APPENDIX D

Excerpts from CARB & SCAQMD Reactivity Study

Reactivity & Availability

SCAQMD Reactivity Study[1]

The following sections have been extracted from the above-referenced report, with some additional summarized results from Dr. William Carter's Presentation pertaining to the reactivity project sponsored by CARB:

As a part of the 1999 amendments to Rule 1113 – Architectural Coatings, the California South Coast Air Quality Management District (SCAQMD) Board approved a resolution, directing the SCAQMD staff to assess the reactivity and availability of solvents typically used in the formulation of architectural coatings. As a part of that effort, staff also included an assessment to further understand the interactions between various architectural coating emissions and mobile emission sources on particulate matter (PM) formation.

As an active member of the Reactivity Research Working Group (RRWG), a public-private partnership with a charter to conduct research on reactivity-based controls to determine whether it is feasible as an alternative compliance option, staff has coordinated their current efforts with CARB and RRWG. The RRWG's efforts to date have found that different VOC species have varying reactive properties to form ozone under the same NO_x environment. However, RRWG's efforts have also highlighted the need for additional work needed to reduce the uncertainty associated with the reactivity values determined using an environmental chamber, especially for the most commonly used solvents in architectural coatings formulations, and their impacts relative to impacts of mobile source emissions. The overall goal is to assess the feasibility of this optional strategy that could potentially allow manufacturers to use greater quantities of less reactive solvents, and reduce the quantity of higher reactive solvents to achieve the same level of ozone reductions, as those achieved through mass reduction. The environmental chambers previously used to develop the existing models had a number of limitations, particularly for evaluating effects on some VOC species. Because of this, in 1998, the U.S. EPA provided $3 million funding to the College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California at Riverside (UCR) for the design, construction and operation of a state-of-the-art, next-generation environmental chamber facility capable of obtaining the data needed for assessing the use of reactivity data as an alternative ozone control strategy to the established mass reduction method(Carter et al, 1999; Carter, 2002a). This chamber was completed in 2003 and successfully employed to evaluate mechanisms for photochemical O_3 formation under low NO_x conditions (Carter 2004) and for other projects, discussed below.

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[1] Reactivity and Availability Studies of VOC Species Found in Architectural Coatings & Mobile Sources, Dr. William P. L. Carter, July 2005

The California Air Resources Board (CARB), along with the SCAQMD, contracted CE-CERT to utilize the new chamber to improve reactivity assessments of some solvent species, with each group funding the evaluation of certain VOC species most commonly used in architectural coatings. Due to limited funding available to both agencies, CARB funded a subset of VOCs most commonly used in solvent-based coating formulations as well as Texanol®, whereas the SCAQMD funding was used exclusively for the most common VOC species used in waterborne formulations.

The CARB project involved conducting ozone reactivity experiments on seven different types of coatings VOCs, which were to be determined in consultation with the CARB staff and the CARB's Reactivity Research Advisory Committee (RRAC). As is the case with the RRWG, the RRAC consists of representatives of industry and regulatory groups, including the SCAQMD. The compounds chosen for study for that project included Texanol®[2], an important compound in water-based coatings, and six different types of petroleum distillates that are utilized in solvent-based and (to a lesser extent) water-based coatings. A report on the CARB study was completed earlier in 2005 (Carter and Malkina, 2005). The results of the study yielded useful information concerning the atmospheric ozone impacts of these compounds and the ability of the current SAPRC-99 detailed chemical mechanism (Carter, 2000a) to accurately simulate these impacts (Carter and Malkina, 2005).

In addition to the verifying the reactivity data for solvents found in waterborne coatings, the SCAQMD study also evaluated the issue of availability of low volatility or highly hydrophilic solvents to react in the gas phase and promote ozone formation, is another area of potential concern when assessing ozone impacts of VOCs. If these compounds tend to be absorbed to any significant extent on surfaces or PM before they have a chance to react in the gas phase, then their actual impact on ozone formation would be less than predicted using gas-phase mechanisms in current models. In 1999, the RRWG identified the need for this type of assessment but to date has funded research focusing on modeling only. The SCAQMD study is the first actual environmental chamber experiments for assessing availability of the VOC species and evaluating model predictions of availability. Furthermore, the SCAQMD study included an objective to assess the PM formation potential of all the solvents studied for the CARB and SCAQMD projects. The specific objectives and work carried out for this project are described below.

– Conduct environmental chamber experiments for reactivity assessment and chemical mechanism evaluation for several types of coatings or solvent VOCs selected by the SCAQMD in conjunction with discussions with the CE-CERT investigators and RRAC. The compounds chosen for study were propylene and ethylene glycols, diethylene glycol n-butyl ether (2-(2-Butoxyethoxy)-ethanol, or dipropylene glycol butyl ether, DGBE), and benzyl alcohol. The two glycols were considered not to have uncertain mechanisms but were studied because of their

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[2] Texanol is a registered trademark of Eastman Chemical Company. It is used throughout this report rather than the generic chemical name for simplicity.

extreme importance in the emissions inventories. DGBE was studied because it is also important in the water-based coatings inventory and has not been experimentally studied previously. Benzyl alcohol was studied because it is also emitted to some extent and had extremely high chemical mechanism uncertainty.

– Conduct measurements of PM formation in reactivity assessment and mechanism evaluation experiments not only for this project but also for the experiments carried out for the CARB coatings reactivity project. The data obtained can then be used to evaluate, at least in a qualitative sense, the PM formation potentials of the types of VOCs studied, and be available for potentially developing and evaluating models for their impacts on PM formation in the atmosphere.

– Carry out a limited number of experiments to characterize background effects related to PM formation that can be used when interpreting or modeling the PM formation in the chamber experiments discussed above, and that can serve as a basis for designing future PM studies in this chamber.

– Evaluate the potential utility of the environmental chamber for testing models for availability of emitted VOCs to react in the atmosphere to form O_3 and secondary PM. After discussion with members of the atmospheric availability subgroup of the RRWG it was decided to focus on conducting several experiments to assess the effects of humidity and seed aerosol on availability, decay rates and reactivities of ethylene and propylene glycol.

The following table summarizes the results of ARB's reactivity study, as documented in the report "Evaluation of Atmospheric Impacts of Selected Coatings VOC Emissions", prepared by W.P.L. Carter and I. Malkina, dated March 21, 2005.

Table E 1.   Summary of solvents studied in the environmental chamber experiments and the overall conclusions from the evaluation results.

Compound or Mixture	MIR [a] Previous	MIR [a] Revised	PM Impact or Approximate SOA Yields [b]	Discussion of Mechanism Evaluation Results [c]
Water Based Coatings VOCs				
Ethylene Glycol	3.36	3.63	Lower PM than base case	The glycolaldehyde product now represented explicitly. This mechanism still underpredicts glycol reactivity by 25-30% in experiments with aromatics in the base ROG surrogate, but there is no chemical justification for glycol mechanism adjustments
Propylene Glycol	2.74	No change	Lower PM than base case	This mechanism underpredicts glycol reactivity by ~20% in experiments with aromatics in the base ROG surrogate, but there is no chemical justification for glycol mechanism adjustments
Texanol® (Isobutyrate monoesters of 2,2,4-tri-methyl-1,3-pentanediol) [d]	0.88	No change	No net effect on PM formed evident	Experimental results for Texanol® and DGBE generally consistent with chamber data. The OH radical rate constants found to be in good agreement with the estimated values used in the mechanism.
2-(2-butoxyethoxy)-ethanol (DGBE)	2.86	No change	14 - 26%	
Benzyl Alcohol	None	4.89	~30%	Mechanism developed for this project and adjusted to fit the chamber data. Mechanism performance comparable to that for other aromatic compounds.
Hydrocarbon Solvents Studied for CARB Project [e]				
VMP Naphtha, Primarily C_7-C_9 mixed alkanes	1.41	1.35	0.1 - 0.7%	The experimental results for the primarily alkane, petroleum distillate-derived hydrocarbon solvents were generally consistent with the chamber data.
Dearomatized Mixed Alkanes, Primarily C_{10}-C_{12} (ASTM-1C)	0.91	0.96	~0.2%	
Reduced Aromatics Mineral Spirits, Primarily C_{10}-C_{12} mixed alkanes with 6% aromatics (ASTM-1B)	1.21	1.26	0.6 - 0.7%	

Compound or Mixture	MIR [a]		PM Impact or Approximate SOA Yields [b]	Discussion of Mechanism Evaluation Results [c]
	Previous	Revised		
Regular mineral spirits, Primarily C_{10}-C_{12} mixed alkanes with 19% aromatics (ASTM-1A)	1.82	1.97	0.3 - 0.8%	The experimental results were generally consistent with the chamber data.
Synthetic isoparaffinic alkanes, primarily C_{10}-C_{12} branched alkanes (ASTM-3C1)	0.81	1.1 - 1.5 [f]	No net effect on PM formed evident	Data not well simulated by the model. Model probably underpredicts atmospheric ozone formation by 25-75%, depending on the cause of the discrepancy.
Aromatic 100 (Primarily C_9-C_{10} alkylbenzenes)	7.51	7.70	0.3 - 0.4%	Experimental results representing MIR conditions generally consistent with model predictions. But model underpredicted O_3 inhibition in low NO_x conditions and has other problems.

[a] Maximum incremental reactivity in gm O_3 per gm VOC. Calculated as described by Carter (1994a,b). Values in "Previous" column are the MIR values incorporated in CARB regulations. The values for the compounds were from the most recent complete MIR tabulation given by Carter (1003). The values for the hydrocarbon solvents were derived using the CARB Bin assignments developed by Kwok et al (2000). No mechanism or MIR value previously existed for benzyl alcohol. Values in the "Revised" column are the best estimate MIRs based on the results of the current study. The changes in MIRs that may result when the mechanism is updated are unknown.

[b] For compounds with measurable positive PM impacts, the secondary organic aerosol (SOA) yields were derived from differences between PM volume levels in the base case and added test compound incremental reactivity experiments after 5 hours of irradiation. These approximate yields were estimated based on assuming same molecular weight for SOA as the starting material, assuming that the PM formed has the same density as water, and using approximate corrections for PM wall losses and approximate estimates of amounts of test compound or hydrocarbon solvent constituents reacted.

[c] Ozone prediction evaluation results are applicable to the SAPRC-99 mechanism (Carter, 2000a).

[d] Texanol was studied for the CARB project; see Carter and Malkina (2005) for details. Texanol is a registered trademark of Eastman Chemical Company.

[e] See Carter and Malkina (2005) for a discussion of the experimental and calculated data for the hydrocarbon solvent reactivities. The ASTM designations are based on the D 235-02 specification (ASTM, 2003).

[f] Range of MIRs for alternative mechanisms adjusted to fit the chamber data with this solvent. The available data are inadequate to distinguish between these mechanisms. See Carter and Malkina (2005).
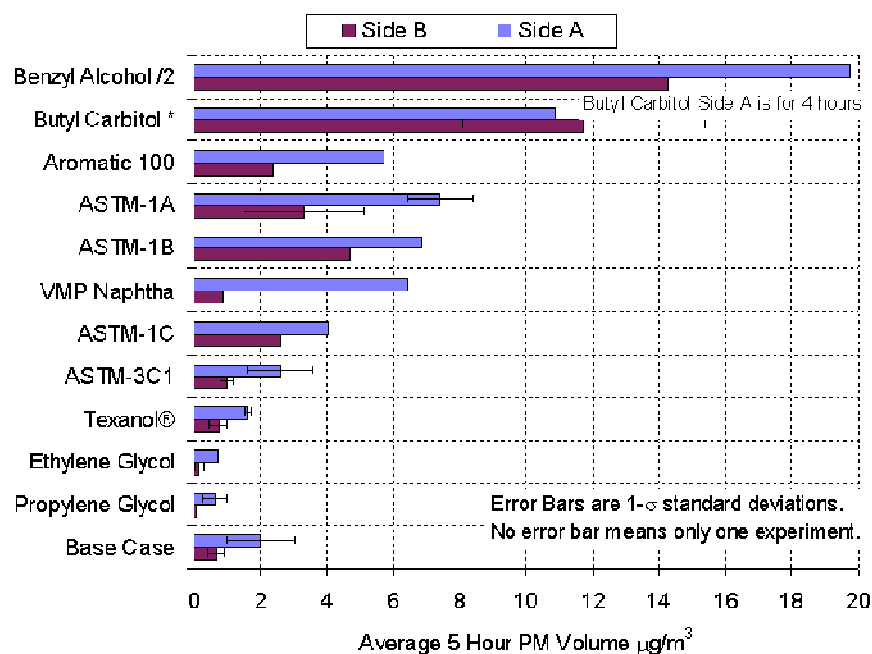
- Chamber data for Texanol®, butyl carbitol, and primarily alkane petroleum distillates are consistent with SAPRC-99 predictions.
- Chamber data for Aromatics-100 consistent with SAPRC-99 for MIR conditions, but O3 inhibition at low NOx underpredicted.

- Reactivities of at least some synthetic hydrocarbon mixtures may be underpredicted by up to a factor of 2 under some experiments.[3]
- Glycol reactivities underpredicted by ~30% in some experiments, but unclear whether adjustments are appropriate.
- New mechanism developed for benzyl alcohol that simulates chamber data about as well as mechanisms for other aromatics

The following chart summarizes the potential PM formation for each of the VOC species tested in the environmental chamber:

Relative secondary PM impacts: benzyl alcohol >> butyl carbitol > petroleum distillates. No measurable PM impacts for others. However, this is a preliminary qualitative analysis to assess the potential use of the environmental chamber for future quantitative studies of PM, and the contribution of VOCs in PM formation.

Summary of PM Volume Reactivity Results

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[3] Personal communication between Naveen Berry & Dr. William Carter to discuss difference in conclusions from a presentation and the final CARB report, September 2005

The following chart summarizes the availability studies:

Glycol Availability Experiments:
Preliminary Conclusions

- No clear effect on glycol consumption rate or ozone reactivity for humidity up to 35% and $(NH_4)_2SO_4$ or NH_4HSO_4 seed aerosol up to 10 $\mu g/m^3$.

- But there still may be a measurable effect at higher humidity or aerosol concentration, with a different type of aerosol

- Upgrades are being made to the chamber facility to facilitate experiments at higher RH, aerosol levels.

- But experiments that measure increases in aerosol mass when exposed to gas-phase VOCs may give a more sensitive measure of VOC uptake on aerosols

The conclusion reached by the study indicates that there was no evidence that humidity and aerosol affects glycol availability at the relatively low aerosol loadings and humidities examined.

The following recommendations/concerns are summarized by the SCAQMD staff pertaining to reactivity, availability, and PM assessment:

- Aromatics mechanisms need to be improved to further reduce uncertainties in reactivity assessments (e.g., glycols)
- Extrapolation of current mechanisms to higher aromatics, such as Aromatics 200, still highly uncertain
- Attempts should be made to improve the direct reactivity measurement method and improve its characterization and variability. The direct reactivity measurement method should be applied to hydrocarbon solvents of interest, including synthetic branched alkane mixtures where there appear to be problems with the current mechanism
- A modified base case experiment that gives better correlations between chamber and atmospheric reactivity would be useful
- The results do not indicate a compelling need to change the hydrocarbon bin assignments for the regulations already in place, but revisions will be needed when the regulatory reactivity scale is updated

- Well-characterized environmental chamber data needed to develop predictive secondary PM models. Work needed on background PM characterization in chambers

2001 Architectural Coatings Survey -Final Reactivity Analysis[4]

The following sections (italicized) have been extracted from the above-referenced report:

In July 2001, the Air Resources Board (ARB or Board) conducted a survey of companies that sold architectural coating products in California in 2000. This report contains a detailed analysis of the photochemical reactivity associated with architectural coatings, based on results from that survey. This document is intended to provide different options for evaluating the reactivity of architectural coatings, but it is not a formal regulatory document. ARB's 2001 Architectural Coating Survey gathered detailed sales information and speciation of VOCs in product formulations, with ingredients reported to the 0.1 weight percent level. When coatings are applied, they release different types of organic compounds that can react in the atmosphere to produce different amounts of ozone. This ozone forming potential is called hydrocarbon reactivity and it is determined by the photochemical reactions in the atmosphere. If a coating contains a small amount of a highly reactive compound, it could have a relatively high reactivity rating even if it has a low level of volatile organic compounds (VOCs). Similarly, a coating that has a high VOC content may have a relatively low reactivity rating, if it contains compounds that aren't very reactive.

The Product-Weighted MIR (PWMIR) represents a compilation of MIR values for all of the individual ingredients in a coating. In one approach, which was used in the ARB's aerosol coatings regulation, the product-weighted MIRs for coatings are calculated as follows:

$$[PWMIR, g\ O_3/g\ product] = [Wt\%]_1*[MIR]_1 + [Wt\%]_2*[MIR]_2 + ... + [Wt\%]_n*[MIR]_n$$

where

   $[Wt\%]_i$ = the weight percent of each ingredient in a coating product (e.g., 0.25 for 25%)
   $[MIR]_i$ = the MIR value of each ingredient in a coating product, g O_3/g TOG
   n = the total number of ingredients in a coating product

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[4] 2001 Architectural Coatings Survey - Final Reactivity Analysis, California Air Resources Board, March 2005

Sales-Weighted Average MIR Values

To determine sales-weighted average MIR values (SWAMIRs), we used the following equation:

$$SWAMIR = \frac{[Sales]1*[PWMIR]1 + [Sales]2*[PWMIR]2 +...+[Sales]n*[PWMIR]n}{[Sales]1 + [Sales]2 +...+[Sales]n}$$

where

> *[Sales, gals]i = the sales of product "i", gallons*
> *[PWMIR]i = the Product-Weighted MIR value, grams ozone/gram product*
> *n = the total number of coating products*

SWAMIRs were calculated for all of the coating categories based on the 2001 survey data. The survey collected sales data for more than 8,000 products and it also gathered data on the chemical ingredients contained in each product. However, there were approximately 100 products for which no ingredient data were submitted. These 100 products only represent 2.0 percent of the total sales volume. Since ingredient data are required to identify MIRs, we did not include the products with missing ingredient data when calculating sales-weighted average MIR values..

The table on the next few pages contains SWAMIRs that were calculated for 50-g/l ranges for all categories. Sales-weighted averages were calculated based on sales volumes (gallons).

As can be gleaned from the data, the SWAMIRs generally decrease as the VOC content (mass of VOC) decreases, based on the 50 g/l increments in data. This is just one of the methods of assessing the potential of reactivity as an alternative approach. However, some members of the architectural coatings industry have indicated that the PWMIR and SWAMIR approach is appropriate for regulating aerosol coatings, but they do not believe this approach is suitable for architectural coatings.

CARB staff has proposed alternative approaches to calculating reactivity data, but the RRAC has not reached a consensus.

The complete report can be downloaded from the following URL:

http://www.arb.ca.gov/coatings/arch/reactivity/final_reactivity_analysis_rpt.pdf

Conclusion

The following represent AQMD staff conclusions on the current status of using reactivity as an alternative ozone control strategy, as well as outline the next steps for CARB and AQMD staff:

CARB and AQMD will continue to assess the reports recently completed by CE-CERT and will work with industry in resolving remaining concerns with the results. In the meantime, CARB staff has initiated another architectural coating survey to collect sales and ingredient data for calendar year 2004. This survey would reflect the coatings being sold in California after all of the SCM VOC limits have taken effect. It is expected that results from this survey would be finalized during 2006. Data from that survey will be analyzed similarly to how the 2001 survey data were analyzed in this report. After the 2005 Architectural Coating Survey data are analyzed, CARB staff will begin the process to revise the 2000 SCM to incorporate lower mass-based VOC limits, or new reactivity-based limits, or some combination of both. This process is anticipated to occur in the 2006-2007 timeframe.

SCAQMD staff will continue to monitor all reactivity-related research at the RRWG, and plans to work closely with CARB staff on the survey and subsequent SCM, as well as with USEPA staff on the Interim Guidance on Control of Volatile Organic Compounds in Ozone State Implementation Plans to assess reactivity. However, based on the latest research and analysis, as well as the recommendations of the researcher to conduct additional analysis, staff supports the continuation of a mass-based ozone control strategy, with future consideration for a reactivity-based approach.

Sales-Weighted Average MIR Values in 50-g/l Ranges (grams ozone/gram product)

Coating Category	VOC Regulatory Ranges (grams/liter)														
	0-50	51-100	101-150	151-200	201-250	251-300	301-350	351-400	401-450	451-500	501-550	551-600	601-650	651-700	> 700
Antenna						0.36		1.37		0.73					
Bituminous Roof	0.00	0.07	0.14	0.28	0.38	0.50	0.52	0.94		0.43					
Bituminous Roof Primer	0.06			0.20			0.84		0.60						
Bond Breakers		0.08		0.06		0.08	0.19					0.82			
Clear Brushing Lacquer														1.51	
Concrete Curing Compounds	0.06	0.07	0.11	0.21	0.10	0.17	1.12			0.01	0.49	1.35	3.68	5.39	1.66
Dry Fog	0.02	0.04	0.08	0.07		0.25	0.30	0.37	0.40		0.82				
Faux Finishing		0.06	0.10		0.20	0.24	0.23	0.31	0.51					0.78	0.95
Fire Resistive	0.04														
Fire Retardant – Clear	0.00														
Fire Retardant – Opaque	0.02	0.04	0.08		1.09	1.04	0.89			0.98		3.91			4.82
Flat	0.04	0.05	0.09	0.13	0.14			0.43	0.25	0.41				0.22	
Floor	0.17	0.06	0.24	0.16	0.25	0.27	0.27	0.64	0.89	0.50	1.05		1.09		
Flow									0.54						
Form Release Compounds		0.07	0.05	0.40	0.31		0.74		0.94						
Graphic Arts		0.03	0.10	0.22	0.28	0.32	0.30	0.86	0.64		0.50				
High Temperature						0.58	0.52	0.78	0.58	1.23	2.54	2.94	1.85	2.88	
Industrial Maintenance	0.04	0.07	0.25	0.33	0.75	0.70	1.20	0.63	0.96	1.45	0.89	2.01	2.49	1.26	3.09
Lacquers	0.01	0.09	0.18	0.22	0.27	0.28	0.36			0.67	0.90	1.00	1.66	1.80	1.90
Low Solids	0.05	0.23													
Magnesite Cement									2.12						
Mastic Texture	0.01	0.08	0.19	0.17	0.12	0.37		0.31							
Metallic Pigmented		0.25	0.08	0.22	0.35	0.84	0.62	0.92	0.82	1.96	1.15	1.74	2.54	4.49	4.59
Multi-Color		0.02	0.10		0.18					0.24	0.43				2.02

Table 2-3: *Sales-Weighted Average MIR Values in 50-g/l Ranges (grams ozone/gram product)*

Coating Category	VOC Regulatory Ranges (grams/liter)														
	0-50	51-100	101-150	151-200	201-250	251-300	301-350	351-400	401-450	451-500	501-550	551-600	601-650	651-700	> 700
Nonflat - High Gloss	0.01	0.06	0.11	0.32	0.26	0.30	0.63	0.64	0.60	0.62	0.92		4.68		
Nonflat - Low Gloss	0.02	0.06	0.10	0.13	0.19	0.20	0.50	0.44	0.79	0.54			4.68		
Nonflat - Medium Gloss	0.00	0.06	0.10	0.13	0.19	0.19	0.34	0.68	1.00	0.45	0.58		4.68	2.49	
Other	0.00	0.18	0.02		0.95	0.42	0.37				0.60	1.68		0.78	
Pre-Treatment Wash Primer 1	0.07	0.07	0.07				0.29	0.29						1.03	1.83
Primer, Sealer, and Undercoater	0.08	0.06	0.10	0.12	0.19	0.21	0.54	0.62	0.62	0.80	0.75	3.29	1.99	3.82	1.89
Quick Dry Enamel				0.20	0.27		0.44	0.58	0.49	1.17	3.04				
Quick Dry Primer, Sealer, and Undercoater	0.00	0.05	0.14	0.02	0.79	0.40	1.29	0.45	0.49	0.71	0.83	1.37	1.15	3.14	3.80
Recycled					0.03	0.03									
Roof	0.03	0.08	0.18	0.15	0.29	0.64	0.72		1.17						1.79
Rust Preventative		0.04	0.11	0.14	0.22	1.25	1.36	0.41	0.64	0.42					1.34
Sanding Sealers				0.14	0.18	0.20	0.17				0.93	1.80		1.04	2.43
Shellacs – Clear												0.90	1.21	1.12	
Shellacs – Opaque											0.74				
Specialty Primer, Sealer, and Undercoater	0.03	0.11	0.09	0.15	0.23	0.60	0.35		0.58	0.87				1.61	
Stains - Clear/Semitransparent	0.00	0.05	0.07	0.15	0.22	0.16	0.51	1.05	0.49	0.76	0.82	0.93	1.38	1.90	1.63
Stains – Opaque	0.01	0.08	0.09	0.14	0.15	0.20	0.49	0.33	0.43	0.55	0.76	3.30	1.08		3.21
Swimming Pool	0.04	0.08	0.08	0.20	0.45	1.09	1.13		1.19		0.48				
Swimming Pool Repair and Maintenance												3.56			
Traffic Marking	0.00	0.03	0.10	0.10	0.24	0.39	0.42	0.58	0.45						1.54
Varnishes - Clear		0.09	0.16	0.14	0.21	0.31	0.68	0.62	0.69	0.73	0.73	1.16		1.55	1.75
Varnishes - Semitransparent					0.22	0.23	0.18	0.29	0.52	1.11	1.94				
Waterproofing Concrete/Masonry Sealers	0.00	0.08	0.10	0.19	0.85	0.21	0.26	0.75	0.74		0.79	3.99		1.81	1.65

Table 2-3: *Sales-Weighted Average MIR Values in 50-g/l Ranges (grams ozone/gram product)*

Coating Category	VOC Regulatory Ranges (grams/liter)														
	0-50	51-100	101-150	151-200	201-250	251-300	301-350	351-400	401-450	451-500	501-550	551-600	601-650	651-700	> 700
Waterproofing Sealers	0.00	0.07	0.10	0.36	0.47	0.60	0.35	0.43	0.65	0.01	0.83	1.13	0.85	1.73	1.54
Wood Preservatives	0.06	0.30	0.10	0.11	0.31	0.26	0.68		0.48	0.72	1.22			1.13	1.67

Blank cells indicate that the SWAMIR could not be calculated for this VOC Regulatory range, because there were no sales or the Form 3 ingredient data was incomplete.

1. These results are questionable because a portion of the sales consists of products that manufacturers chose to categorize as Pretreatment
   Wash Primers, but could potentially qualify as Specialty PSUs.