. A simple trapezoidal rule was applied to the spreadsheet for the calculation to give a total VOC emission for the 60 minute drying period. These relative emissions (ppmv minutes) are compared in Table 1.

Table 1. 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

All additives increased emissions over that of the control panel. The siloxane group emitted substantially more than the wax group. Within each of the wax and siloxane groups, increasing the dosage increased the total emissions proportionately. The second block of emissions (Can) confirm these trends as shown above in Figure 6. ARCADIS estimates of the VOC emissions of the 12 pounds/msf siloxane and 90 pounds/msf wax and the control no WR additive systems were 152.1 tons/year VOC, 22.4 tons/year VOC, and 5.3 tons/year VOC respectively, for a manufacturing plant running full time water resistant product. These estimates show the increased risk of air quality violations due to VOCs with the use of siloxanes instead of waxes.

For siloxane, a 33% increase in dosage increased emissions by approximately 55%. For wax, an 80% increase in dosage increased emissions by around 142%. If an emissions ratio is calculated, the siloxane emissions ratio is 1.67 (that is 55/33) and the wax emissions ratio is 1.78, again implying that the increase in emissions is related to the increase in the raw material component estimated to cause the emissions. The similar emissions ratios imply that there are few statistical interactions in the emissions responses and that the mathematical system is somewhat simple and straightforward.

It is important to note the significantly larger amount of emissions from siloxane versus wax emulsion on a relative basis in the context of air permits and subsequent modifications. Initial calculations using these data suggest that the models used to determine increases in VOCs stated in many air permit modifications required when switching from wax emulsion to siloxane may be significantly understated and should be re-evaluated.

**Henry Company Research & Development Center
VOC Data**

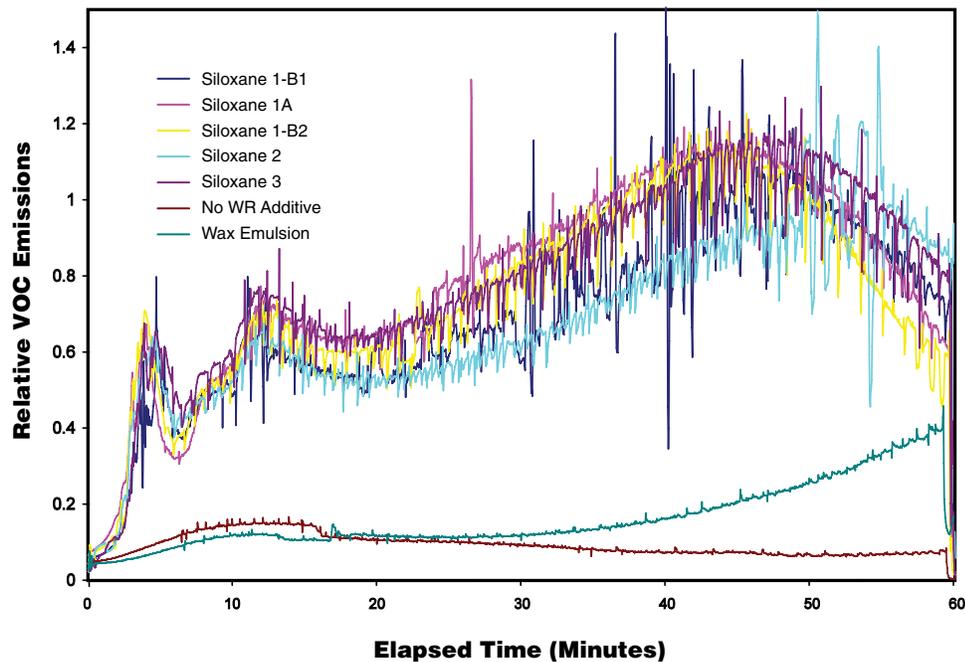
VOC measurements using the Henry Company Emissions Oven with a FID THC analyzer were used to confirm the trends among the control, wax, and siloxane formulations in test panels. The highest dosage rate of both the wax emulsions (39% solids; 90 pounds/msf) and the siloxane (100% solids; 12 pounds/msf) were evaluated. Four different siloxanes, one wax emulsion, and one control panel (no WR additives) are compared in Figure 7. A duplicate of Siloxane 1 was also done (this siloxane had also been used for the ARCADIS testing).

The siloxane panels all showed similar VOC emission patterns, with emissions substantially higher than either the wax emulsion panel or the control panel. A consistent trend in siloxane emission was the appearance of three characteristic peaks which may be indicative of three different siloxane products.

Two sets of the same formulations were run and emissions gases collected for chemical compound speciation using the TO-15 method of GC/MS and sent to ALS in Cincinnati, Ohio and Air Toxics Ltd. in Folsom, California for testing.

The lowest emissions over the 60 minute drying schedule were from the control panel whose trace is shown along the bottom of the graph. The next lowest emission was the 90 pounds/msf wax emulsion panel whose trace is shown next to the control panel at the bottom of the graph.

Figure 7. Relative Board Drying Emissions from Five Siloxane Panel Samples, One Wax Emulsion Panel Sample and a Control Panel without WR Additives from Henry Company Emissions Oven



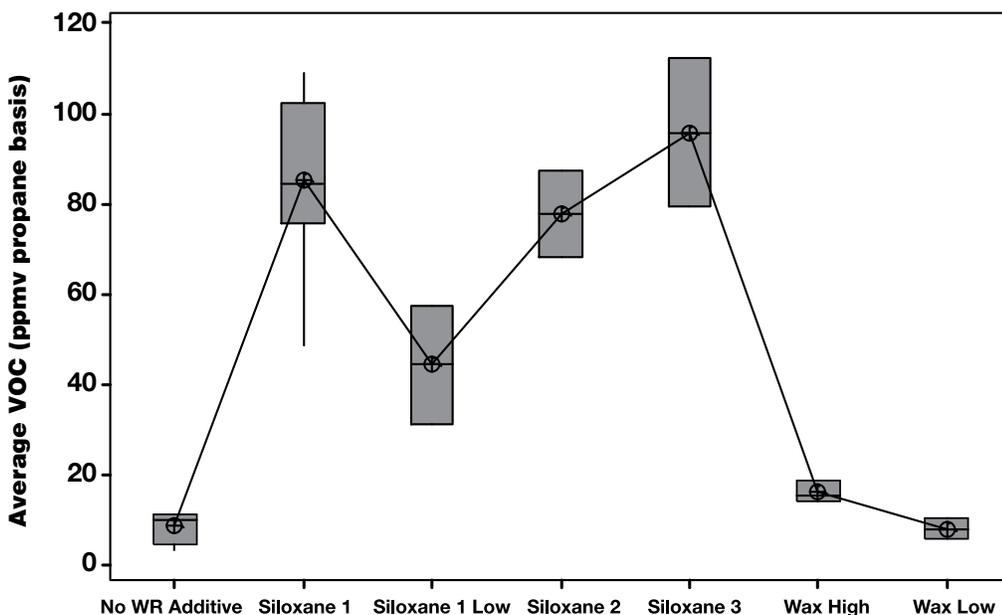
Since VOC emissions of drying panels were assumed to vary due to WR additives or dosage of an additive, average VOC data for test panels from ARCADIS, ALS, and ATL were compared using analysis of variance (ANOVA) using a "MINTAB15." VOC was found to be a statistically significant source of variation at a 99.9% confidence level as shown in Table 2. Based on this statistical confirmation, additional inferences in differences between additives and dosages could be made.

Table 2. One Way Statistical Analysis of Variance Comparing VOC Values From Two Levels of Wax, Two Levels of Siloxanes, and Three Siloxanes

Source	DF	SS	MS	F	P
Additive	6	29,129	4,855	20.69	0
Error	16	3,754	235		
Total	22	32,883		$F_{crit,6,16,.001}=6.81$	

A method to visualize the variation and differences between WR additives and dosages is shown in the box plot of the results in Figure 8. The values from the control boards without any WR additives and the lowest wax dosage level panels are grouped into the lowest VOC emissions, with the higher wax dosage panel slightly higher. The grouping of the high dosage level of the siloxanes is much higher than the control/wax group. The lower dosage level of siloxane group is higher than the wax/control group, yet lower than the higher dosage level of siloxanes. Although the Siloxane 3 VOC mean is higher than the other siloxanes, due to variability, it is not statistically significantly higher. However, based on certain species identified via GC/MS generated with Siloxane 2, if VOC emissions were a concern and siloxane must be used, Siloxane 3 should be chosen for use before Siloxane 2. Based on the statistical analysis of this group of data, siloxane addition to wallboard panels emits significantly more VOC emissions during the kiln drying process than wax emulsion addition.

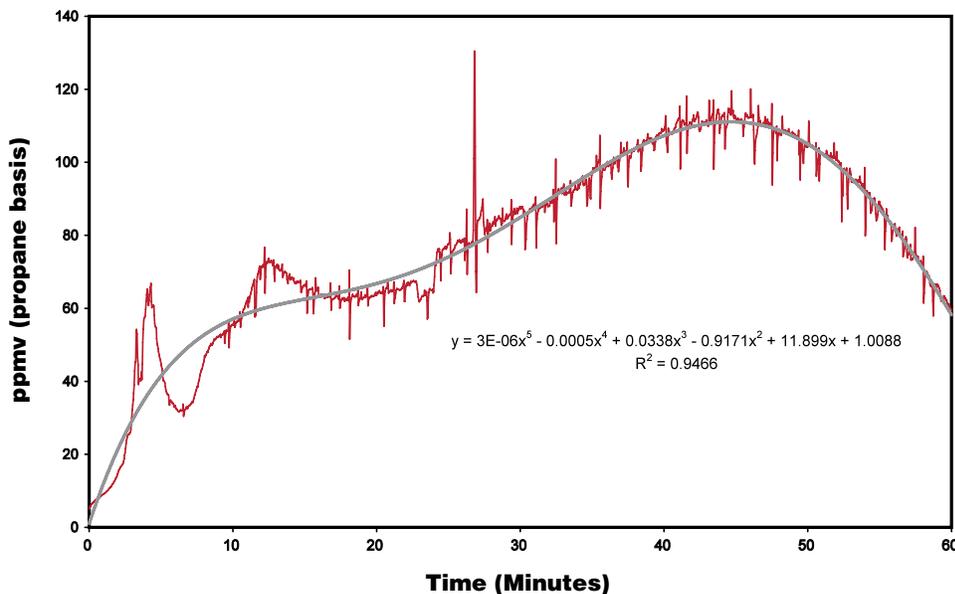
Figure 8. Statistical Box Plot Comparison of Average VOC Emissions Over 60 Minute 232°C Drying for Panels with Two Levels of Wax, Two levels of Siloxane and Three Siloxanes



Similar trends in VOC generation over the 60 minute drying schedule were seen for all siloxanes, as shown in Appendix C. The VOC emission traces from the emissions oven testing were fit to polynomial curves to develop models. Although siloxane polynomials tended to minimize the first and second peaks of VOC generation, model fitting to the data was excellent. An example of the model curve fitting is shown in Figure 9.

Models were developed from 720 to 1,800 data points for each sample. Initially 720 points were used for the first experiment at ARCADIS. Once the three-peak nature of the siloxane panel emissions was recognized, the sampling was increased to 1,800 points per 60 minute period to improve peak resolution. These models of the data allow comparisons of VOC emissions at the same point in the drying process, as shown at the bottom of Appendix C.

Figure 9. Example of Curve Fitting of VOC Emissions Data for ATL Siloxane Panel Drying



To calculate comparative VOC emissions at the same point in the drying process, the desired time (in minutes) was input to the appropriate cell of the spreadsheet and the VOC calculated for each of the types of panels at that point in the drying process. These models could be used by wallboard manufacturers to estimate relative emission changes when contemplating WR additive changes and corresponding equipment design changes. For example, Table 3 shows a comparison of siloxane VOC emissions with wax VOC emissions at corresponding points in the drying process, calculated from the models of the

emissions curves in Appendix C. The emissions from siloxane panels are greater than from wax panels at any corresponding point in the drying process. The three siloxane peaks at five, 12 and 47 minutes indicate up to 21 times the VOC emission compared to wax. Although the models somewhat bias the emissions from the first and second emissions peaks towards lower values (see Figure 9), the highest emissions from the first and second peaks are much lower contributors than that from the third peak.

Table 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

As shown in Table 3, the average ppmv emissions for the 60 minute period for each siloxane additive is greater than the maximum VOC emissions of either the first or second peaks. This indicates the greatest amount of VOC emissions to occur during the last peak of the siloxane drying. The wax additive panels show a lower and more uniform emission rate over the 60 minute drying period.

The lower dosage, eight pounds/msf, of Siloxane 1 appears to be most distinctly separated from the 12 pounds/msf dosage rate during the last and most massive siloxane emissions peak at around 47 minutes into the 60 minute drying process. Although all three siloxane MSDS listed them as methyl hydrogen siloxanes, the total VOC emissions from their reaction products in the kiln varied between them. Although Siloxane 3 had the highest average VOC emission over the 60 minute period, Siloxane 2 appeared to have a stronger VOC emission in the third peak, implying either a difference in reaction products and/or a retardation of the reaction yielding the WR silicone end product.

In a manufacturing plant situation, if exhaust gas treatment is needed to meet stack emissions, an entire oven exhaust treatment may be prohibitively expensive. Even if only certain zones of the kiln are generating the largest emissions, the discharge stack of that zone may have to be run through a thermal oxidizer or other VOC removal treatment to lower the overall total plant emissions. For example, with a three zone kiln, based on the data in Table 3 and Appendix G, exhaust gas VOC reduction treatment should be targeted in the third zone. The added treatment step would further increase the cost of siloxane use, however it may be necessary in areas where attainment of VOC emissions permits is not possible when siloxane is used as a WR additive in place of wax. Due to the higher PM generated during siloxane use, life of the thermal oxidizer could be extended by installation of an electrostatic precipitator or other particulate removal system to remove the silicon dioxide solids upstream of the VOC reduction. However, this would further increase the cost penalty of using siloxane instead of wax and further increase the initial capital cost of changeover from wax to silicone.

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. This allowed a comparison of wax versus siloxane and the high and low dosages of each. Columns list relative safety comparisons based on National Fire Protection Association (NFPA) and Hazardous Materials Identification System (HMIS) safety ratings as well as the required Department of Transportation (DOT) placards. PEL TWA values are used for comparisons of the risks of the VOC in Table 4. PEL TWA is the OSHA Permissible Exposure Limits based on a Time Weighted Average for an eight hour day over a 40-hour work week.

Table 4. 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)
108-88-3	Toluene	476.0	1,240.0	1,390.0	2,130.0	2	2	500	200
74-87-3	Chloromethane	98.9	41.5	21.5	24.8	3	3	2,000	100
107-02-8	Acrolein	62.0	37.0	56.4	57.7	4	4	2	0.1
111-65-9	n-Octane ³	20.4	23.9	23.7	17.7	2	0	1,000 ³	500
87-68-3	Hexachloro-1,3-butadiene	0.8	6.8	ND*	ND*	3	3	na**	0.02
115-07-1	Propylene	12.2	6.7	9.8	10.9	0	0	na**	na
67-66-3	Chloroform	3.8	5.0	4.1	3.9	2	2	500	50
75-05-8	Acetonitrile	1.8	2.9	44.9	17.9	2	2	500	40
95-63-6	1,2,4-Trimethylbenzene	8.3	1.6	3.5	2.0	2	1	na**	none
108-38-3	m-Xylene	8.6	1.4	3.1	4.9	2	2	900	100
106-42-3	p-Xylene	8.6	1.4	3.1	4.9	2	2	900	100
75-15-0	Carbon Disulfide	2.0	1.3	2.1	2.0	2	2	500	20
74-86-2	Acetylene	1.7	1.0	1.4	1.6	1	1	na**	none
71-43-2	Benzene	1.3	0.9	1.7	2.3	2	3	500	1
100-41-4	Ethylbenzene ³	2.7	0.7	1.2	3.0	3	2	800 ³	100
108-67-8	1,3,5-Trimethylbenzene	1.9	0.6	1.1	1.1	2	2	na**	none
95-47-6	O-Xylene	2.3	0.5	1.2	2.0	2	2	900	100
78-93-3	Methyl Ethyl Ketone	24.1	ND	23.5	24.3	1	2	3,000	200

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

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

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

⁴OSHA 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

⁵DOT 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 or the raw materials used in their manufacture. For example, one would expect toluene, acrolein and acetonitrile to be associated more with the wax, and chloromethane, hexachloro-1,2-butadiene and chloroform to be more abundant in the siloxane emissions.

Some paper edge discoloration was evident in the test samples as shown in Appendix E. The worst of the panels were remade and retested. Within the group of boards in Table 4, paper edge discoloration was considered comparable. Typically true paper burning in this test generates a spike in emissions at the end of the test. In many cases, over-drying of panels and burnt corners or edges may be an additional source of emissions in a manufacturing environment.

Hexachloro1, 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 types of board. As shown in Table 4, HCBD has the highest risk factors of the compounds in the table (0.02 ppmv HCBD basis, 0.24 mg/m³ PEL TWA toxicity) for the PEL TWA systems. HCBD gives health concerns from a chemistry perspective by both its chlorine constituents and the double carbon bonds. Chlorine compounds are quite reactive and may pose risks of reaction or interaction with metabolic cycles in living creatures. Likewise, double-bond carbon compounds tend to be more reactive than their single-bond counterparts and may pose risk of reaction with biological tissues closer to room temperature.

DOT Placard⁶

Irritant, Flammable
 Toxic, Flammable
 Poison, Inhalation Hazard, Flammable Liquid
 Flammable Liquid
 Poison, Toxic, Irritant, Carcinogen
 Flammable Gas
 Irritant, Carcinogen
 Flammable Liquid
 Combustible Liquid
 Irritant, Flammable Liquid, Reproduction Hazard
 Irritant, Flammable Liquid, Reproduction Hazard
 Flammable Liquid
 Flammable Gas
 Toxic, Carcinogen, Flammable
 Flammable Liquid, Irritant, Carcinogen
 Combustible Liquid, Irritant
 Irritant, Flammable Liquid, Reproduction Hazard
 Flammable Liquid

Toluene (100 ppmv toluene basis, 375 mg/m³PEL TWA toxicity) was the most abundant TO-15 air toxic in the drying emissions gas stream, with both wax and siloxane generating more than the board without any WR additive. Toluene increased as the level of either wax or siloxane increased, with the wax panels generating around twice as much as the siloxane panels. Since toluene is one of the solvents of choice for purification of paraffin and Montan wax, the toluene may be residual from the wax supplier's manufacturing process.

Similarly, acetonitrile (40 ppmv acetonitrile basis, 70 mg/m³PEL TWA toxicity) levels were higher with the wax panels than the siloxane panels by about an order of magnitude. However, since the VOC level decreased as the wax level was increased, the wax may not have been the source of the acetonitrile but rather the paper facers.

Chloromethane (50 ppmv chloromethane basis, 105 mg/m³PEL TWA toxicity) levels were higher in the siloxane boards than the wax boards, but again, the VOC level decreased as the siloxane level increased, implying that the siloxane may not have been the only source of the chloromethane. The paper used in wallboard facing can contain a variety of recycled papers. Papermaking typically involves two steps: pulping to separate fiber bundles, and bleaching to brighten the pulp. Traditionally, chlorine compounds or ozone have been used for bleaching. Some of these previously bleached recycled papers may have been used in the manufacture of the wallboard paper facing with the residual chlorine as a possible contributor to chloromethane generation.

As a result, there may be two sources of the chloromethane, the decomposition of the paper and the residual raw materials from the manufacture of the siloxane. The higher level in the control may be due to more paper edge discoloration in that sample than in the siloxane or wax panels. The highest level of chloromethane in the four panels arose from the low siloxane panel, which may have had contributions from the siloxane component as well as from the paper edge discoloration, since this panel was also the second-most discolored panel behind the control.

Acrolein (0.1 ppmv acrolein basis, 0.25 mg/m³PEL TWA toxicity) and hexachloro-1,3-butadiene (HCBd) (0.02 ppmv HCBd basis, 0.24 mg/m³PEL TWA toxicity) are some of the more toxic compounds from the EPA TO-15 list. There appears little distinction between the siloxane and the wax in acrolein emissions, and since the control board was nearly three times the emissions of either, little can be inferred for this compound. HCBd, however, is only present when siloxane is used as the additive.

Although the ERG SIM method is much more sensitive to some VOC compounds than common GC-MS specified by EPA TO-15, additional samples were prepared and sent to two other labs for TO-15 analysis (Table 5 and Appendix G). These samples focused more on differences between siloxane sources as well as on separating the three peaks common to the siloxane VOC emissions curve.

For the second and third blocks of VOC data, gas was also sampled separately during each of the three major peaks occurring at around five minutes, 12 minutes, and 47 minutes into the 60 minute drying schedule as shown in Table 5. In this case, no acrolein-2-propanol was not found in the wax board but was found in the siloxane panels.

Table 5. 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	60	60	7	13	40	60	60	PEL TWA ¹ ppmv
		ALS2 Control Board	ALS3W Wax	ALS4 BSF Siloxane 1	ALS5 BS7 Siloxane 1 1st peak	ALS5 BS8 Siloxane 1 2nd peak	ALS5 BS9 Siloxane 1 3rd Peak	ALS5 OM Siloxane2	ALS5 MO Siloxane3	
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	0.02
107-02-8	Acrolein-2-Propanal	36.0	ND	126.0	97.0	210.0	196.0	ND	280.0	0.1
108-88-3	Toluene	17.0	67**	220**	220**	220**	140**	12.0	11.0	200
74-87-3	Chloromethane	6.8	9.5	19.0	15.0	90**	390**	29**	690**	100
142-82-5	Heptane	ND	1.2	ND	3.7	1.3	6.5	1.0	9.1	500
110-54-3	Hexane	ND	1.5	ND	2.0	1.3	ND	1.1	ND	500
67-66-3	Chloroform	1.2	ND	1.1	ND	1.0	2.9	ND	5.7	50
75-15-0	Carbon Disulfide	2.8	1.8	1.5	20.0	2.9	11.0	4.6	18.0	20
95-63-6	1,2,4-Trimethylbenzene	36**	23.0	44**	8.1	11.0	9.5	9.7	14.0	none
108-67-8	1,3,5-Trimethylbenzene	10.0	6.3	ND	ND	ND	ND	2.9	ND	none
67-64-1	Acetone	150**	110**	78**	81**	99**	460**	90**	700**	1000
67-63-0	2-Propanol	12.0	13.0	4.7	14.0	9.6	32**	8.4	48**	400
78-93-3	Methyl Ethyl Ketone	39**	29**	ND	ND	ND	ND	ND	ND	200
115-07-1	Propylene-Propene	ND	ND	ND	ND	ND	ND	ND	59.0	na
100-42-5	Styrene	ND	ND	ND	ND	ND	ND	ND	1.3	100
71-43-2	Benzene	ND	ND	ND	ND	ND	4.2	ND	5.7	1
79-01-6	Trichloroethene	0.8	0.4	ND	ND	ND	ND	ND	ND	100
98-82-8	Cumene	2.2	ND	ND	ND	ND	ND	ND	ND	50
108-10-1	4-Methyl-2-Pentanone	2.2	1.4	ND	1.6	ND	ND	1.2	ND	100
110-82-7	Cyclohexane	ND	3.1	ND	ND	ND	ND	ND	ND	300
74-83-9	Bromomethane	ND	ND	ND	ND	1.1	5.3	ND	8.1	20
75-09-2	Methylene Chloride	ND	ND	ND	ND	ND	2.1	ND	ND	25
108-38-3	M,P-Xylene	23.0	10.0	17.0	9.9	16.0	7.4	8.6	10.0	100
106-42-3										
622-96-8	4-Ethyltoluene	8.9	5.5	9.4	2.5	2.9	1.8	2.6	3.6	na
95-47-6	O-Xylene	7.3	3.7	6.1	3.6	4.5	2.5	3.0	3.5	100
591-78-6	2-Hexanone	7.7	7.2	5.1	3.0	4.3	2.8	3.3	4.0	100
100-41-4	Ethylbenzene	3.9	1.8	3.2	3.0	3.5	1.8	2.3	2.5	100

¹OSHA 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

Other

Poison, Toxic, Irritant, Carcinogen
 Poison, Inhalation Hazard, Flammable Liquid
 Irritant, Flammable
 Toxic, Flammable
 n-Heptane, $\text{CH}_3(\text{CH}_2)_5\text{CH}_3$
 Hexyl Hydride, Normal-Hexane, $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$
 Irritant, Carcinogen
 Flammable Liquid
 Combustible Liquid
 Combustible Liquid, Irritant
 Dimethyl Ketone, Ketone Propane, 2-Propanone, $(\text{CH}_3)_2\text{CO}$
 Isopropyl Alcohol, Dimethyl Carbinol, IPA, Isopropanol, Sec-Propyl Alcohol,
 Rubbing Alcohol, $(\text{CH}_3)_2\text{CHOH}$
 Flammable Liquid, 2-Butanone
 Flammable Gas
 Ethenyl Benzene, Phenylethylene, Styrene Monomer Styrol, Vinyl Benzene,
 $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$
 Toxic, Carcinogen, Flammable
 Ethylene Trichloride, TCE, Trichloroethene, Trilene, $\text{ClCH}=\text{CCl}_2$
 Cumol, Isopropyl Benzene, 2-Phenyl Propane, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$
 Hexone, Isobutyl Methyl Ketone, Methyl Isobutyl Ketone, MIBK
 Benzene Hexahydride, Hexahydrobenzene, Hexamethylene, Hexanaphthene, C_6H_{12}
 Methyl Bromide, Monobromomethane, CH_3Br
 Methylene Dichloride, Dichloromethane, CH_2Cl_2
 Irritant, Flammable Liquid, Reproduction Hazard

p-Ethyl Toluene, 4-Methyl Ethyl Benzene, 1-Ethyl-4-Methyl Benzene
 Irritant, Flammable Liquid, Reproduction Hazard
 Butyl Methyl Ketone, MBK, Methyl Butyl Ketone, Methyl n-Butyl Ketone,
 $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CH}_3$
 Flammable Liquid, Irritant, Carcinogen

ALS TO-15 Speciation Results

ALS had significant problems with the large amount of siloxane-based materials in the VOC samples, which introduced instrumental interference. As a result, speciation of VOC was less accurate than the ARCADIS/ERG testing; however, ALS did estimate the major siloxane-based species in the samples. In particular, trimethyl silanol, 2,4,6,8-tetramethyl cyclotetrasiloxane, as well as another unidentified higher molecular weight siloxane are shown in the top lines of Table 5. As mentioned earlier, trimethyl siloxane is thought to be a reaction product as the siloxane converts to the more WR silicone form. These large and broad siloxane compound gas chromatograph peaks may have obscured some of the compounds detected in the more sensitive ARCADIS/ERG analysis.

Siloxane 3 showed unique compound emissions of heptane, chloroform, styrene, benzene, propylene, and bromomethane. As a result, this siloxane would not be recommended for use if other alternatives were available. The heptane is most likely a co-solvent or carrier for the siloxane. Obviously, different siloxane products can produce different VOC emissions and HAPS based on their formulation and purity. This highlights the need for siloxane MSDS to be more forthcoming regarding additives or impurities that can impact emissions.

The high levels of isopropyl alcohol, methyl ethyl ketone and acetone were considered to be laboratory contaminates and not considered further.

Samples were taken during a VOC test of Siloxane 1 around the first siloxane peak (one to seven minutes), the second siloxane peak (8 to 20 minutes) and the third siloxane peak (21 to 60 minutes). Siloxane emission increased from the first through the third peaks.

Overall, compared to the wax panel and the control panel, the siloxane samples generated a much larger amount of VOC, which was predominately siloxanes as shown in numbers 1-3 of Table 5 and numbers 1-6 of Appendix G. This clarifies that the large peaks on the VOC traces over the 60 minute drying period are predominately siloxane-based materials.

Air Toxics Ltd. TO-15 Results

The Air Toxics Ltd. VOC speciation from samples made and collected from the Henry Emissions Oven is shown in Appendix G. A duplicate set of ATL3, the wax panel, was run by ATL to confirm the repeatability of their GC-MS method. Both values are listed in the table, separated by a comma. This shows the repeatability of their procedure to be extremely good. Since the acetone, ethanol, MEK, isopropyl alcohol and methyl chloride were seen in the sample from the oven emissions with no board present, and they are common solvents used to clean analytical equipment, their source is most likely from residual cleaning before the samples were run and not from the panel emissions, as has also been mentioned previously for the isopropyl alcohol, methyl ethyl ketone, and acetone from the ALS analysis.

ATL was able to identify more siloxanes present in the VOC emissions as shown in numbers 1 to 6 of Appendix G. Analyzing the large quantities of these siloxanes in the samples forced ATL to do substantial dilution prior to the instrumentation to eliminate the instrument problems observed with the ALS samples. Unfortunately, this also may have diluted the samples below the detection limits for some of the lower concentration constituents, such as the hexachlorobutadiene.

As with the ALS data, the predominant VOC compounds are siloxane-based compounds, which almost exclusively appeared in the siloxane panel emissions but not in the wax or control panel emissions. Several additional unknown compounds were found and are listed as 7 to 9 in the table. Number 7 and number 8 are most likely also siloxane-based compounds due to their similar concentrations to other siloxane compounds from the siloxane panels.

Comparing the three siloxanes, as with the ALS data, Siloxane 3 appeared to generate more siloxane compounds than the other siloxanes and should be the last choice of the three siloxanes if siloxane must be used instead of the much lower VOC wax. The VOC siloxane compounds also varied between the three siloxanes with Siloxanes 1 and 3 containing tetramethyldisilane (number 5), but not Siloxane 2. However, only Siloxane 2 emitted the heptamethyltrisiloxane (number 6). This characteristic might be used to determine the siloxane source used in a wallboard process if samples are taken at the wet end and immediately tested in an emissions test oven similar to that of Henry Company.

In comparing the three peaks of siloxane VOC emission (see Figure 9 and Appendix G), a progression is seen with the first four siloxane compounds in the table (numbers 1, 2, 3, 4) of increasing concentrations of these VOCs from the first through the third siloxane reaction peaks. The trimethylsilanol appears to be the primary siloxane based compound in the first peak, which corresponds with the initial hydration reaction of the siloxane and the expected cleavage of trimethyl silanol end groups to allow endwise polymerization. The phenylenetrimethylsilane (number 1) appears to predominate in the second peak and may be either a siloxane starting material contaminant that has found its way to the surface of the wallboard panel or a condensation and rearrangement product of the trimethylsilanol. The fluorotrimethylsilane is much more common in the second and third siloxane peaks and due to fluorination, would appear to more likely be a residual from the siloxane raw material than a product formed during the kiln drying siloxane reactions.

A second comparison that was done in the ATL study was the effect of aging of siloxane in an opened container. VOC emissions were similar to unaged siloxane, except that they contained substantially less phenyltrimethylsilane (number 1 in Appendix G). If it is a contaminant in the starting siloxane, it may imply that aging allows more of it to be lost to the atmosphere before it can be used in the wallboard manufacturing process or that this material reacts with atmospheric components to form other compounds. These compounds could be higher in molecular weight and not collected in the TO-15 list, or are of a higher molecular weight that cannot be carried to the panel surface and lost to the drying air.

As a final note, substantially more VOCs are generated than can be measured by the EPA TO-15 method. Formaldehyde, for example, and similarly methanol, methane, other alcohols, aldehydes and alkanes, etc. would be measured by the flame ionization detector for total VOC, but not by the TO-15 method.

CONCLUSIONS AND RECOMMENDATIONS

With average siloxane emissions of greater than ten times that of wax, and peak emissions greater than 100 times, to equal the reduced emissions of wax, the siloxane dosage would need to be reduced from a typical eight to 12 pounds/msf to around one pound/msf. This level to date has not been found to achieve ASTM requirements for water resistant gypsum panels.¹² Increased VOC emissions will also impact plant EPA air emissions permitting. Based on these results, plants switching from wax to siloxane may face EPA penalties or permit modification requirements. Based on these data, plants may need to re-evaluate air permits and WR gypsum wallboard production levels, paying specific attention to hazardous air pollutants if they contemplate changing from wax to siloxane.

This paper presented models for the VOC emissions of wax or siloxane panels during a 60 minute 232°C drying schedule. These models could be used by manufacturers to estimate increased VOC at various points in the drying process or for total VOCs in the full drying process with various wax and siloxane additives.

If a plant switches from wax to siloxane and still wants to maintain historical production levels of WR product, plant stack emissions will increase and may result in either EPA penalties or costs associated with permit modifications and/or costs associated with pollution control equipment and hazardous waste handling and disposal. Siloxane generates a toxic air pollutant that wax does not. This particular compound, HCBP, 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 large increase in PM as well. Siloxane use in wallboard plants generates significant quantities of PM 10 and specifically PM 2.5. The question of whether utilization of siloxane creates or contributes to the formation/liberation of crystalline silica in the kiln is a serious worker safety issue and requires more investigation.

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ABBREVIATIONS

CaSO ₄	Calcium Sulfate
CaSO ₄ * 2H ₂ O	Calcium Sulfate Dihydrate
CFR	Code of Federal Regulations
EPA	Environmental Protection Agency
ERG	Easter Research Group
FID	Flame Ionization Detector
GC/MS	Gas Chromatography/Mass Spectrometry
H ₂	Hydrogen Gas
HMIS	Hazardous Materials Identification System
K ₂ SO ₄	Potassium Sulfate
MEK	Methyl Ethyl Ketone
MHS	Methylhydrogensiloxane
MR	Moisture Resistant/Resistance
MSDS	Materials Safety Data Sheet
MSW	Municipal Solid Waste
NFPA	National Fire Protection Association
OSHA	Occupational Safety & Health Administration
PEL	Permissible Exposure Limit
PM	Particulate Matter
PMHS	Polymethylhydrogensiloxane (siloxane)
PSD	Prevention of Significant Deterioration
PTFE	Polytetrafluoroethylene (DuPont brand – Teflon)
SARA	Superfund Amendments and Reauthorization Act
SiO ₂	Silicon Dioxide
THC	Total Hydrocarbon
TWA	Time Weighted Average
UHP	Ultra High Purity
VOC	Volatile Organic Compound
WR	Water Resistant/Resistance

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Marion R. Surgi, Ph.D., has been a consultant to Fortune 10 companies for the last 15 years. Dr. Surgi directs large scale remediation programs as well as other process related statistical projects. He holds a Ph.D. in analytical chemistry from Louisiana State University, as well as a bachelor's degree in chemistry from the University of New Orleans.

Chris Lyons, M.S., has four years of experience in the development of wax emulsions and their use in waterproof applications in construction. He is responsible for product development at H&R ChemPharm UK, a manufacturer of a wide product range of water blocking compounds specifically developed for applications in the construction, communication and energy cable industry. Mr. Lyons graduated from the University of Bath with a master's degree in chemistry.

APPENDIX A: 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

APPENDIX B: ARCADIS EMISSIONS TEST OVEN SETUP



APPENDIX C: MODEL OF VOC EMISSIONS OVER 60 MINUTE DRYING CYCLE AT 450°F IN VOC EMISSIONS OVEN

Additive	Dosage (lb/msf)	AVE VOC (ppmv)	Polynomial Fit (R ²)	VOC Emission Curve Equation (720 to 1800 Values Each)
Control	0	3.42	0.8718	$y = 2E-07x^5 - 3E-05x^4 + 0.0021x^3 - 0.0657x^2 + 0.8506x + 0.863$
Control	0	9.39	0.9277	$y = 4E-07x^5 - 8E-05x^4 + 0.0055x^3 - 0.1775x^2 + 2.3746x + 2.4104$
Control	0	10.87	0.8379	$y = -7E-06x^4 + 0.0013x^3 - 0.0792x^2 + 1.6914x + 3.1231$
ControlCan	0	11.48	0.9674	$y = 3E-07x^5 - 6E-05x^4 + 0.0043x^3 - 0.1493x^2 + 2.1187x + 1.61$
No Board	0	0.05	0.8069	$y = -4E-10x^5 + 4E-08x^4 - 3E-07x^3 - 4E-05x^2 + 0.0005x + 0.0032$
Siloxane 1	8	31.44	0.9170	$y = -1E-05x^4 + 0.0011x^3 - 0.0611x^2 + 2.6127x - 1.8606$
Siloxane 1	8	57.45	0.8656	$y = 6E-06x^5 - 0.0008x^4 + 0.037x^3 - 0.7318x^2 + 9.0185x - 6.8294$
Siloxane 1	12	77.62	0.9466	$y = 3E-06x^5 - 0.0005x^4 + 0.0338x^3 - 0.9171x^2 + 11.899x + 1.0088$
Siloxane 1	12	90.90	0.9385	$y = -0.0002x^4 + 0.0151x^3 - 0.5107x^2 + 9.1786x + 2.3471$
Siloxane 1	12	96.96	0.9609	$y = -0.0002x^4 + 0.0168x^3 - 0.513x^2 + 7.9136x - 5.309$
Siloxane 1 Old	12	74.97	0.9072	$y = -0.0001x^4 + 0.0127x^3 - 0.4571x^2 + 7.7643x + 11.801$
Siloxane 1 Old	12	109.00	0.9190	$y = 7E-06x^5 - 0.0012x^4 + 0.0726x^3 - 1.901x^2 + 22.072x - 1.9049$
Siloxane 1 Peak	12	78.10	0.9279	$y = -0.0001x^4 + 0.0109x^3 - 0.3697x^2 + 6.3951x + 16.037$
Siloxane 2	12	68.30	0.8771	$y = 2E-06x^5 - 0.0005x^4 + 0.0335x^3 - 0.9987x^2 + 12.76x + 0.1546$
Siloxane 2	12	87.40	0.9265	$y = 4E-06x^5 - 0.0007x^4 + 0.0478x^3 - 1.3623x^2 + 17.373x - 6.8015$
Siloxane 3	12	79.30	0.9479	$y = 3E-06x^5 - 0.0006x^4 + 0.0413x^3 - 1.1835x^2 + 15.116x - 3.7536$
Siloxane 3	12	112.30	0.9345	$y = 5E-06x^5 - 0.001x^4 + 0.066x^3 - 1.77x^2 + 20.647x + 2.3759$
Wax	50	5.91	0.9798	$y = 3E-07x^5 - 4E-05x^4 + 0.0023x^3 - 0.0657x^2 + 0.8462x + 1.6732$
Wax	90	14.30	0.9476	$y = 1E-05x^4 - 0.0005x^3 - 0.0038x^2 + 0.5559x + 4.2019$
Wax	90	19.03	0.9785	$y = 0.0008x^3 - 0.0638x^2 + 1.5284x + 5.3105$
WaxCan	50	10.62	0.9258	$y = 0.0005x^3 - 0.0417x^2 + 0.9818x + 2.3699$
WaxCan	90	15.48	0.9295	$y = 0.0007x^3 - 0.0511x^2 + 1.2786x + 2.3642$

Worksheet to calculate VOC at specific times into the drying process

Additive	Average (ppmv)	Point (ppmv)*	Polynomial Fit (R ²)	6th	5th	4th	3rd	2nd	1st	Intercept
Wax 50	10.62	8.31	0.9258	0	0	0	0.0005	-0.0417	0.9818	2.3699
Wax 90	19.03	19.27	0.9785	0	0	0	0.0008	-0.0638	1.5284	5.3105
Silox1-12	78.10	143.64	0.9279	0	0	-0.00010	0.0109	-0.3697	6.3951	16.037
Silox1-8	57.45	114.27	0.8656	0	6.00E-06	-8.00E-04	0.037	-0.7318	9.0185	-6.8294
No WR	10.87	8.48	0.8379	0	0	-7.00E-06	0.0013	-0.0792	1.6914	3.1231
Silox3-12	112.30	182.22	0.9345	0	5.00E-06	-1.00E-03	0.066	-1.77	20.647	2.3759
No Bd	0.05	0.01	0.8069	0	-4.00E-10	4.00E-08	-3.00E-07	-4.00E-05	5.00E-04	3.20E-03
Silox2-12	87.40	264.75	0.9265	0	4.00E-06	-7.00E-04	0.0478	-1.3623	17.373	-6.8015
				1.08E+10	2.29E+08	4.88E+06	1.04E+05	2209.00	47.00	

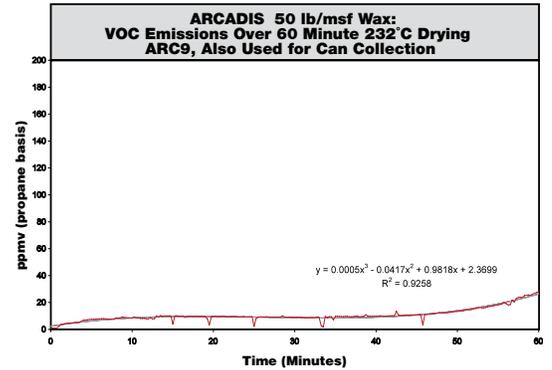
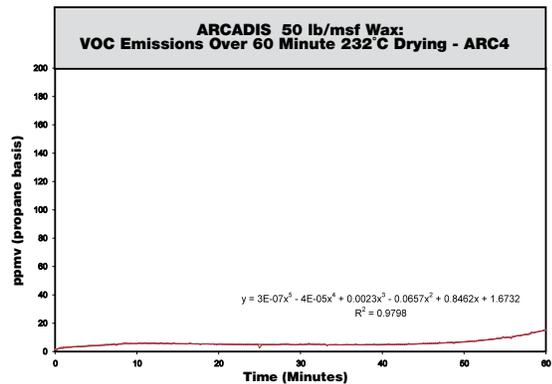
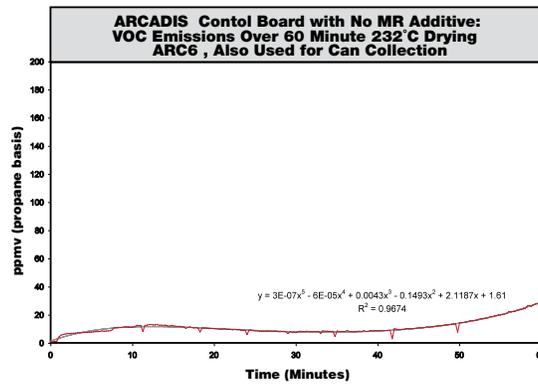
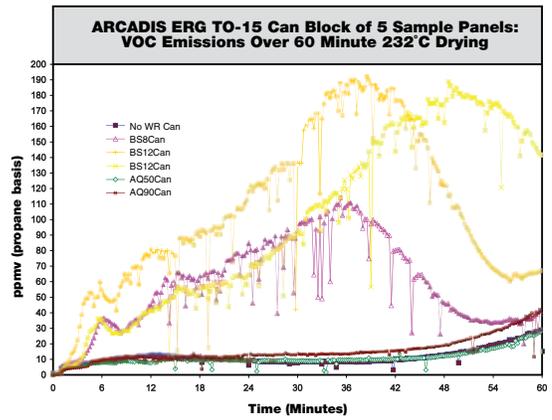
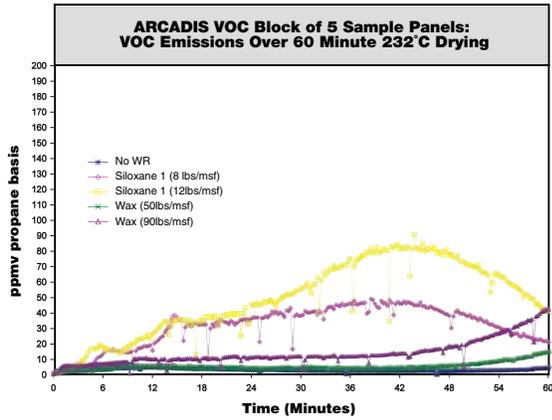
Additive	Full Equation
Wax 50	$y = 0.0005x^3 - 0.0417x^2 + 0.9818x + 2.3699$
Wax 90	$y = 0.0008x^3 - 0.0638x^2 + 1.5284x + 5.3105$
Silox1-12	$y = -0.0001x^4 + 0.0109x^3 - 0.3697x^2 + 6.3951x + 16.037$
Silox1-8	$y = 6E-06x^5 - 0.0008x^4 + 0.037x^3 - 0.7318x^2 + 9.0185x - 6.8294$
No WR	$y = -7E-06x^4 + 0.0013x^3 - 0.0792x^2 + 1.6914x + 3.1231$
Silox3-12	$y = 5E-06x^5 - 0.001x^4 + 0.066x^3 - 1.77x^2 + 20.647x + 2.3759$
No Bd	$y = -4E-10x^5 + 4E-08x^4 - 3E-07x^3 - 4E-05x^2 + 0.0005x + 0.0032$
Silox2-12	$y = 4E-06x^5 - 0.0007x^4 + 0.0478x^3 - 1.3623x^2 + 17.373x - 6.8015$

*Point (ppmv) is calculated from the input time value below. Input desired time point (x) in minutes below.

Point in time (x) is minutes.

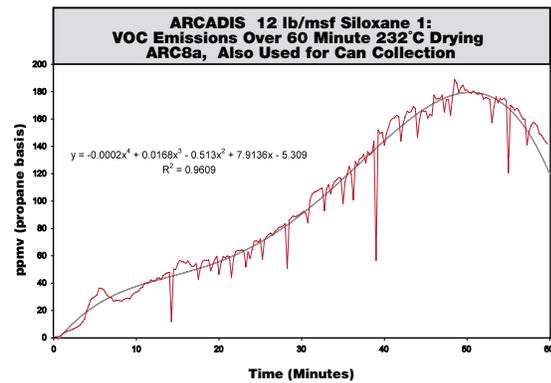
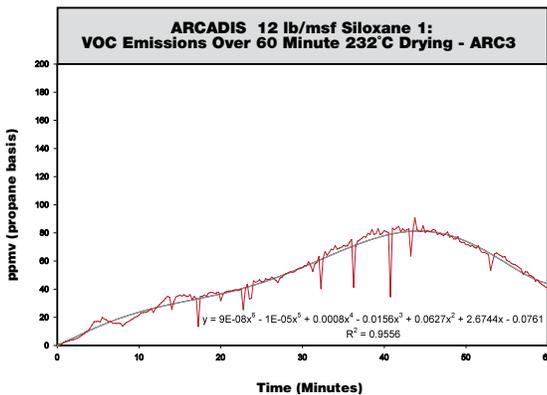
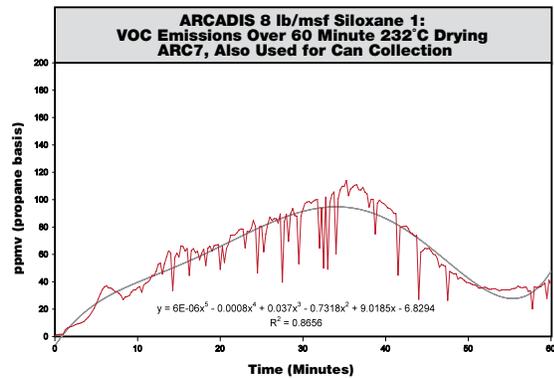
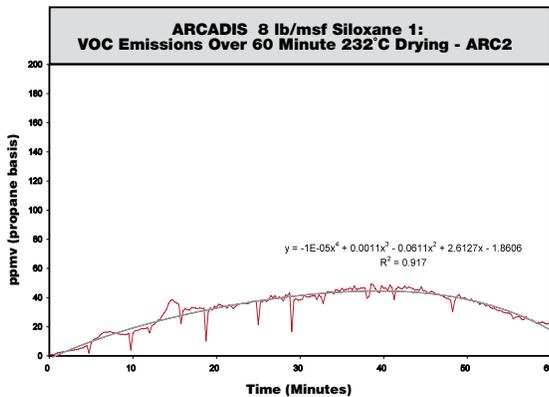
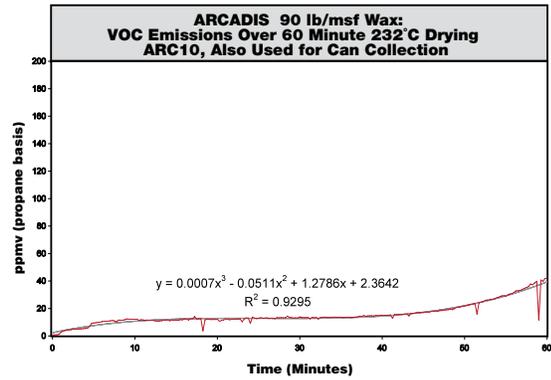
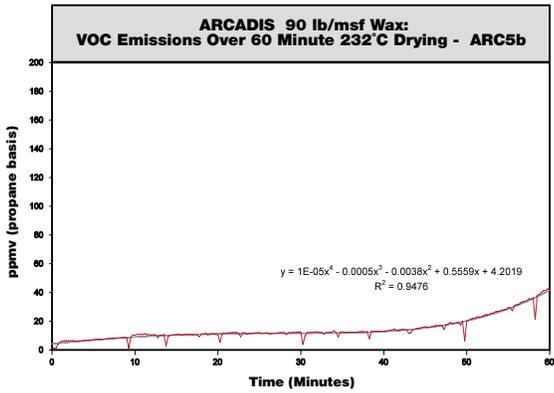
APPENDIX D: VOC EMISSIONS OVER 60 MINUTE DRYING CYCLE

ARCADIS Boards VOC Data



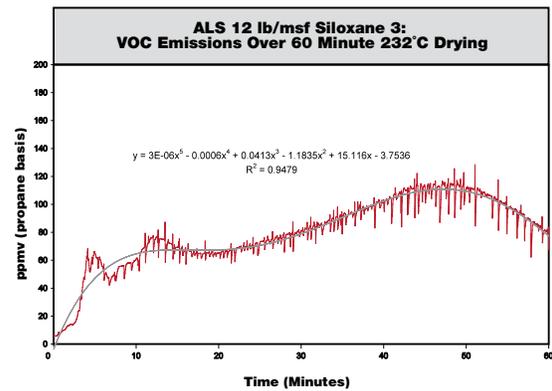
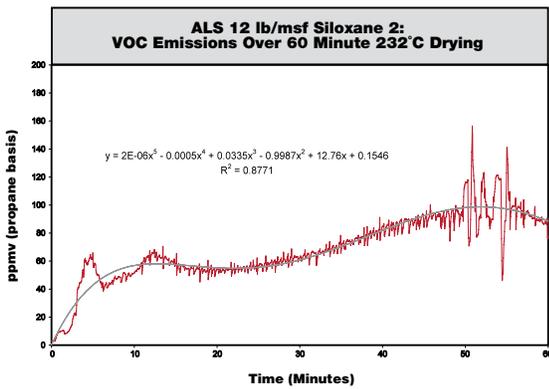
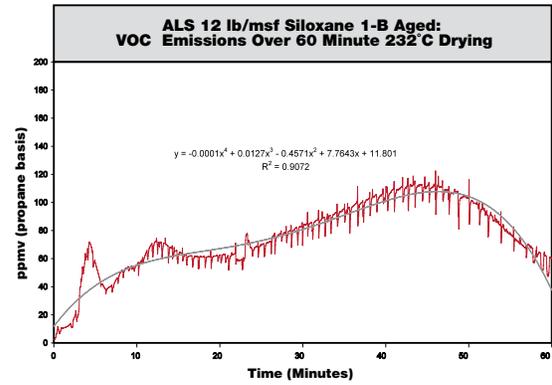
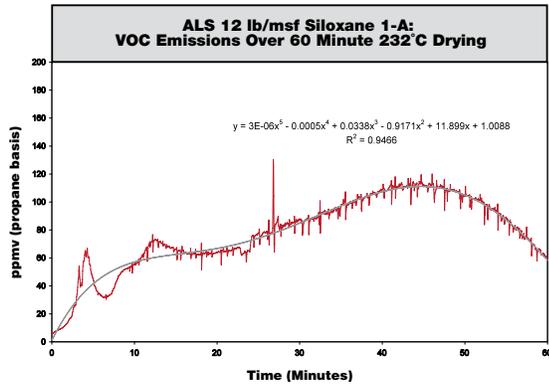
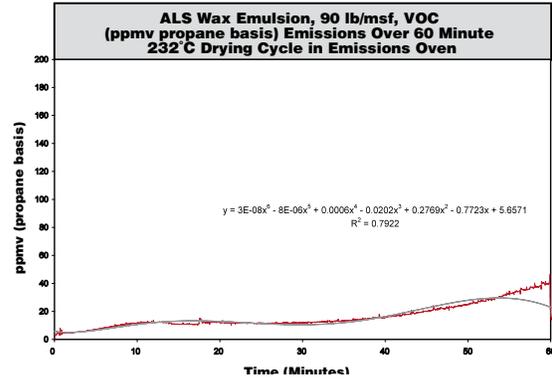
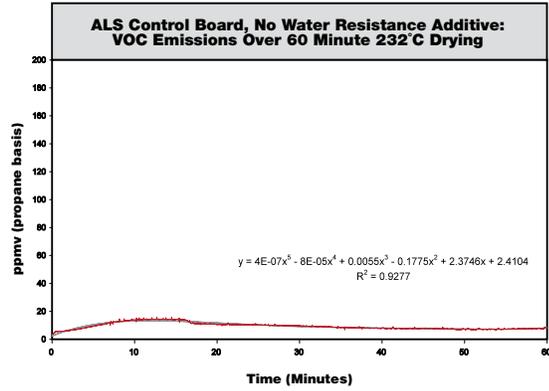
APPENDIX D: VOC EMISSIONS OVER 60 MINUTE DRYING CYCLE

ARCADIS Boards VOC Data



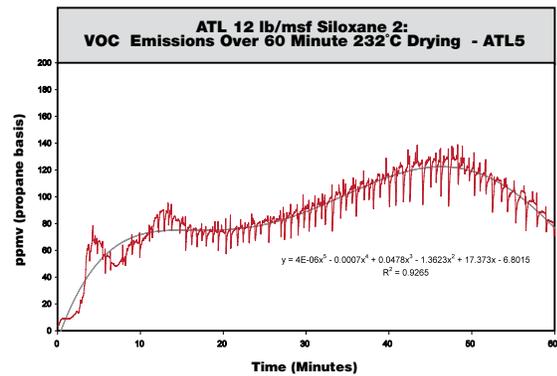
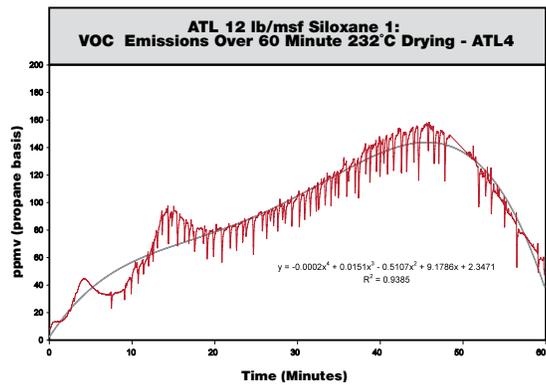
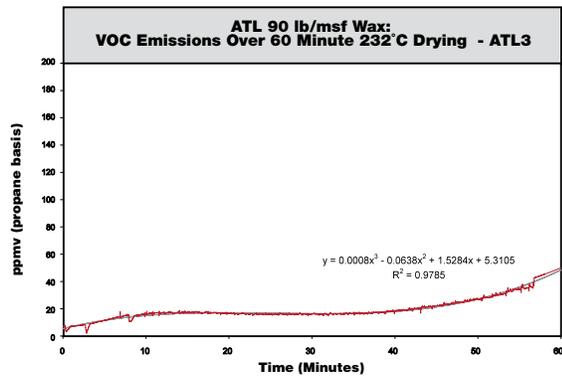
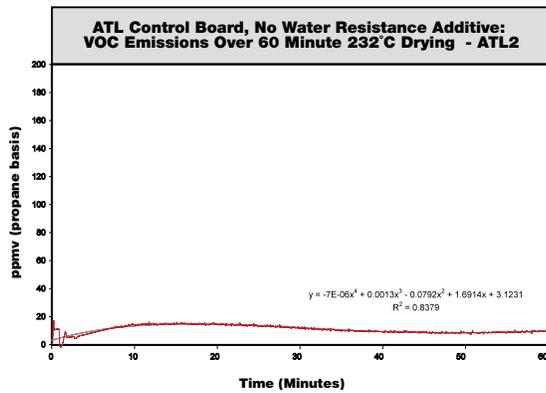
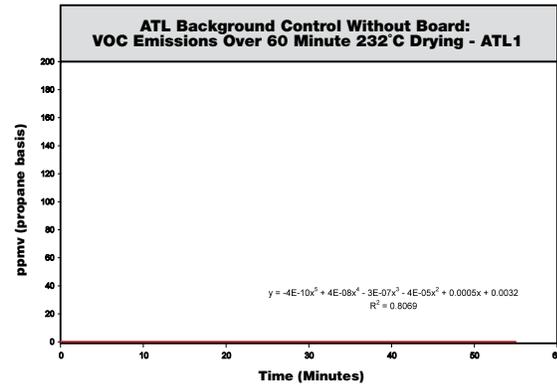
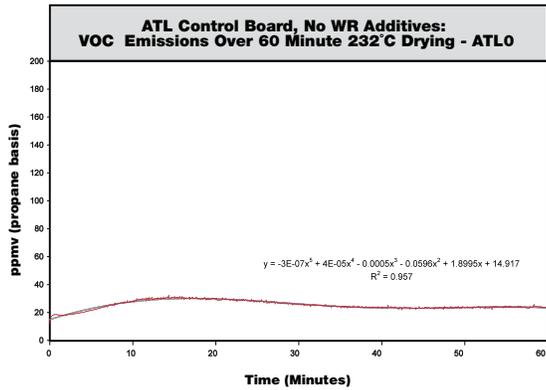
APPENDIX D: VOC EMISSIONS OVER 60 MINUTE DRYING CYCLE

ALS Boards VOC Data



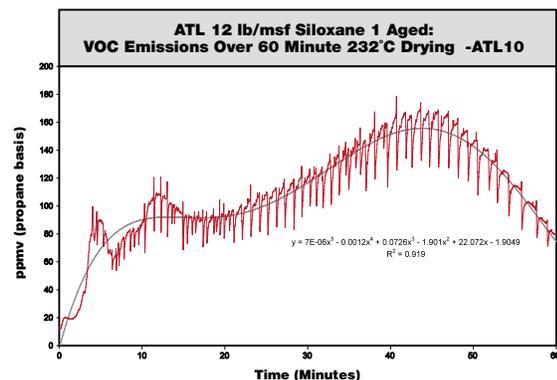
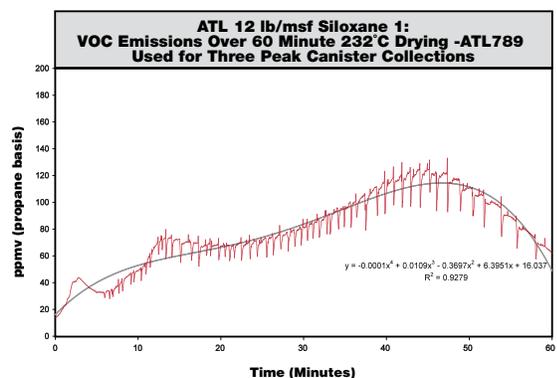
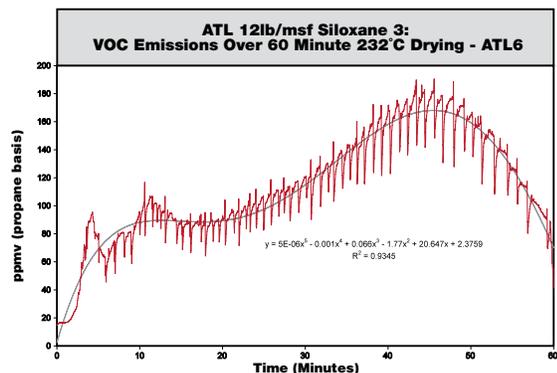
APPENDIX D: VOC EMISSIONS OVER 60 MINUTE DRYING CYCLE

ATL VOC Testing Data

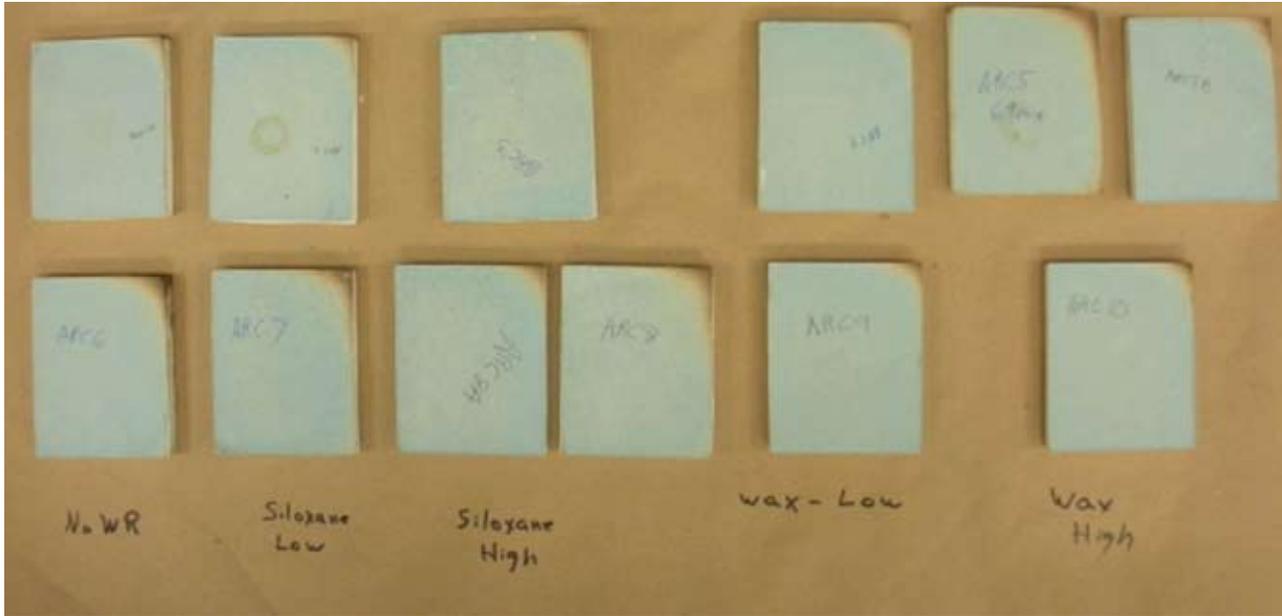


APPENDIX D: VOC EMISSIONS OVER 60 MINUTE DRYING CYCLE

ATL VOC Testing Data



APPENDIX E: RANGE OF DISCOLORATION OF PANEL CORNERS DURING ARCADIS TESTING (THE WORST PANELS WERE DISCARDED AND REPEATED)



APPENDIX F: SYNONYMS AND CHEMICAL DATA FOR VOCS FOUND BY ARCADIS-ERG IN SAMPLE PANEL EMISSIONS

Safety		Safety	Compounds	bp °F	CAS#	Synonyms	Structure
NFPA	HMIS ¹	DOT Placard ⁴					
2	2	Irritant, Flammable	toluene	232	108-88-3	toluol, methyl benzene, phenyl methane, methyl benzol	C ₆ H ₅ CH ₃
3	3	Toxic, Flammable	chloromethane	-12	74-87-3	methyl chloride, monochloromethane	CH ₃ Cl
4	4	Poison, Inhalation Hazard, Flammable Liquid	acrolein	127	107-02-8	acraldehyde, acrylaldehyde, acrylic aldehyde, allyl aldehyde, propenal, 2-propenal	CH ₂ =CHCHO
2	0	Flammable Liquid	n-octane	258	111-65-9	octane, l-octane	CH ₃ (CH ₂) ₆ CH ₃
3	3	Poison, Toxic, Irritant, Carcinogen	hexachloro-1,3-butadiene	419	87-68-3	hcbd, hexachlorobutadiene, 1,3-hexachlorobutadiene, perchlorobutadiene	Cl ₂ C=CClCCl=CCl ₂
0	0	Flammable Gas	propylene	-	115-07-1	propene	C ₃ H ₆
2	2	Irritant, Carcinogen	chloroform	143	67-66-3	methane trichloride, tricholomethane	CHCl ₃
2	2	Flammable Liquid	acetonitrile	178-180	75-05-8	cyanomethane, ethyl nitrile, methyl cyanide	CH ₃ CN
2	1	Combustible Liquid	1,2,4-trimethylbenzene	334	95-63-6	asymmetrical trimethylbenzene, psi-cumene, pseudocumene	C ₆ H ₃ (CH ₃) ₃
2	2	Irritant, Flammable Liquid, Reproduction Hazard	m,p-xylene	282 281	108-38-3 106-42-3	(1,3-dimethylbenzene, meta-xylene, m-xylol), (1,4-dimethylbenzene, para-xylene, p-xylol)	C ₆ H ₄ (CH ₃) ₂
2	2	Flammable Liquid	carbon disulfide	116	75-15-0	carbon bisulfide	CS ₂
1	1	Flammable Gas	acetylene	sublimes	74-86-2	ethine, ethyne	C ₂ H ₂
2	3	Toxic, Carcinogen, Flammable	benzene	176	71-43-2	benzol, phenyl hydride	C ₆ H ₆
3	2	Flammable Liquid, Irritant, Carcinogen	ethylbenzene	277	100-41-4	ethylbenzol, phenylethane	CH ₃ CH ₂ C ₆ H ₅
2	2	Combustible Liquid, Irritant	1,3,5-trimethylbenzene	329	108-67-8	mesitylene, symmetrical trimethylbenzene, sym-trimethylbenzene	C ₆ H ₃ (CH ₃) ₃
2	2	Irritant, Flammable Liquid, Reproduction Hazard	o-xylene	292	95-47-6	1,2 dimethylbenzene, ortho-xylene, o-xylol	C ₆ H ₄ (CH ₃) ₂
1	2	Flammable Liquid	methyl ethyl ketone (MEK)	175	78-93-3	2-butanone, MEK, methyl acetone, ethyl methyl ketone	CH ₃ COCH ₂ CH ₃

¹ HMIS Codes:

4	Extreme
3	High
2	Moderate
1	Slight
0	Least

APPENDIX G: TO-15 CHEMICAL COMPOUND SPECIATION RESULTS FROM AIR TOXICS LTD. SAMPLES (ppbv)

No.	Compound	CAS#	ATL1 No Board	ATL2 No WR Board	ATL3 Wax (90 lbs/msf)	ATL4 Siloxane 1 (12 lbs/msf)	ATL7 Siloxane 1 Peak 1	ATL8 Siloxane 1 Peak 2	ATL9 Siloxane 1 Peak 3	ATL5 Siloxane 2 (12lbs/msf)	ATL6 Siloxane 3 (12lbs/msf)	ATL10 Siloxane 1 Aged
1	silane, 1,4-phenylenebis (trimethyl-	13183-70-5	nd	nd	nd	160,000	3,900	50,000	130,000	120,000	130,000	86,000
2	silanol, trimethyl-	1066-40-6	320	800	450, 430	14,000	4,900	14,000	26,000	23,000	22,000	20,000
3	silane, fluorotrimethyl-	420-56-4	320	44	240, 230	12,000	42	14,000	140,000	120	6,100	13,000
4	cyclotetrasiloxane,2,4,6,8-tetramethyl-	2370-88-9	nd	nd	nd	9,900	1,300	2,200	9,200	nd	7,300	6,600
5	9,9,10,10-tetramethyl-9,10-disila-9,10-d	33022-24-1	nd	nd	nd	400	nd	nd	300	nd	300	nd
6	1,1,1,3,5,5,5-heptamethyltrisiloxane	1873-88-7	nd	nd	nd	nd	nd	nd	nd	98	nd	nd
7	unknown	NA	nd	nd	nd	4,200	nd	nd	3,900	nd	2,600	2,900
8	unknown	NA	nd	nd	nd	1,800	280	480	1,400	nd	1,200	1,200
9	unknown	NA	nd	nd	72, 74	360	57	420	300	nd	110	190
10	toluene	108-88-3	nd	9.7	620, 630	560	180	540	74	nd	nd	330
11	tetrachloroethene	127-18-4	nd	nd	nd	360	38	78	330	nd	260	240
12	dodecane	112-40-3	nd	nd	54, 59	260	23	nd	nd	nd	nd	nd
13	acetone	67-64-1	30	57	85, 87	230	70	210	110	170	160	180
14	undecane	1120-21-4	nd	66	56, 55	110	22	nd	nd	nd	nd	nd
15	1,2,4-trimethylbenzene	95-63-6	nd	19	37	64	8.9	54	29	43	38	44
16	ethanol	64-17-5	8.4	nd	40, 52	56	35	140	140	52	85	170
17	4-ethyltoluene	622-96-8	nd	16	44, 43	49	7.4	48	21	34	30	35
18	cumene	98-82-8	nd	nd	2, 2	47	nd	nd	41	nd	29	32
19	2-butanone (methyl ethyl ketone)	78-93-3	11	31	26, 25	29	120	nd	nd	nd	nd	nd
20	1,3,5-trimethylbenzene	108-67-8	nd	6.6	18, 17	23	3.4	21	nd	15	13	16
21	m,p-xylene	108-38-3 106-42-3	nd	9.5	22, 21	12	3.7	nd	nd	13	14	12
22	o-xylene	95-47-6	nd	3.3	8.9, 8.0	nd	1.5	nd	nd	nd	nd	nd
23	2-propanol (isopropyl alcohol)	67-63-0	6.2	nd	24, 13	nd	25	nd	nd	nd	nd	50
24	chloromethane (methyl chloride)	74-87-3	5.4	2.8	19, 16	nd	nd	nd	nd	110	140	250
25	decane	124-18-5	nd	nd	240, 230	nd	nd	240	160	nd	280	nd
26	2-hexanone	591-78-6	nd	4.9	nd	nd	nd	nd	nd	nd	nd	nd
27	2-propenal	107-02-8	nd	6.4	11	nd	nd	nd	nd	nd	nd	nd
28	4-methyl-2-pentanone	108-10-1	nd	1.4	nd	nd	nd	nd	nd	nd	nd	nd
29	benzaldehyde	100-52-7	nd	32	39, 39	nd	nd	nd	nd	nd	nd	nd
30	benzene	71-43-2	nd	nd	3.9, 3.8	nd	nd	nd	nd	nd	nd	nd
31	benzotrile, 2-chloro-	873-32-5	nd	nd	nd	nd	45	nd	nd	nd	nd	nd
32	carbon disulfide	75-15-0	2.3	1.9	4.7, 4.7	nd	nd	nd	nd	11	nd	16
33	chloroform	67-66-3	nd	9.7	4.5, 4.4	nd	5.9	nd	nd	nd	nd	nd
34	decane, 2,3,6-trimethyl-	62238-12-4	nd	420	nd	nd	nd	nd	nd	nd	nd	nd
35	ethylbenzene	100-41-4	nd	1.5	2, 2	nd	nd	nd	nd	nd	nd	nd
36	heptane	142-82-5	nd	2.1	nd	nd	nd	nd	nd	nd	nd	nd
37	heptane, 2,4-dimethyl-	2213-23-2	nd	43	nd	nd	nd	nd	nd	nd	nd	nd
38	hexanal	66-25-1	nd	42	52, 50	nd	38	nd	nd	nd	nd	nd
39	methylene chloride	75-09-2	nd	nd	nd	nd	8.9	nd	nd	nd	nd	nd
40	nonanal	124-19-6	nd	97	nd	nd	nd	nd	nd	nd	nd	nd
41	nonane	111-84-2	nd	64	100, 100	nd	51	nd	nd	nd	nd	nd
42	octadecane	593-45-3	nd	nd	nd	nd	nd	nd	nd	120	nd	nd
43	octanal	124-13-0	nd	nd	46, 45	nd	nd	nd	nd	nd	nd	nd
44	octane	111-65-9	nd	460	32, 30	nd	nd	nd	nd	nd	nd	nd
45	propylbenzene	103-65-1	nd	2.4	6.4, 6.7	nd	nd	nd	nd	nd	nd	nd
46	tetradecane	629-59-4	nd	190	nd	nd	nd	nd	nd	nd	nd	nd
47	tetrahydrofuran	109-99-9	0.74	nd	nd	nd	nd	nd	nd	nd	nd	nd
48	trichloroethene	79-01-6	nd	1.4	nd	nd	nd	nd	nd	nd	nd	nd
49	undecane, 3-methyl-	1002-43-3	nd	nd	nd	nd	nd	nd	nd	270	nd	320