Quarterly Progress Report on

Standard Agreement No. 04-329

For the Period

September 1, 2007 through February 29, 2008

Development of an Improved VOC Analysis Method for Architectural Coatings

Prepared for California Air Resources Board
and the California Environmental Protection Agency

Dane R. Jones, Professor
Max T. Wills, Professor Emeritus

Department of Chemistry and Biochemistry
California Polytechnic State University

February 29, 2008

Disclaimer-

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Acknowledgements

This report was submitted in partial fulfillment of ARB Standard Agreement Number 04-329*, Development of an Improved VOC Analysis Method for Architectural Coatings,* by the Cal Poly Foundation under sponsorship of the California Air Resources Board.

I. Work This Reporting Period

This report summarizes work performed on the project from September 1, 2007 through February 29, 2008.

A. Task 2 Activities

During this time period, work was continued on Task 2 activities including

- Completion of analysis of all coatings
- Summarizing results for coatings in different classes
    - Two-component coatings
    - Single component air-dry coatings
    - Coatings containing exempt solvents
- Validation of test methods
- Analysis of high-boiling substances remaining in coating films

B. Samples

A list of the coatings included in this study is given in Table 1.

Table 1. Coatings undergoing VOC analysis

					WATERBORNE					SOLVENTBORNE		
in	run	split		Coating Category	Low VOC	High VOC	High Multi	Low Solids	High Multi	Low Solids	High Solids	High Exempt
y	y	y	1	Fire Resistive	X							
y	y		2	Recycled	X							
y	y	y	3	Industrial Maintenance					X-2K			
y		y	4	Bituminous Roof	X							
y		y	5	Bituminous Roof		X						
y		y	6	Driveway Sealer	X							
y		y	7	Metallic Pigmented	X							
y	y	y	8	Faux Finishing		X						
y	y	y	9	Stains - Clear/Semitransparent				X				
y	y	y	10	Stains - Opaque	X							
			13	Varnishes - Clear		X	X					
y			14	High Temperature								X
y	y	y	14-1	Industrial Maintenance							X-2K	
y	y	y	14-2	Industrial Maintenance							X-2K	
y	y	y	14-3	Industrial Maintenance							X-2K	
y	y	y	15-1	Industrial Maintenance							X-2K	
y	y	y	15-2	Industrial Maintenance							X-2K	
	y	y	15-3	Industrial Maintenance							X-2K	
y	y	y	24	High Temperature								X
y	y	y	25	Swimming Pool					X-2K			
y	y	y	26	Swimming Pool			X-2K					
y			29	Varnishes-clear		X						
y	y	y	32-1	Lacquers	X							
y	y	y	32-2	Primer/stainblock	X							
y	y	y	34	Dry Fog	X							
y	y	y	35	Dry Fog	X							
y			36	Faux Finishing	X							
y	y	y	37	Roof	X							
y	y	y	38	Waterproofing Concrete/Masonry Sealers	X							
y	y	y	39	Bituminous Roof	X							
y	y	y	40	Driveway Sealer	X							
y	y	y	41	Driveway Sealer	X							
y	y	y	43	Roof	X							
y			44	Magnesite Cement								X
y			44-2	Magnesite Cement								X
y	y	y	45	Varnishes - Clear			X-2K					
y			48	Wood Preservatives				X				
y	y	y	50	Mastic Texture	X							
y	y	y	51	Waterproofing Concrete/Masonry Sealers	X							

Table 1. Coatings undergoing VOC analysis (con't.)

					WATERBORNE				SOLVENTBORNE			
in	run	split		Coating Category	Low VOC	High VOC	High Multi	Low Solids	High Multi	Low Solids	High Solids	High Exempt
y			52	Bond Breakers				X				
y			53	Form Release Compounds							X	
y	y	y	55	Rust Preventative		X						
y		y	56	Low Solids	X			X				
y	y	y	57-1	Lacquers						X		X
y	y	y	57-2	Lacquers						X		X
y	y	y	57-3	Lacquers						X		X
y			59	Floor		X-2K						
y			60	Metallic Pigmented		X						
y			61	Varnishes - Clear		X						
y			62	Stains - Clear/Semitransparent								X
y	y	y	63	Floor		X						
y	y	y	64	Waterproofing Sealers				X				
y	y	y	65	Waterproofing Sealers	X			X				
y			73	Traffic Marking	X							
y	y	y	75	Bituminous Roof	X							
y	y	y	76-1	Faux Finishing		X		X				
y		y	76-2	Faux Finishing		X		X				
y	y	y	76-3	Faux Finishing		X		X				
y		y	76-4	Faux Finishing		X		X				
y	y	y	76-5	Faux Finishing		X		X				
y	y	y	76-6	Faux Finishing		X		X				
y			77	Lacquer								X
y	y	y	79	Sanding Sealers				X				
y	y	y	80	Stains - Opaque	X			X				
y	y		81-1	Concrete Curing Compounds	X			X				
y	y		81-2	Concrete Curing Compounds	X			X				
y			82-1	Waterproofing Concrete/Masonry Sealers	X			X				
y			82-2	Waterproofing Concrete/Masonry Sealers	X			X				
y	y	y	83	Quick Dry Primer, Sealer, and Undercoater	X							
y	y	y	84	Shellacs - Clear						X		
y	y	y	85	Shellacs - Clear						X		
y	y	y	86	Wood Preservatives	X			X				
y	y	y	87	Varnish						X		

1. "Low VOC": <=3% VOCs by weight. "High VOC": >=10% VOCs by weight. "High Exempt": >=10% Exempt Compounds by weight.
2. "High Multi": Categories that have more than 10% multi-component products, by sales volume.
3. "Low Solids": 0-20% solids by volume. "High Solids": 80-100% solids by volume.
4. "Low Solids" and "High Solids" products only include single-component coatings.
   The other classifications include both single-component and multi-component coatings.

C. Summary of Results for Two-component Coatings

Table 2 gives a summary of the results obtained by Cal Poly for the analysis of two-component (2-K) architectural coatings. The solvent-borne coatings were analyzed by both EPA Method 24 and a GC method developed by Cal Poly. The water-borne coatings were analyzed by the GC method only. Five of the coatings were sent to three laboratories for independent analysis by the Cal Poly GC method. To date, results have been received from one of the three laboratories. (See Section F for details on these coatings).

Table 2. Summary of the VOC results obtained by Cal Poly for 2-K Coatings

Sample #	Solids fraction	Coating VOC, EPA 24	Material VOC by GC, avg	Coating VOC by GC, avg	Material VOC, reported	Coating VOC, reported	water fraction
#3	0.8803	168		178		179.7	
#14-1	0.9697	41		46		7	
#14-2	0.8557	241		261		296	
#14-3	0.8826	209		216		170	
#15-1	0.9739	34		19		10	
#15-2	0.9612	54		87		12	
#15-3	0.8448	225		211		214	
#25	0.8147	291		305		325	
#26-WB	0.5682		138	226	122	236	0.3191
#45-WB	0.2824		83	247	82	244	0.6363
#59-WB	0.6447		54	90		<100	0.3147

On October 2, 2007 the US EPA received a request from Mr. Frederick Gelfant (Stonhard/Epoplex Company) to approve two modifications to EPA Method 24 (Appendix A of 40 CFR Part 60) for modification of ASTM Method 2369 as it relates to high solids multi-component coatings. The EPA approved the request to carry out the total volatile determination omitting addition of a diluent solvent before curing the test sample and also agreed that the sample weight used should be representative of how the coating is applied. The net result of this change, in general, will be that larger sample weights will be used to test the total volatile content. An effort is currently underway to conduct an ASTM round robin with selected high solids (>90% solids) coatings. The EPA approval letter follows:

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

OCT 24 2007

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Mr. Frederick Gelfant
Vice President
Stonhard/Epoplex
One Park Avenue
Maple Shade, New Jersey 08052

Dear Mr. Gelfant:

Thank you for your letter dated October 2, 2007, in which you requested a modification to EPA Method 24 (Appendix A of 40 CFR Part 60), used to determine the volatile matter content of coatings. In your letter, you stated that Method 24 results are biased high when used to test very high solid (>90%), multi-component resins. The two modifications you requested are omitting the addition of the diluent solvent before curing the test sample, and using a larger sample weight, which is representative of how the coating is actually used.

We have reviewed your letter and the supporting information and have concluded that the modifications to Method 24 which you requested are acceptable for very high solids (>90%), multi-component resins. Therefore, we are approving the proposed modifications when testing these specific resins (very high solid (>90%) multi-component) using Method 24

If you have any additional questions concerning this matter, please contact Candace Sorrell of my staff at 919-541-1064.

Sincerely,

Conniesue B. Oldham, Ph.D., Group Leader
Measurement Technology Group

cc: Gary McAlister, MTG, AQAD
Dave Salman, SPPD

Three of the 2-K coatings in the present ARB study meet the definition of >90% solids (#14-1, 15-1, and 15-2). Two of these high solids coatings were reanalyzed using the provisions of the two EPA approvals. The results of this retesting are presented in Tables 3a and 3b.

Table 3a Results for Sample 14-1 using different film thicknesses

Sample 14-1. Recommended film thickness = 12-20 mils					
	volatile fraction				
	trial 1	trial 2	trial 3	average	coating VOC based on average
D2369, FT=12 mils	0.0220	0.0194	0.0199	0.0204	27
D2369, FT=6 mils	0.0258	0.0319	0.0314	0.0297	40
GC, 12 mils, extract 5 sec	0.0102	0.0078		0.0090	12
GC, 12 mils, extract 24 hour	0.0406	0.0414		0.0410	55
benzyl alcohol, uncured mixture	0.0426	0.0421		0.0424	57
Reported Coating VOC					7

Table 3b Results for Sample 15-2 using different film thicknesses

Sample 15-2. Recommended film thickness = 6 - 12 mils					
	volatile fraction				
	trial 1	trial 2	trial 3	average	coating VOC based on average
D2369, FT=6.5 mils	0.0349	0.0350	0.0357	0.0352	49
D2369, FT= 11.4 mils	0.0242	0.0239	0.0205	0.0229	32
GC, 6.5 mils, extract 5 sec	0.0383	0.0459		0.0421	58
GC, 6.5 mils, extract 24 hour	0.0625	0.0484		0.0554	77
benzyl alcohol, uncured mixture	0.1158	0.1164		0.1161	161
Reported Coating VOC					12

Samples 14-1 and 15-2 contain benzyl alcohol as the major VOC component. The literature boiling point of benzyl alcohol is 205^{o}C and benzyl alcohol is apparently not released completely from coatings which cure by cross-linking. Based on manufacturer formulation VOC values, it would appear that benzyl alcohol is not counted as a VOC. Both coatings were analyzed for total benzyl alcohol content by gas chromatographic determination of the coating immediately after mixing the components, i.e., before onset of the cure reaction. Uncured coating 14-1 contained 4.24% benzyl alcohol and coating 15-2 contained 11.61% benzyl alcohol. If all of the benzyl alcohol in these coatings were to evaporate during a total volatile determination (ASTM Method 2369), the coating VOC values would have been 57 and 161 g/L , respectively. When the D2369 determination was carried out on 14-1, the VOC content when using the manufacturer's recommended minimum film thickness (12mils) was 27g/L. If a film thickness of half the minimum recommended application thickness is used to measure total VOC content, the value increases to 40g/L. Similarly, for coating 15-2, the recommended minimum application film thickness (6mils) gives a VOC value of 49g/L and the recommended maximum application film thickness (12mils) gives a the lower VOC value of 32g/L. So clearly, benzyl alcohol evaporates only partially under the test conditions of ASTM 2369.

In the Cal Poly GC method the uncured coating mixture is placed into a closed headspace vial, is allowed to cure for 24 hours at room temperature, and is then heated for 1 hour at 110^{0}C (ASTM D2369). After cooling, a weighed amount of acetone containing an internal standard is injected into the sealed vial, the contents are mixed, and the resulting solution is then analyzed by GC. Apparently the mixing time in this procedure is critical in measuring only the evolved volatiles. When the mixing time is kept very short (5 seconds), the results obtained by GC match the D2369 results more closely while mixing for a long period of time (24 hours) gives higher GC results which match the total benzyl alcohol content more closely. At the outset of this project we postulated that the EPA Method 24 would probably give sufficient accuracy for solvent-borne coatings and that a GC method is not required as long as mass-based VOC regulations are in effect..

The EPA Method 24 results (ASTM D2369) of solvent-borne multi-component coatings with a solids content less than 90% and containing either none or small quantities of benzyl alcohol are nearly the same as those obtained by the Cal Poly GC method. EPA Method 24 can not be used reliably with waterborne multi-component coatings and the Cal Poly GC method gives excellent results as judged by comparison with manufacturer's formulation VOC values.

D. Summary of Results for Single Component Air-dry Coatings Not Containing Exempt Solvents

Table 4 contains data in summary form for the results obtained for those coatings not containing exempt solvents curing by solvent evaporation (air-dry).

Table 4 Summary results for single component coatings without exempt solvents

Sample #	Solids fraction	density (lbs/gal)	density (g/L)	VOC fraction, avg	water fraction, avg	Lwater per L coating, avg	lbs solids/gal	Material VOC by GC, avg	Coating VOC by GC, avg	Coating VOC by EPA 24	Material VOC, reported	Coating VOC, reported
#1	0.4780	8.743	1047	0.0053	0.5169	0.5412	4.18	5	12		9	
#4	0.5257	8.637	1035	0.00034	0.4740	0.4904	4.54	0.35	0.69		0	0
#5	0.4649	7.029	842	0.0911	0.4440	0.3739	3.27	77	123		Not rptd	Not rptd
#6	0.5617	11.451	1372	0.0000	0.4383	0.6013	6.43	0	0		0	0
#7	0.3630	9.145	1096	0.0208	0.6161	0.6750	3.32	23	70			40max
#8	0.2140	8.876	1063	0.1019	0.6840	0.7273	1.90	108	397			<350
#9	0.1771	8.498	1018	0.0305	0.7923	0.8067	1.51	31	161			<250
#10	0.4391	9.506	1139	0.0279	0.5330	0.6070	4.17	32	81		Not rptd	Not rptd
#29	0.3239	8.720	1045	0.0962	0.5799	0.6058	2.82	100	255		106.2	265.5
#32-1	0.5043	11.339	1358	0.0027	0.4930	0.6697	5.72	4	11		17.1	50.6
#32-2	0.5663	10.714	1284	0.0175	0.4162	0.5342	6.07	22	48		28.7	60.7
#34	0.5160	10.410	1247	0.0244	0.4596	0.5732	5.37	30	71		Not rptd	Not rptd
#35	0.5426	11.207	1343	0.0128	0.4446	0.5969	6.08	17	43		Not rptd	Not rptd
#37	0.6534	11.308	1355	0.0107	0.3359	0.4551	7.39	14	26		Not rptd	Not rptd
#38	0.5801	10.927	1309	0.0302	0.3897	0.5101	6.34	40	81		Not rptd	Not rptd
#39	0.4736	8.440	1011	0.0013	0.5251	0.5309	4.00	1	3			0
#40	0.5744	11.418	1368	0.0008	0.4249	0.5812	6.56	1	2			<50
#41	0.4988	10.317	1236	0.0215	0.4797	0.5929	5.15	27	59			< 96
#43	0.4752	10.329	1237	0.0137	0.5111	0.6324	4.91	17	46			< 50
#48	0.1737	8.420	1009	0.0716	0.7547	0.7612	1.46	72	295			< 260
#50	0.6427	11.634	1394	0.0199	0.3375	0.4704	7.48	28	52		31	60
#51	0.2194	8.430	1010	0.0291	0.7515	0.7590	1.85	29	122		29	126
#52	0.0870	8.140	975	0.1061	0.8069	0.7869	0.71	103	485		< 120	
#53	Soap											
#55	0.4330	10.328	1237	0.1076	0.4594	0.5684	4.47	133	308			318
#56	0.0520	8.231	986	0.0357	0.9124	0.8997	0.43	35	351		< 120	< 600
#58	0.1031	8.480	1016	0.0040	0.8929	0.9071	0.87	4	44			< 100
#60	0.4981	10.020	1200	0.1257	0.3762	0.4516	4.99	151	275			< 250
#61	0.2866	8.700	1042	0.1096	0.6038	0.6293	2.49	114	308			259
#62	0.7061	9.110	1091	0.2815	0.0124	0.0135	6.43	307	311	321		< 250
#63	0.4120	9.471	1135	0.0651	0.5230	0.5934	3.90	74	179			< 100
#64	0.2002	8.584	1028	0.0643	0.7354	0.7563	1.72	66	271			< 100

Table 4 (con't.)

Sample #	Solids fraction	density (lbs/gal)	density (g/L)	VOC fraction, avg	water fraction, avg	Lwater per L coating, avg	lbs solids/gal	Material VOC by GC, avg	Coating VOC by GC, avg	Coating VOC by EPA 24	Material VOC, reported	Coating VOC, reported
#65	0.0978	8.426	1009	0.0065	0.8957	0.9041	0.82	7	69			< 100
#73	0.7841	13.720	1644	0.0513	0.1646	0.2705	10.76	84	116		50	75
#75	0.5149	7.319	877	0.0239	0.4612	0.4044	3.77	21	35			50
#76-1	0.1516	8.966	1074	0.2962	0.5522	0.5932	1.36	318	781		Not rptd	Not rptd
#76-3	0.1345	8.832	1058	0.3153	0.5502	0.5822	1.19	334	796		Not rptd	Not rptd
#76-5	0.1485	8.926	1069	0.2689	0.5825	0.6229	1.33	288	763		Not rptd	Not rptd
#76-6	0.1485	8.926	1069	0.2783	0.5732	0.6130	1.33	298	769		Not rptd	Not rptd
#79	0.2211	8.514	1020	0.0616	0.7173	0.7316	1.88	63	234		Not rptd	Not rptd
#80	0.0676	8.553	1025	0.0089	0.9236	0.9464	0.58	9	169		Not rptd	Not rptd
#81-1	0.1894	8.303	995	0.0042	0.8064	0.8022	1.57	4	19			< 100
#81-2	0.3485	8.138	975	0.0058	0.6456	0.6294	2.84	6	14			< 100
#82-1	0.1129	8.444	1012	0.0132	0.8740	0.8841	0.95	13	115			< 200
#82-2	0.2932	8.624	1033	0.0487	0.6537	0.6754	2.53	50	155			< 200
#83	0.5128	10.620	1272	0.0032	0.4840	0.6157	5.45	4	11			< 5
#84	0.2280	7.283	872	0.7247	0.0473	0.0413	1.66	632	659		Not rptd	Not rptd
#85	0.2222	7.308	875	0.7259	0.0518	0.0454	1.62	636	666			< 730
#86	0.0391	8.373	1003	0.0185	0.9424	0.9453	0.33	19	339			< 350
#87	0.2706	6.954	833	0.7105	0.0190	0.0158	1.88	592	599	608	Not rptd	Not rptd

E. Summary of Results for Coatings Containing Exempt Solvents

All of the coatings containing exempt solvents were analyzed by ASTM Method 6886. The only exempt solvents present included acetone, parachlorobenzotrifluoride (PCBTF), and methyl acetate. Acetone was found in coatings 24, 44, 44-2, 57-1, 57-2, 57-3, and 77 at fairly high levels (18-55%), PCBTF was found in one coating (#14) at a level of 47%. Methyl acetate was found in coating 57-3 at about 4% and in 57-1 and in 57-2 in trace amounts.

One of the difficulties in measuring the acetone content in coatings by ASTM D6886 or by ASTM D6133 is that acetone and isopropyl alcohol (IPA) co-elute on the column specified in both of these ASTM methods. Acetone and IPA can be separated on a Carbowax™ GC column or may be separated by GC/MS in the selected ion monitoring mode (SIM). We have used both of these methods to determine the acetone/IPA content and will incorporate language into both ASTM methods to include the GC/MS/SIM methodology for determining acetone and IPA. In the SIM method the coating is dissolved in THF, a known amount of deuterated acetone is added and the solution is analyzed using mass spectrometry. The exempt solvent content results obtained using these two methods is given in Table 5.

The summary VOC results obtained by GC analysis of coatings containing exempt solvents are presented in Table 6.

Table 5 Exempt solvent content of samples

Method	sample #	acetone fraction	IPA fraction	methyl acetate fraction	acetone fraction, rptd	IPA fraction, rptd	methyl acetate fraction,rptd
GC/MS	24	0.1832	0		0.154	0	0
GC/MS	24	0.1875	0				
GC/MS	24	0.1743	0				
GC/MS	44	0.2531			0.2633	0	0
GC/MS	44	0.2509	0.0014				
GC/MS	44	0.2398	0.0014				
GC/MS	44-2	0.4700			0.4844	0	0
GC/MS	44-2	0.4688	0.0010				
GC/MS	57-1	0.3760	0.0267		0.455	0.035	0
GC/MS	57-1	0.3746	0.0495				
GC/FID	57-1	0.3900	0.0329	0.0040			
GC/FID	57-1	0.3890		0.0044			
GC/FID	57-2	0.5447	0.0337	0.0017	0.52	0.04	0
GC/FID	57-2	0.5420		0.0015			
GC/MS	57-2	0.5230	0.0248				
GC/FID	57-3	0.3794	0.0345	0.0416	0.38	0.035	0.04
GC/FID	57-3	0.3734		0.0420			
GC/FID	57-3	0.3681		0.0417			
GC/MS	57-3	0.3674	0.0294				
GC/MS	77	0.2517	0.0338		0.32	0.05	
GC/MS	77	0.2991	0.0323				
GC/MS	77	0.2991	0.0323				
GC/MS	77	0.2881	0.0301				

Table 6 Summary VOC results for coatings containing exempt solvents

Sample #	#14	#24	#44	#44-2	#57-1	#57-2	#57-3	#77
Solids fraction	0.4021	0.5670	0.4931	0.3241	0.2614	0.2106	0.2438	0.3278
density, coating, (lbs/gal)	9.79	9.44	8.84	7.37	7.59	7.38	7.49	7.85
density, coating, (g/L)	1173	1130	1059	883	910	884	898	940
density, acetone, g/L	791	791	791	791	791	791	791	791
density, PCBTF, g/L	1353	1353	1353	1353	1353	1353	1353	1353
density, methyl acetate, g/L	940	940	940	940	940	940	940	940
total organic volatile fraction, avg	0.6495	0.4778	0.5216	0.7111	0.7639	0.8289	0.7787	0.6111
calcd water fraction, avg	-0.0516	-0.0448	-0.0147	-0.0352	-0.0253	-0.0395	-0.0225	0.0611
L water per L coating, avg	-0.0605	-0.0506	-0.0156	-0.0310	-0.0230	-0.0350	-0.0202	0.0575
lbs solids/gal	3.94	5.35	4.36	2.39	1.98	1.55	1.83	2.57
acetone fraction, avg		0.1816	0.2480	0.4694	0.3824	0.5366	0.3674	0.2845
PCBTF fraction, avg	0.4700							
methyl acetete fraction, avg					0.0042	0.0016	0.0418	
direct VOC fraction by GC, avg	0.1795	0.2961	0.2736	0.2417	0.3773	0.2908	0.3695	0.3266
indirect VOC fraction by EPA 24	0.1279	0.2513	0.2589	0.2066	0.3520	0.2512	0.3470	0.3877
L acetone per L coating		0.2596	0.3320	0.5239	0.4398	0.5997	0.4169	0.3383
L PCBTF per L coating	0.4075							
L methyl acetete per L coating					0.0041	0.0015	0.0399	
Material VOC, GC, avg	211	335	290	213	343	257	332	307
Coating VOC, GC, avg	355	452	434	448	617	645	611	464
Material VOC, EPA 24	150	284	274	182	320	222	312	365
Coating VOC, EPA 24	253	384	410	383	576	557	573	551
Material VOC, reported			269	192	269	232	294	343
Coating VOC, reported	312	<420	416	419	550	550	550	547

F. Validation of Test Methods

An important part of this project is independent validation of the methods we have developed. We have selected coatings in three categories to send to other laboratories: two-component coatings, unusual coatings (low solids, high VOC, unusual solvents) and coatings containing exempt solvents. Coatings selected for validation studies are listed in Table 7. Specific VOCs we identified in these coatings are also listed in the table. We sent the two-component coatings to three laboratories several months ago and have received results from one laboratory. Samples in the other categories are being sent this week. The laboratories were provided with samples of the coatings split from our original samples along with whatever information we have on the coatings from the manufacturers. We also informed the laboratories of what VOCs might be present so they can determine response factors for these VOCs. We provided the laboratories with copies of the analysis procedures we have developed. We hope to present results from these studies in our next report.

Table 7 Samples selected for validation study

Sample #	Company	Category	Product	Type	solids (lb/gal)
3	Ameron International	Industrial Maintenance	Amerlock	2K, high solids	10.31
VOCs	furfuryl alcohol	ethylbenzene	m,p-xylene	o-xylene	Aromatic 100
15-2	Carboline Company	Industrial Maintenance	Carboguard 992	2K, high solids	11.11
VOCs	benzyl alcohol				
15-3	Carboline Company	Industrial Maintenance	Carboguard 890	2K, high solids	10.24
VOCs	1-butanol	toluene	ethylbenzene	m,p-xylene	o-xylene
	cumene	Aromatic 100	benzyl alcohol		
26	ELLIS PAINT COMPANY	Swimming Pool	Propoxy	2K	5.77
VOCs	2-propoxyethanol	Aromatic 100			
45	Hillyard Industries, Inc.	Varnishes - Clear	Contender Gym Finish	2K	2.46
VOCs	propylene glycol monomethyl ether	benzyl alcohol			
86	Zinsser Co., Inc.	Wood Preservatives	WoodLife Classic	low solids, high water	0.33
VOCs	ethylene glycol	propylene glycol monopropyl ether	1-iodo-2-propynyl butyl carbamate		
76-1	Valspar Corporation	Faux Finishing	Decorative Effects Color Glaze	very high VOC	1.36
VOCs	methyl ethyl ketone	propylene glycol			

Table 7 Samples selected for validation study (con't.)

Sample #	Company	Category	Product	Type	solids (lb/gal)
61	Rust-Oleum Corp.	Varnishes - Clear	Varathane Semi-gloss Renewal	high VOC	2.49
VOCs	triethyl amine	propylene glycol	dipropylene glycol monomethyl ether	N-methyl pyrrolidinone	propylene glycol monobutyl ether
	Surfynol				

55	Ponderosa Paint Co., Inc.	Rust Preventative	Aqua Clad	high VOC	4.47
VOCs	2-butanol	2-butoxyethanol	butyl carbitol		

60	Rust-Oleum Corp.	Metallic	Stops Rust	unusual solvents	4.99
VOCs	propylene glycol	diethylene glycol monomethyl ether	propylene glycol monobutyl ether	2-(2-ethylhexyl) ethanol	triethylene glycol
	dibutyl phthalate				

14	Carboline Company	High Temperature	Thermaline 4900 VOC	exempt solvent(s)	3.94
VOCs	toluene	metachloro benzotrifluoride	parachloro benzotrifluoride	ethylbenzene	m,p-xylene
	o-xylene	Aromatic 100	naphthalene		

44-2	Hill Brothers Chemical Co.	Magnesite Cement	Classic Sealer Clear	exempt solvent(s)	2.39
VOCs	acetone	ethylbenzene	m,p-xylene	o-xylene	Aromatic 100
	naphthalene				

57-3	R.J. McGlennon Co. Inc.	Lacquers	precatalyed gloss base	exempt solvent(s)	1.83
VOCs	methanol	acetone	2-propanol	methyl acetate	MEK
	1-butanol	butyl acetate	ethylbenzene	m,p-xylene	2-heptanone
	o-xylene	2-butoxyethanol	4-methyl-3-heptanone		

G. Analysis of Specific VOCs Remaining in Coating Film

One of the areas of interest for high boiling solvents is the fraction remaining in the coating film after analysis by ASTM 2369. EPA Method 24 defines the amount of volatiles by this method and thus any solvent remaining in the film after heating for one hour at 110^{o}C is not counted as a VOC. For the direct method, ASTM 6886, the total amount of each solvent in the coating is determined. We have analyzed several of the coatings in this study to determine the fraction of certain high boiling solvents remaining in the film. This is done by extracting the film after ASTM 2369 analysis with an appropriate solvent and then quantifying the amount of solvent recovered from the film by direct gas chromatographic analysis as is done in ASTM 6886. High Boiling substacnes identified and quantified in the films include Texanol, bis (2-ethylhexyl maleate), 2-(2-ethylhexyl) ethanol, triethylene glycol, dibutyl phthalate, benzyl butyl phthalate, polynuclear aromatic hydrocarbonds (PNAH) and wax. Results for several samples are given in Table 8 below.

Table 8 High boiling substances remaining in coatings film after ASTM 2369 analysis

Sample #	Ret time	high boiling substance	fraction remaining in film
#8	13.523	Texanol	0.02
#34	13.607	Texanol	0.23
	22.353	bis (2-ethylhexyl) maleate	0.93
#41	12.4-21.2	PNAH's	0.50-0.60
#51	13.611	Texanol	0.06
#60	12.507	2-(2-ethylhexyl) ethanol	0.04
	14.423	triethylene glycol	0.15
	18.458	dibutyl pthalate	0.83
#63	26.559	benzyl butyl phthalate	0.99
#73	13.61	Texanol	0.35
#79	13.608	Texanol	0.21
#81-1	18.0-30.5	wax	1.18

The fraction of Texanol remaining in the film varies from 0.02 to 0.35. In general, compounds with boiling points higher than that of Texanol (longer retention times) show larger fractions remaining in the film. The fraction of wax remaining in the film was found to be greater than one, but this consists of many specific compounds which were analyzed separately which results in much lower precision for the result. These results indicate Texanol might be a suitable boiling point (or retention time) marker for determining what is and what is not a VOC when performing direct analysis of VOCs.

II. Future Work

We will be preparing the final form for the analysis methods and compiling the results of the validation studies, as they become available.

III. Overall Progress of Project.

Project is on budget. We have requested a one-year no-cost time extension for completion of the project since results form the validation study will not be available in time to complete the final report by the end of June, 2008.