Quarterly Progress Report on

Standard Agreement No. 09-428

For the Period

October 1, 2010 through December 31, 2010

Low Volatile Organic Compound (VOC) Stain Blocking Specialty Primer Coating

Prepared for California Air Resources Board

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Disclaimer-

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Acknowledgements

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A. Summary

Local air districts' architectural coating rules that are based on the California Air Resources Board's (ARB) 2007 architectural coatings Suggested Control Measure are scheduled to reduce the volatile organic compound (VOC) limit of specialty primers, sealers, and undercoaters (SPSU) from 350 g/L to 100 g/L in January of 2012. Currently the stain blocking primers that are considered most effective are solvent based primers that have VOC contents much higher than 100 g/L. The goal of this study is to determine if primers on the market today with a VOC content of 100 g/L or less can provide acceptable performance in comparison to primers with VOC contents greater than 100 g/L. The first quarterly report of this project (1) described the preliminary work performed in preparation of a more systematic and comprehensive study to evaluate the performance of paints sold to the SPSU market. During the current reporting period, fifteen primers, both water based and solvent based, were chosen for testing and comparison. Basic primer characterization was completed, including solids content, density, sag, leveling, contrast ratio and VOC content. Stain-blocking testing, including marker and tannin stains, will begin in the next quarter.

B. Introduction

Current regulations in California allow SPSU paints, also referred to as stain blocking primers, to have a VOC content of up to 350 g/L. By January 2012, several air districts' rules will lower the VOC limit to 100 g/L. The best performing stain blocking primers currently on the market, as accepted within the industry, are shellac-based primers, with a VOC limit of 550 g/L, and several oil based primers with a VOC limit of 350 g/L. A survey of published literature, outlined in the first quarterly report, did not uncover any study comparing stain blocking performance of less than 100 g/L VOC SPSU coatings with those containing higher VOC levels. Our discussions with industry experts led to the conclusion that there is currently no industry standard for what classifies a stain blocking primer as having "acceptable" performance. For this project, it is necessary to create a set of guidelines to determine if a stain blocking primer shows "acceptable performance". To define "acceptable performance" and to select candidate primers for comprehensive testing, an industrial panel was gathered by the ARB. This panel is made up of following companies and organizations:

- American Coatings Association
- Akzo Nobel Company
- Behr Process Company
- Benjamin Moore Company
- Byk USA Company
- California Air Resources Board
- Dunn-Edwards Company

- Eliokem Company
- Kelly Moore Company
- Rustoleum Company
- Sherwin Williams Company

To begin testing, fifteen primers listed in the Materials and Methods section below were chosen based on recommendation by industry panel. It was agreed that, when a primer coating and a top coating is needed for the purpose of preparing substrates and test panels for performance testing of the 15 stain blocking primers, paints manufactured by Dunn-Edwards Company would be used. No Dunn-Edwards paint is included in the list of 15 stain blocking primers.

A series of standard characterization tests such as sag, leveling, and density determination were performed on all paints selected. This paper presents the results from the characterization of the fifteen chosen primers, along with the five Dunn-Edwards topcoats and primers that were chosen as standard paints.

C. Materials and Methods

Primer, Topcoat, and Substrate Selection.

Stain blocking primers were chosen based on industry panel recommendations from three VOC categories: less than 550g/L, less than 350 g/L, and less than 100 g/L. The first category represents shellac-based primers; the second category contains oil based specialty primers, sealers, and undercoaters; and, the third category contains waterborne latex primers. The fifteen stain blocking primers selected for testing are,

- Zinsser Shellac-Based B-I-N (shellac based)
- Zinsser High-Hide Cover Stain (oil based)
- Zinsser Odorless (oil based)
- Zinsser Smart Prime (water based)
- Zinsser Bulls Eye Zero (water based)
- Zinsser Waterborne Cover Stain
- KILZ Complete (oil based)
- KILZ Premium (water based)
- Behr Premium Plus Interior/Exterior Primer and Sealer (oil based)
- Behr Premium Plus Interior Primer and Sealer (water based)
- Benjamin Moore Fresh Start Alkyd Primer
- Benjamin Moore Fresh Start All-Purpose 100% Acrylic Primer
- Kelly Moore Weather Shield Exterior Alkyd Primer for Stain Blocking (oil based)
- Sherwin Williams Multi-Purpose Latex Primer, and
- Akzo Nobel P&P Gripper Stain Killer (water based)

This list contains one primer in the shellac category (VOC content of 550 g/L or less), six oil based primers with VOC content of 350 g/L or less, and eight waterborne primers with VOC content of 100 g/L or less. As mentioned above, Dunn-Edwards company's topcoats and primers were chosen as standard paints when topcoated or primed substrates become necessary for preparing stained samples for testing. All of these paints are water based. Vinylastic Premium Wall Sealer was chosen as the primer to be used for sealing drywall substrates to be used in stain testing; ENSO Interior Primer Low Odor Zero VOC was chosen as the standard interior primer; ENSO Interior Eggshell paint was chosen as the standard interior topcoat; UltraGrip Premium Interior/Exterior Multi-Purpose Primer was chosen as the standard exterior primer; and, Evershield Exterior Eggshell paint was chosen as the standard exterior topcoat.

The substrates used in tests reported in this report were black and white BYK Byko-Charts. In future stain testing, cedar and redwood boards, drywall, and field substrates containing various stains will also be used along with the Byko-Charts. These substrates were selected with agreement of the industry panel.

Primer Characterization.

The sections below provide details of several tests conducted to characterize the paints used in this study, along with relevant ASTM method.

Sag and Leveling. Three sag and leveling draw downs were made for each primer. Sag draw downs were made using the Leneta Anti-Sag Meter ASM-1 Standard Range. The sag draw downs were allowed to dry vertically, at room temperature. Sag ratings were recorded from 0 – 10, with 10 being best (i.e., none of the paint stripes ran together). ASTM D4400-99 was followed for sag measurements.

Leveling draw downs were made using the NYPC Level Test Blade. The leveling draw downs were allowed to dry on a flat countertop surface at room temperature The values for leveling were recorded from 0 – 5, with 5 being the best, where all leveling double stripes merged together. ASTM D4062-99 was followed for leveling measurements.

Contrast Ratio and Gloss. Three draw downs with a wet film thickness of 3 mils were made for each primer on black and white BYK Byko-Charts. Contrast ratio data was obtained using a DataColor Mercury spectrophotometer by taking the ratio of the Y tristimulus values from the black portion of the chart over the white. ASTM D6441-05 was followed for contrast ratio measurements.

Gloss measurements were taken as an average of ten data points over the white portion of the draw down chart using a BYK Gardener Micro-TRI-Gloss gloss meter at 60º. ASTM D523-08 was followed for gloss measurements.

Density and Percent Solids. A stainless steel pycnometer was used to determine the density of each primer in pounds per gallon, according to the procedure outlined in ASTM D1475-98.

The percent of solids by weight in each primer was determined according to ASTM D2369-07. To determine the percent solids by weight, an aluminum pan was weighed and approximately 0.5 g of paint was added and weighed. Latex paint samples had 3 mL of water added to each pan. All samples were then placed in an oven at 110 ºC for exactly 1 hour. The weight of the paint and the pan was then recorded after and the percent solids by weight was determined from this information.

Rheology. Viscosity versus shear rate data was obtained for all primers from 0.02 s^{-1} to 200 s^{-1} with 10 points per decade at 25 ºC. All measurements were made with a Texas Instruments AR 2000 Rheometer using a cone-and-plate geometry. Each primer was run at least twice to obtain consistent results.

VOC Determination. The volatile organic compound (VOC) level in each paint was determined according to ASTM D6886-03. HPLC grade methanol or acetone was used as the solvent for sample preparation for waterborne paints and HPLC grade tetrahydrofuran (THF) was used as the solvent for solvent based paints. An Agilent GC/MS/FID was used for all runs.

Stain Blocking Testing.

Stain blocking testing has not yet been completed. The following paragraphs outline the expected procedures for testing in the near future. Common stains are important to include in testing to assess the blocking capabilities of each primer. The stains that will be tested are discussed below, including both marker stains and wood tannin stains.

Marker Stains. Marker, pen, and highlighter will be used to test the stain blocking abilities of each primer in accordance with ASTM D7514-09. For each staining agent, two colors will be used. In this test method, several straight lines, each of a different staining agent, are drawn at least 3 mm apart on the white portion of BYK Byko-Charts. The stains are allowed to dry for 24 hours and primer is applied perpendicular to the stains at a 3 mil wet film thickness. The primer is then allowed to dry for 24 hours and a topcoat is applied parallel to the staining agents (perpendicular to the primer). Three charts will be made for each primer.

Another test method to be conducted uses select staining agents from the test above. 4cm x 4cm squares were filled in on BYK Byko-Charts using the staining agents that proved difficult to block in preliminary testing (1). The staining agents selected were red and black permanent marker, yellow and green highlighter, and blue pen. These staining agents are applied to the white portion of the charts, allowed to

dry for 24 hours, and the color data are collected as an average of three readings using the DataColor Mercury spectrophotometer. Primer is applied at a 3 mil wet film thickness, allowed to dry for 24 hours, and color data are collected as an average of three readings. The topcoat is then applied, allowed to dry for 24 hours, and color data is collected as an average of three readings. Three charts are made for each primer.

Tannin Stains. Cedar and Redwood boards will be purchased and cut into approximately 12”x7” size. A section of the board will be measured for accurate area measurements and painted. The boards will be weighed before and after painting, and average film thickness determined from this information. The primer will dry for at least 24 hours and the topcoat will then be applied to approximately half of the primed area.

D. Results and Discussion

Primer Characterization

All results for sag, leveling, contrast ratio, gloss, density, and weight fraction of solids can be found in **Tables 1 - 3**. From these tables it can be seen that the sag and leveling values are in close agreement - generally the paints with the best sag resistance have poor leveling capabilities. As a group, waterborne paints perform better in sag test and worse in leveling test when compared to with the solvent based group of paints. This is consistent with the expected trend between the two groups of paints.

Appearance properties of the coatings are shown in terms of contrast ratio and gloss values at 60º. There is no clear trend between the gloss values of the two groups of coatings (i.e. solvent based and water based). The gloss values are low, and consistent with what is expected of primers that would be formulated at near or above the critical pigment volume concentration. Contrast ratios, however, show a clear trend – the waterborne group has higher contrast ratios than does the solvent based group. It should be noted that higher contrast ratios, while indicate better hiding, are not necessarily indicative of better stain blocking performance. Typically, stain blocking primers are formulated to block stains by preventing the staining agent from migrating into the topcoat applied on over the primer. Another clear trend is observed in solids weight fraction results between solvent based and water based groups. The solvent based group, with the exception of SB4, has significantly higher solids (by weight) compared to the water based group of primers. Also, the solvent based group, with the exception of SB4, has higher densities than the densities of primers in the water based group. The combined trends of solids (by weight) and density data indicate that the solvent based group is more highly filled with inorganic fillers. Although the primers in water based group appears to be less filled, the higher contrast ratio of that group indicate presence of more TiO_2 in those formulations. The solid weight fraction data was useful in calculation of the VOCs discussed later in this report. The numbers presented are based on averages of three trials per paint.

Rheology.

Coating rheology has a direct influence on critical properties such as application film thickness, dewetting of applied film, sag, leveling, and diffusion of molecules including staining agents through the wet film. Although full rheological analysis of all coatings can be a highly resource consuming endeavor, determination of viscosity as a function of rate of shear can be accomplished with reasonable ease using a semi-automated rheometer such as the AR-2000 rheometer used in this work. Viscosity as a function of shear rate was determined for each primer at least in duplicate. A representative plot of one run for each primer can be found in **Figures 1&2** (Figure 1 – solvent based primers; Figure 2 – water based primers). As expected, all paints exhibit shear thinning behavior. Viscosities at low shear rate region should correlate with the sag and leveling properties of the paint, with low viscosity resulting in poor sag and good leveling. There is good agreement between the sag and leveling data reported in **Tables 1** and **2** and the rheology plots in **Figures 1** and **2**. However, as seen in **Table 1**, SB4 primer showed poor sag and good leveling values, but it appears to have the highest viscosity at low shear rate region. Careful examination showed that this primer dries fast within the cone-and-plate fixture of the rheometer, leading to high viscosity responses. The erratic nature of the data points supports this observation. Visually, the paint appears as though it has a low viscosity at low shear rates, in agreement with the sag and leveling data. In the water based primer group (Table 2 and Figure 2), WB6 performed worst in sag test and it has the lowest viscosity at low shear rate region.

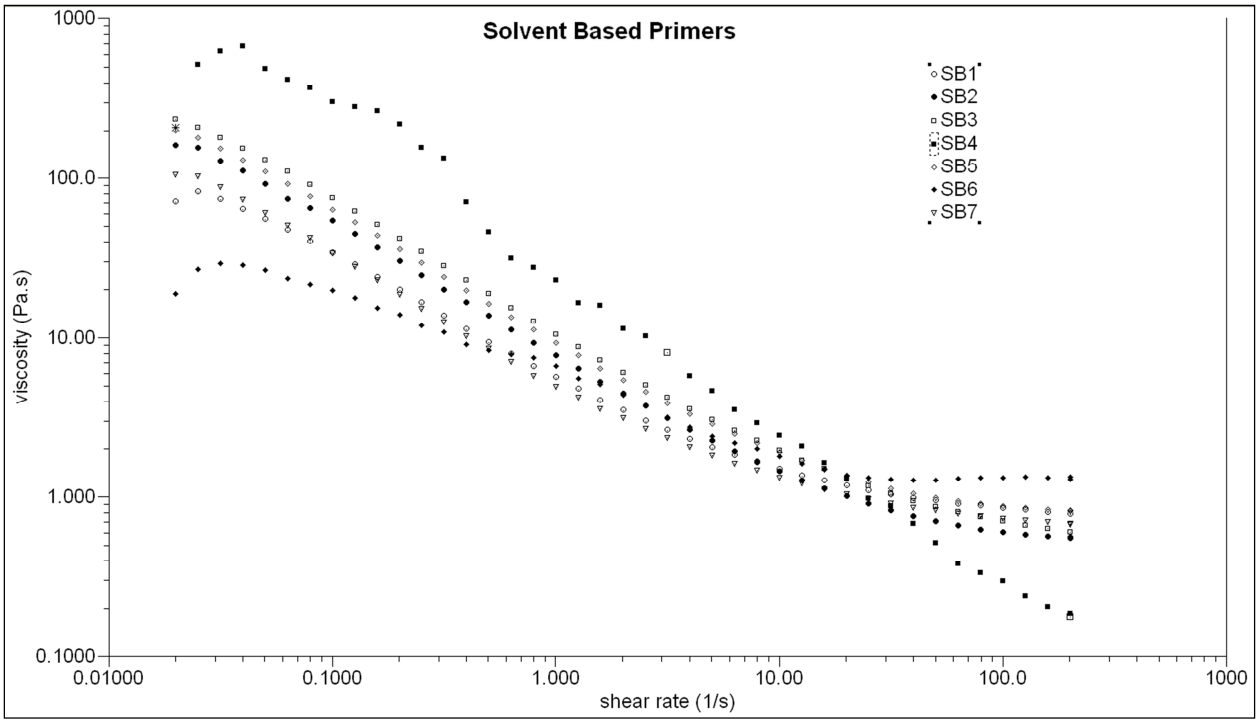

Figure 1. Viscosity versus shear rate plots for solvent based stain blocking primer coatings

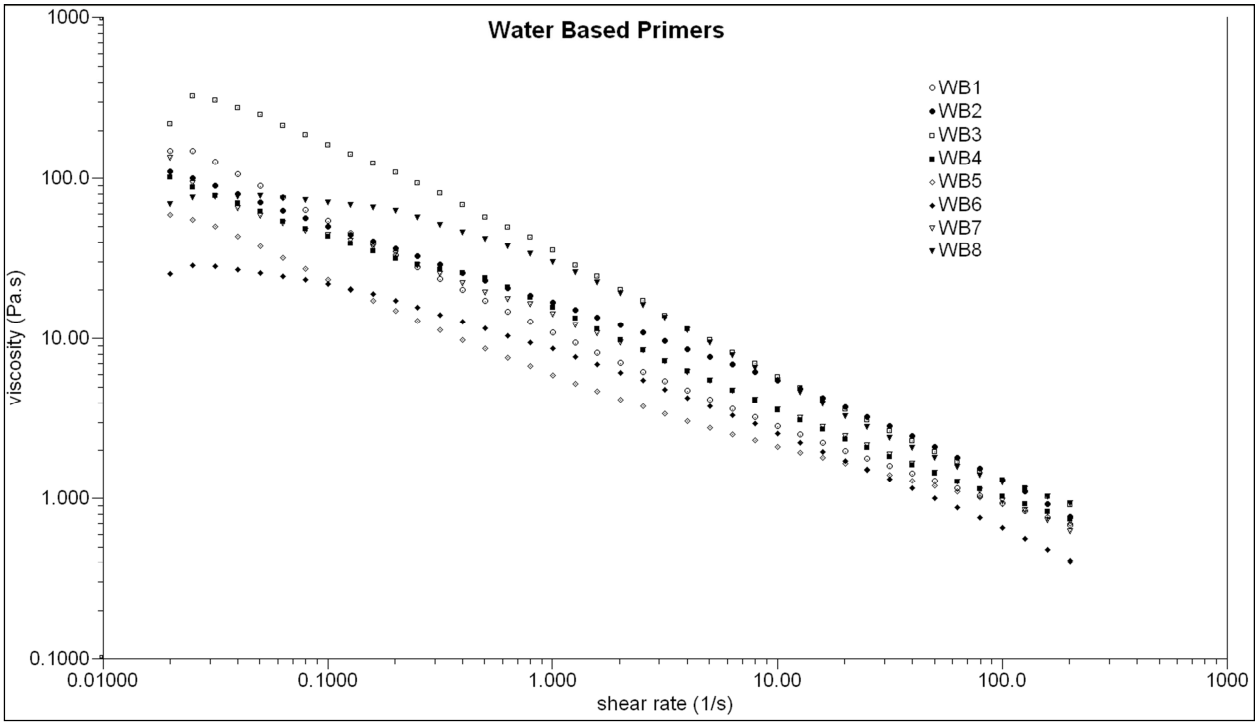

Figure 2. Viscosity versus shear rate plots for water based stain blocking primer coatings

Table 1. *Primer characterization values for sag, leveling, contrast ratio, gloss, solids weight fraction, and density of solvent based primers.*

	Sag	Leveling	Contrast Ratio	Gloss (60º)	Solids (wt fraction)	KU Viscosity	Density (lbs/gal)
SB1	8	1	0.91	4.8	0.768	95	11.8
SB2	10	0	0.90	3.3	0.754	89	11.4
SB3	10	0	0.89	2.5	0.791	89	13.3
SB4	6	3	0.93	5.8	0.516	68	9.80
SB5	10	0	0.91	2.5	0.774	91	12.5
SB6	5	3	0.91	5.1	0.742	91	11.3
SB7	9	0	0.94	7.0	0.770	93	11.9

Table 2. *Primer characterization values for sag, leveling, contrast ratio, gloss, solids weight fraction, and density of waterborne primers.*

	Sag	Leveling	Contrast Ratio	Gloss (60º)	Solids (wt fraction)	KU Viscosity	Density (lbs/gal)
WB1	10	0	0.96	3.4	0.444	99	10.1
WB2	10	0	0.98	14	0.488	110	10.5
WB3	10	0	0.95	6.5	0.533	120	10.8
WB4	10	0	0.97	3.5	0.517	100	11.0
WB5	10	2	0.96	3.5	0.470	100	10.8
WB6	7	3	0.97	11	0.495	96	10.9
WB7	10	0	0.95	5.1	0.505	110	10.9
WB8	9	0	0.95	5.7	0.554	110	11.1

Table 3. *Primer characterization values for sag, leveling, contrast ratio, gloss, solids weight fraction, and density of waterborne Dunn Edwards paints and primers.*

	Sag	Leveling	Contrast Ratio	Gloss (60º)	Solids (wt fraction)	KU Viscosity	Density (lbs/gal)
Drywall Sealer	6	3	0.97	3.5	0.473	88	10.7
Int WB Primer	10	2	0.95	8.3	0.504	110	10.8
Ext WB Primer	10	1	0.95	18	0.529	110	10.8
Int Topcoat	10	0	0.97	14	0.540	110	10.9
Ext Topcoat	10	0	0.98	14	0.531	91	10.5

VOC Determination.

Table 4 shows the VOC values that have been obtained for select primers as well as the expected VOC content as provided in the technical data sheets (TDS) from the manufacturer. As shown in the table, these values are consistent with the expected values, as provided by the manufacturers.

Table 4. *VOC content as determined experimentally and as provided by the manufacturer. Manufacturer values are coating VOC values. All values are in grams per liter.*

Coating	Material VOC	Coating VOC	TDS VOC
SB1	340	340	340
SB2	280	300	350
SB3	320	320	<350
SB4	460	510	550
SB5	250	280	<350
SB6	260	290	340
SB7	320	320	350
WB1	16	47	100
WB2	3.6	10	"zero"
WB3	34	79	95
WB4	32	81	96
WB5	20	59	81
WB6	8.0	23	"zero"
WB7	9.7	27	<100
WB8	24	56	92

E. Conclusion

The stain blocking primers tested in this study were selected based on industry recommendation. The testing completed to date shows the similarities and differences in basic characteristics between selected primers. The stain blocking tests discussed in this paper will be conducted in the near future to assess the stain blocking capabilities of each primer.

F. References

1. "Low Volatile Organic Compound (VOC) Stain Blocking Specialty Primer Coating", R. H. Fernando and D. R. Jones, First Quarterly Report of Project Sponsored by California Air Resources Board (Standard Agreement No. 09-428), September 30, 2010