Final Report on

Standard Agreement No. 09-428

For the Period

June 23, 2010 through January 31, 2012

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

This report was submitted in partial fulfillment of ARB Standard Agreement Number 09-428, Low Volatile Organic Compound (VOC) Stain Blocking Specialty Primer Coating, by the Cal Poly Corporation under sponsorship of the California Air Resources Board.

A. Summary

This report describes work performed between June 2010 and January 2012 under Standard Agreement Number 09-428, Low Volatile Organic Compound (VOC) Stain Blocking Specialty Primers Coatings. At the time of initiation of the project, local air districts' architectural coating rules that are based on the California Air Resources Board's (ARB) 2007 architectural coatings Suggested Control Measure were 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. Generally, 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 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. With the help of an advisory panel, fifteen stain blocking primers, both water based and solvent based, were chosen for testing and comparison. All primers were characterized with respect to their solids content, density, sag, leveling, contrast ratio, gloss and VOC content. Characterization results are included in this report. The fifteen primers' stain-blocking performance against household markers, tannin stains from redwood and cedar, and stains from smoke and fire damaged wood substrates were determined The substrates included coating draw-down paper, drywall, redwood, cedar, and wood panels burned under controlled laboratory conditions and retrieved from real fire and water damage sites.

Results of the study indicated that as a class, water-based stain-blocking primers performed similarly to solvent-based primers in blocking stains from household markers. Tannin blocking tests on cedar boards indicated there are water based coatings in the market that can match the performance of best solvent based coatings. However, solvent based coatings outperformed water based coatings in blocking redwood stains. Tests indicated that several water based primers, when applied as two coats, can match the best performing solvent based primers in blocking redwood stains. Results also indicate that there are water based primers that can match the best solvent based primers in blocking stains caused by fire and water damage on wood panels.

B. Introduction

At the time of initiation of this project (June 2010), regulations in California allowed specialty primers, sealers, and undercoaters (SPSU), also referred to as stain blocking primers, to have a VOC content of up to 350 g/L. Several air districts had plans to lower the VOC limit for this category to 100 g/L by January 2012. The best performing stain blocking primers 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. However, there have been a number of recent advancements in developing low VOC waterborne stain blocking primers (1-7). A number of recent products with less than 100 g/L VOC also have been introduced to this market by paint and coating companies in recent years.

Typical stains that require blocking include tannins, various household markers, and smoke and fire related stains. Tannins are naturally occurring, plant-based polyphenolic compounds that are found in all wood species (8). Knots in the wood usually contain a higher concentration of tannins and other staining agents. These staining agents can leach out of the wood and into the coating, causing significant discoloration in the case of woods like redwood and cedar. Tannins form water-soluble compounds when exposed to the basic conditions typically associated with waterborne paints. A solvent based primer usually is more effective than a water based primer at preventing migration of tannins into the topcoat; however there are ways of preventing migration using a water based primer. Tannins can be made to bind chemically in the primer so they would not migrate. The conventional approach to this method is to use a cationic polymer dispersion with a reactive pigment, such as zinc oxide and other inorganic compounds, which form complexes with tannin compounds (9). Another approach is the use of a chemical pre-treatment to remove staining agents from wood (10). This method is undesirable because it adds another costly step in coating wood and also because it could have negative effects on the physical properties of the wood.

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 was 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 made up of companies and organizations having a vested interest in the project were gathered by the ARB. This panel was 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

This panel recommended fifteen stain-blocking primer coatings for testing, along with five other coatings to be used as standard primers and topcoats when needed during the course of testing. 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 solids content, VOC content, density, sag, leveling, viscosity, gloss, and contrast ratio, were performed on all paints selected. Following that, stain blocking tests were conducted with household markers according to ASTM D7514-09 and tannin blocking tests were conducted with cedar and redwood substrates. Other substrates such as wood panels from real fire and water damage sites, and wood panels burned under controlled conditions were also tested. Results of these evaluations, previously presented in quarterly progress reports available at an ARB website (11), are combined and presented in this final project report.

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 were:

- 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. In order to conceal the identity of stain-blocking primers the seven solvent based coatings were assigned the codes SB1, SB2, SB3, SB4, SB5, SB6, and SB7, whereas the eight water based coatings were assigned the codes WB1, WB2, WB3, WB4, WB5, WB6, WB7, and WB8. 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 were black and white BYK Byko-Charts, cedar and redwood boards, drywall, Douglas fir, and field substrates with fire and water damage. These substrates were selected with agreement of the industry panel. Cedar, redwood, Douglas fir, and drywall substrates were purchased from a local Home Depot store.

Some of the redwood and Douglas fir panels were burned under controlled conditions in an attempt to simulate burning in a real fire. The level of burning was such that the panels would be painted over rather than discarded in a restoration effort. Controlled burning involved subjecting the redwood and Douglas fir panels to a Coleman propane torch. The torch was applied directly to the surface of the wood (about 3 inches from the surface) for about 90 seconds, which resulted in an even burn of the panel surface. Figure 1 shows a Douglas fir panel before and after being burned. Figure 2 illustrates the typical degree of burning achieved for all panels used for testing.

Figure 1: Photograph of a wood panel before (left) and after (right) being subjected to the flame from Coleman burner

The burned panels were left undisturbed for 24 hours. Each panel then had the test primer applied on three sections. After 24 hours of drying time of the primer, the Dunn Edwards ENSO Interior Eggshell top coat was applied over the primer and allowed to dry for an additional 24 hours. Stain blocking primer performance was ranked the same way as described elsewhere in this report, visually within a scale from 1-10, with 1 being the worst and 10 being the best.

Figure 2: Photograph of a batch of wood panels after being subjected to the flame from Coleman burner

A fire damaged piece of wood (2”x4” cross-section, 36” long) from the ceiling of a local restaurant in San Luis Obispo was obtained. The piece of wood had been burned in a fire that occurred in March 2010. The wood surface contained charred material but was still intact when obtained for the study (Figure 3). The wood surface was wiped clean before application of coatings. Narrow stripes of each stain blocking primer and topcoat were applied across the length of the panel according to the procedure described above for panels burned under controlled conditions.

Figure 3: Photograph of wood sample obtained from a restaurant fire in San Luis Obispo, CA.

The water damaged wood samples were obtained from a residence in San Luis Obispo. Two wood panels (9”x18” each), that were put together in a checkerboard pattern (see Figure 4) were left in the garage in an area where there was a leak in the ceiling. The panels had been subjected to water damage for approximately two months. They were dry but slightly moldy when obtained for the study. The extent of water damage related

staining was similar on the two panels. Both of the panels were initially wiped with de-ionized water and dried with clean tissue paper. One of the panels was used for testing the solvent based primers, whereas the other panel was used for testing the waterborne primers. One of the wood panels coated with a solvent based stain blocking primer is shown in Figure 4. The other solvent based primers were applied on the remaining area. The panel was left to dry for 24 hours at ambient temperature, and then the Dunn Edwards ENSO Interior Eggshell topcoat was applied on each primer. The top coat was also allowed to dry for 24 hours. The same procedure was repeated for waterborne primers using the remaining wood panel. Performance of each stain blocking primer was ranked visually in the same scale (1-10) as before.

Figure 4. Photograph of a water damaged wood panel recovered from a residence in San Luis Obispo, CA. One of the test primers has been applied on the panel.

Several brand new acoustical ceiling tile panels were supplied by a member of the industrial advisory panel for inclusion in the study. Attempts were made to create stains on the face of the tiles by wetting the back side with water that was allowed to diffuse to the face of the panel. This approach produced water marks on the face, but the stains were not severe at all. It was determined that the stain severity on the ceiling tiles were not high enough to differentiate the performance of the fifteen test primers. No coating tests were conducted on the ceiling tiles.

Primer Characterization.

This section provides details of the 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.

Viscosity. Viscosity versus shear rate data were obtained for all primers from 0.02 s^{-1} to 200 s^{-1} shear rate range in a logarithmic scale with 10 points per decade at 25 ºC. All measurements were made with a TA Instruments AR 2000 Rheometer equipped with a cone-and-plate geometry. Each primer was tested at least twice to obtain consistent results. In addition, the Stormer KU viscosities were measured.

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.

Common stains are important to include in testing to assess the blocking capabilities of each primer. The stains that were tested are discussed below, including both marker stains and wood stains.

Marker Stains. Marker, pen, and highlighter were used to test the stain blocking abilities of each primer in accordance with ASTM D7514-09. For each staining agent, two colors were 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 the Dunn-Edwards ENSO Interior Eggshell interior topcoat is applied parallel to the staining agents (perpendicular to the primer). Three charts are made for each primer.

Tannin Stains. Cedar and redwood boards were purchased from a local Home Depot store and cut into approximately 12”x36” size. Each board was lightly sanded to ensure more uniformity between samples. The test primer was applied at a 7 mil wet film thickness in two areas along the length of the board (see Figure 5). Each board was also coated with a 7 mil layer of Dunn-Edwards UltraGrip Premium Interior/Exterior Multi-Purpose Primer, across the width at the center. The boards were weighed before and after painting, and the average film thickness was determined from this information and the density of the coating. The primers were allowed to dry for at least 24 hours and the topcoat, Dunn-Edwards Exterior Waterborne Eggshell Paint, was then applied over a portion of the primed area at a wet film thickness of 7 mils. Half of the area coated with the UltraGrip Premium Interior/Exterior Multi-Purpose Primer was also coated with the Dunn-Edwards Exterior Waterborne Eggshell Paint. The center portion of every wood panel was coated the same way to use as a consistent visual reference. Following a 24 hour drying period of the topcoat, wet sponges, approximately 1 inch by 1 inch, were placed on top of the primed areas and the areas with both primer and topcoat. The sponges were covered with plastic cups to prevent evaporation and contamination. After 24 hours the cups and sponges were removed, the test area was gently dried, and both stain intensity and blistering were ranked on a scale of 1 to 5, with the ranking of 5 representing no visible tannin bleed-through and no blistering. This test method and the ranking scale of 1-5 are based on a procedure provided by Kelly-Moore Company. During a teleconference with the industry panel involved in this project it was agreed that the 1-5 ranking would be converted to a 1-10 scale in order to keep the scales consistent among various test methods. Results presented later on in this report are based on the 1-10 scale.

Figure 5. Photograph of a redwood panel (12”X36”) prepared for tannin blocking test

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 6&7 (Figure 6 – solvent based primers; Figure 7 – 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 6 and 7. 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 7), WB6 performed worst in sag test and it has the lowest viscosity at low shear rate region.

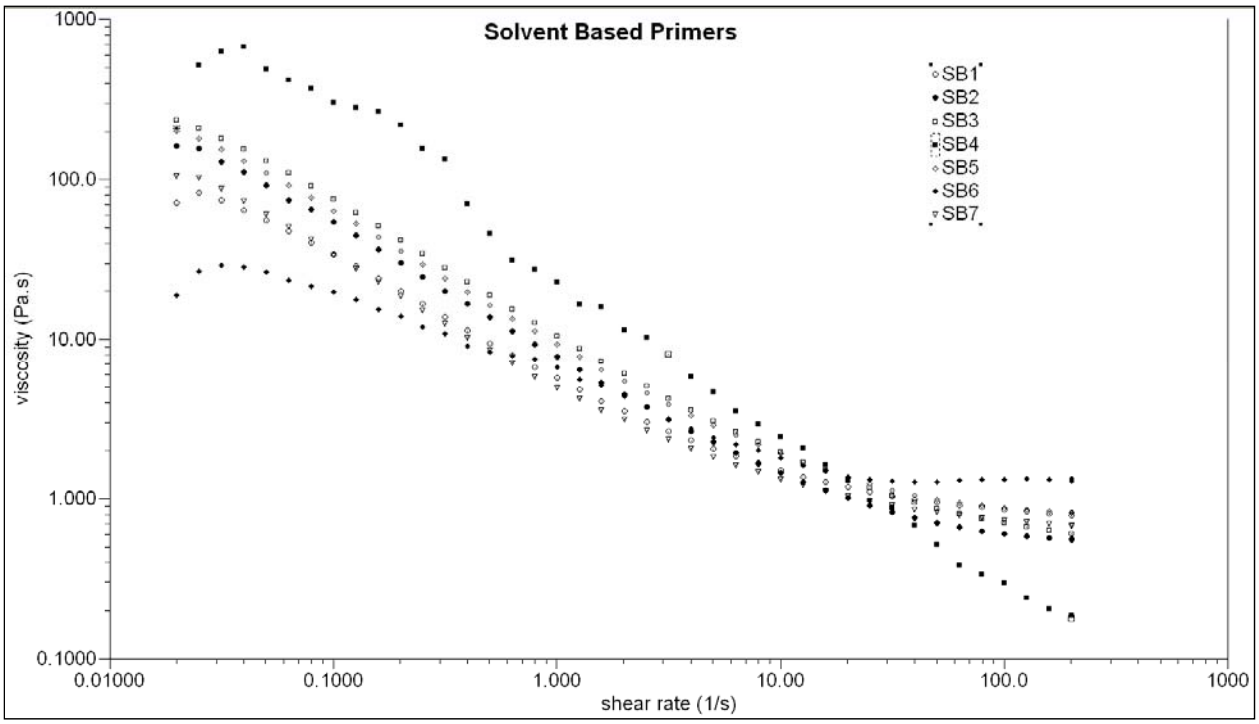


Figure 6. Viscosity versus shear rate plots for solvent based stain blocking primer coatings

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.

Marker Stain Blocking Testing

Table 5 contains the data for the stain blocking ranking of each stain for each primer. The score presented is an average of 3 trials with a maximum score of 10 representing perfect stain blocking. The values presented in Table 5 are very reproducible with a maximum possible error of ± 1 ranking value. A systematic statistical analysis was conducted on a sampling of results to quantify the error in stain blocking rating. Average marker stain-blocking rankings in Table 5 are represented in a bar chart in Figure 8. As seen in Table 5 and Figure 8, the solvent based primer SB5 performed best among all primers, while the waterborne primer WB3 performed best among waterborne primers. The overall performance of water based and solvent based primers is comparable.

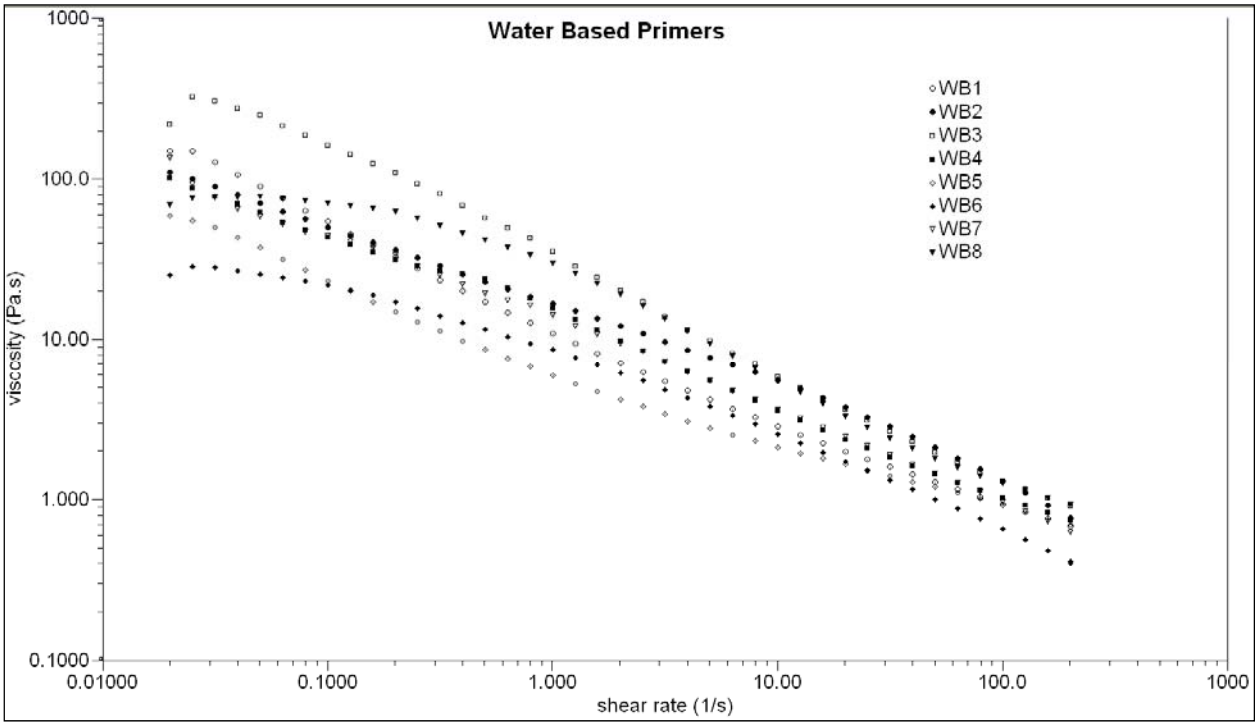


Figure 7. Viscosity versus shear rate plots for water based stain blocking primer coatings

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

Primer	Sag	Leveling	Contrast Ratio	Gloss (60º)	Solids (% by wt.)	Viscosity (KU)	Density (lbs/gal)
SB1	8	1	0.91	4.8	76.8	95	11.8
SB2	10	0	0.90	3.3	75.4	89	11.4
SB3	10	0	0.89	2.5	79.1	89	13.3
SB4	6	3	0.93	5.8	51.6	68	9.80
SB5	10	0	0.91	2.5	77.4	91	12.5
SB6	5	3	0.91	5.1	74.2	91	11.3
SB7	9	0	0.94	7.0	77.0	93	11.9

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

Primer	Sag	Leveling	Contrast Ratio	Gloss (60º)	Solids (% by wt.)	Viscosity (KU)	Density (lbs/gal)
WB1	10	0	0.96	3.4	44.4	99	10.1
WB2	10	0	0.98	14	44.8	100	10.5
WB3	10	0	0.95	6.5	53.3	120	10.8
WB4	10	0	0.97	3.5	51.7	100	11.0
WB5	10	2	0.96	3.5	47.0	100	10.8
WB6	7	3	0.97	11	49.5	96	10.9
WB7	10	0	0.95	5.1	50.5	110	10.9
WB8	9	0	0.95	5.7	55.4	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.*

Primer	**Sag**	**Leveling**	**Contrast Ratio**	**Gloss (60º)**	**Solids (% by wt.)**	**Viscosity (KU)**	**Density (lbs/gal)**
Drywall Sealer	6	3	0.97	3.5	47.3	88	10.7
Int WB Primer	10	2	0.95	8.3	50.4	110	10.8
Ext WB Primer	10	1	0.95	18	52.9	110	10.8
Int Topcoat	10	0	0.97	14	54.0	110	10.9
Ext Topcoat	10	0	0.98	14	53.1	91	10.5

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

During testing it was noted that several primers performed poorly in blocking the red Sharpie and green highlighter stains. These stains were interesting because the black Sharpie and the yellow highlighter did not present a problem for most primers. The average stain-blocking scores for all primers were recalculated omitting the red Sharpie and green highlighter scores. The results are significantly different, as seen below in Figures 9 and 10. A final plot was made excluding both red Sharpie and green highlighter as seen in Figure 11. All recalculated values can also be seen in Table 6. When the score for the red Sharpie is omitted, there is a

significant change in the results (Figure 9, Table 6). The most noticeable change is the increase in average score for the solvent based primers. It appears that there is some component in the red Sharpie that is not blocked by the solvent based primers. When the green highlighter is omitted from the total score, there is also a significant change in the results (Figure 10, Table 6). The most noticeable change is the increase in the average scores of the water based primers. It appears that there is some component in the green highlighter that is not blocked by the water based primers. Finally, the scores for both the red Sharpie and the green highlighter were omitted in order to remove all outliers (Figure 11, Table 6). From this data it can be seen that several of the primers, both solvent based and water based, had average rankings of 10 (best possible ranking), including SB2, SB5, SB6, SB7, WB2, WB3, WB4, and WB7.

Two Coat Marker Stain Testing

A test was conducted using two coats of the water based primers in order to determine if two coats of water based primers can perform as well as or better than one coat of the solvent based primers. Two coats of water based primer emit much less VOC than one coat of solvent based primer. The results of this test are shown in Table 7. Two solvent based primers were included in testing to ensure consistent results were obtained. From Table 7 it can be seen that there was at least a one ranking point increase in the average stain blocking capabilities of all water based primers with the use of a second coat.

Table 5 : Average Marker Stain Blocking Rankings for All Stains and Primers. (Best: 10)

Primer	Blue pen	Red pen	Black Sharpie	Red Sharpie	Black Expo	Red Expo	Green Highlighter	Yellow Highlighter	Primer Average
SB1	8	10	8	6	10	10	9	10	8.9
SB2	10	10	8	4	10	10	10	10	9.0
SB3	8	10	8	7	8	10	8	10	8.7
SB4	8	10	6	7	10	10	5	10	8.2
SB5	10	10	10	7	10	10	10	10	9.7
SB6	10	10	8	5	10	10	10	10	9.2
SB7	9	10	9	3	10	10	10	10	8.8
Average SB	9.0	10.0	8.2	5.7	9.6	10.0	8.9	10.0	8.9
WB1	9	9	9	9	10	10	3	10	8.5
WB2	10	10	10	10	10	10	3	10	9.1
WB3	9	10	8	9	10	10	8	10	9.3
WB4	10	10	9	8	10	10	3	10	8.8
WB5	8	10	7	5	10	10	3	10	7.7
WB6	7	8	10	10	10	10	3	10	8.3
WB7	10	10	10	10	10	10	2	10	9.0
WB8	8	10	7	9	10	10	6	10	8.8
Average WB	8.8	9.6	8.6	8.7	10.0	10.0	4.0	10.0	8.7

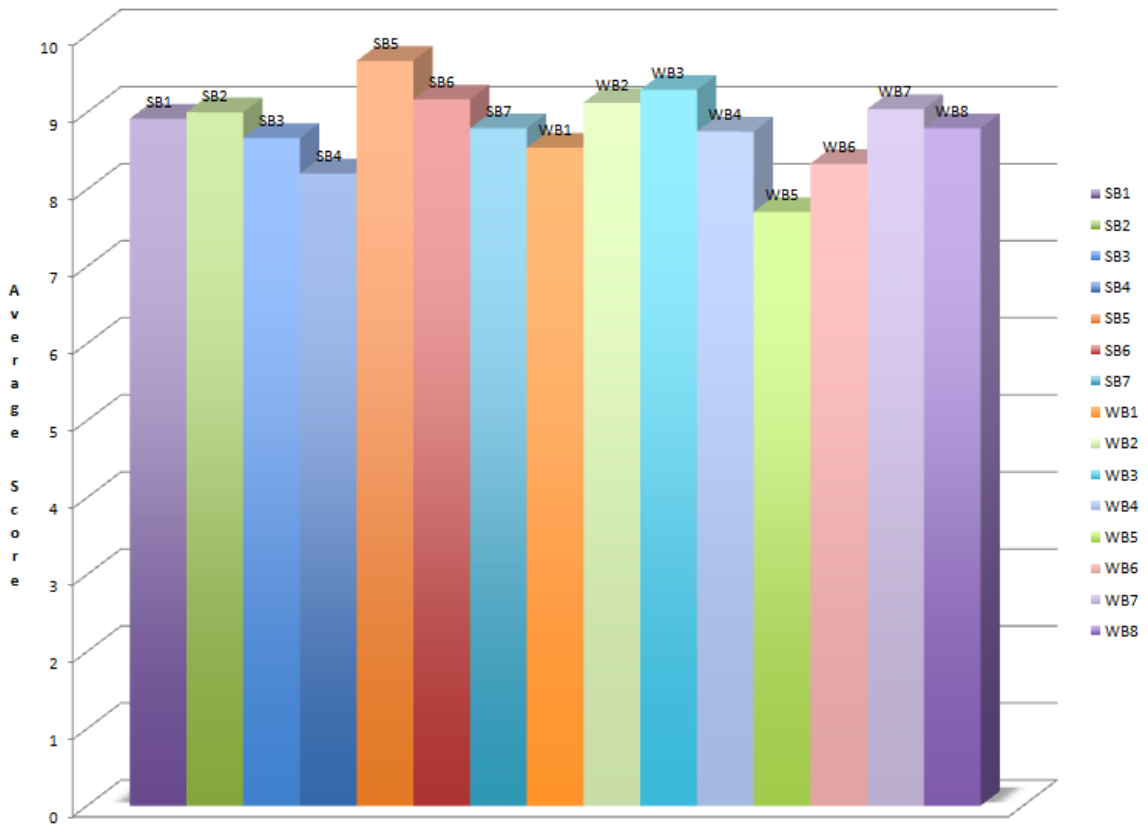


Figure 8: Average Marker Stain Test Rankings for all Primers and Stains (Best: 10)

Table 6: Average Marker Stain Rankings for All Primers and Select Stains. (Best: 10)

Primer	Average Score	Without Red Sharpie	Without Green Highlighter	Without Red Sharpie and Green Highlighter
SB1	8.9	9.3	8.9	9.3
SB2	9.0	9.7	8.9	9.7
SB3	8.7	8.9	8.7	9.0
SB4	8.2	8.4	8.7	8.9
SB5	9.7	10.0	9.6	10.0
SB6	9.2	9.7	9.0	9.7
SB7	8.8	9.6	8.7	9.6
WB1	8.5	8.5	9.3	9.4
WB2	9.1	9.0	10.0	10.0
WB3	9.3	9.3	9.5	9.5
WB4	8.8	8.9	9.6	9.8
WB5	7.7	8.1	8.4	9.0
WB6	8.3	8.1	9.1	9.0
WB7	9.0	8.9	10.0	10.0
WB8	8.8	8.8	9.1	9.2

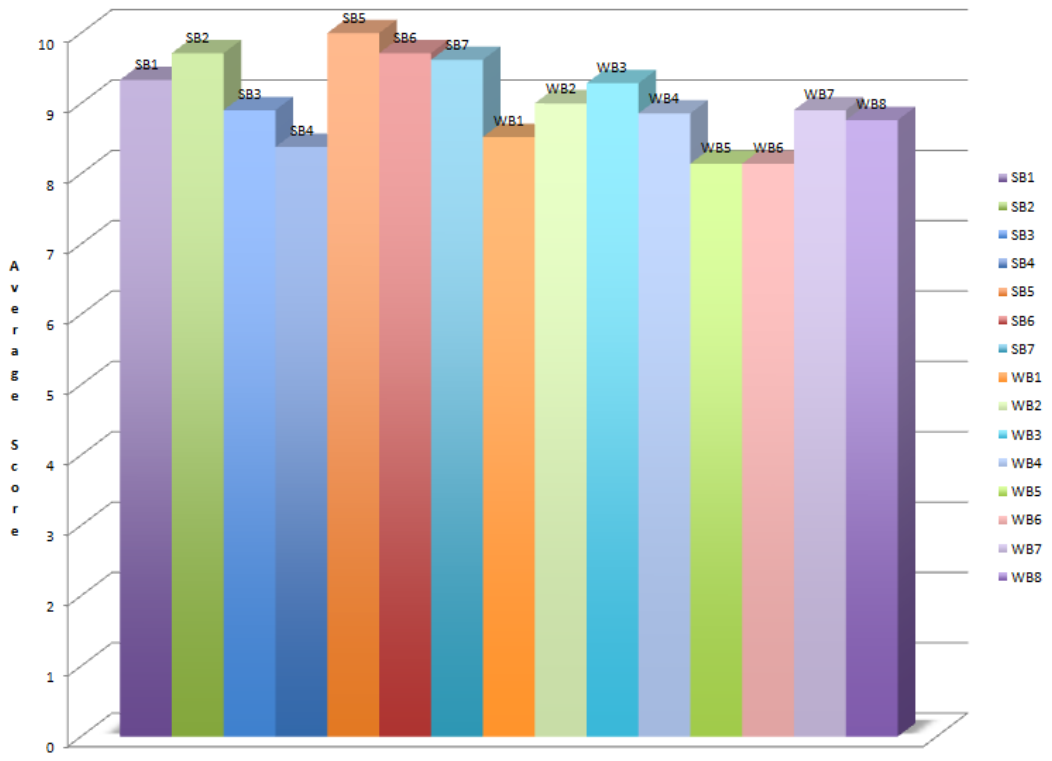


Figure 9: Marker Stain Test Rankings for all Primers and Stains, Excluding Red Sharpie. (Best: 10)

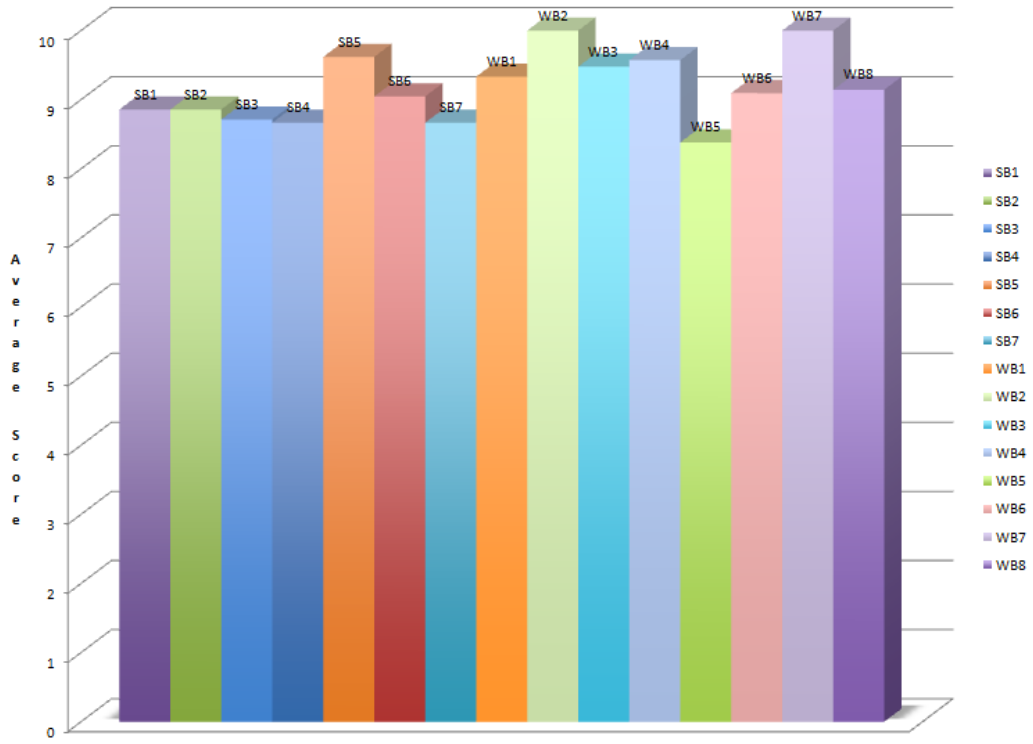


Figure 10: Marker Stain Test Rankings for all Primers and Stains, Excluding Green Highlighter. (Best: 10)

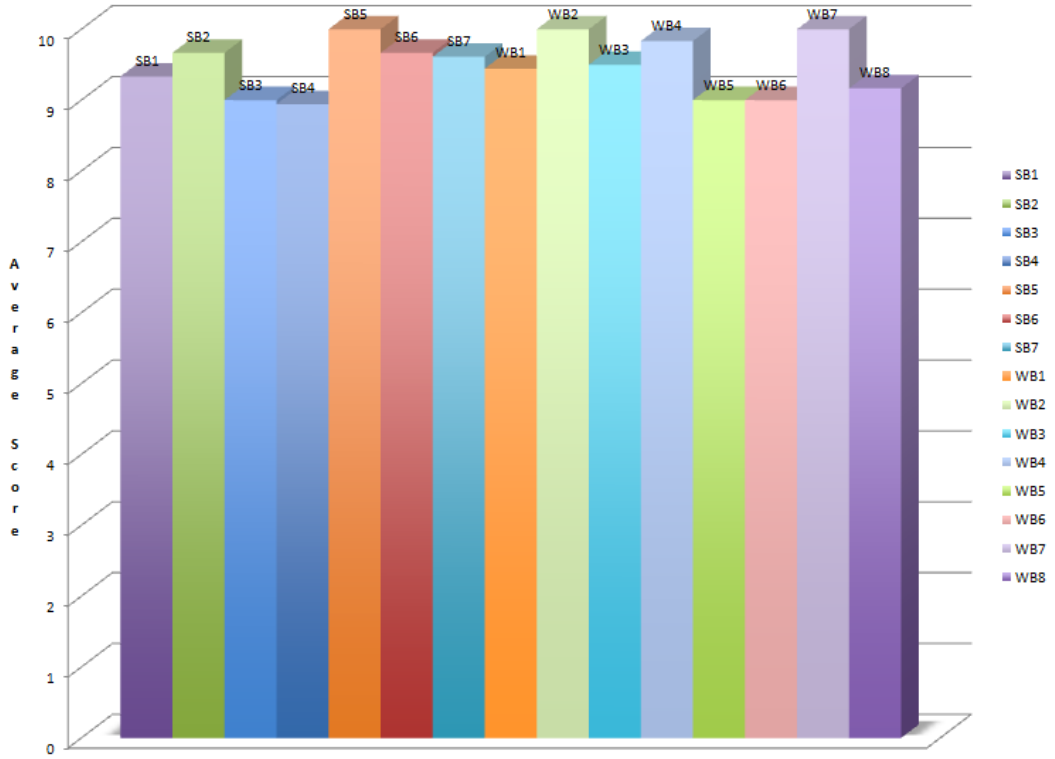


Figure 11: Marker Stain Test Rankings for all Primers and Stains, Excluding Green Highlighter and Red Sharpie. (Best: 10)

Table 7: Average Marker Stain Rankings for Two Coats of Water Based Primer Test. (Best: 10)

Primer	One Coat	Two Coats
SB2	9.0	--
SB5	9.7	--
WB1	8.5	9.8
WB2	9.1	9.8
WB3	9.3	9.8
WB4	8.8	9.5
WB5	7.7	9.0
WB6	8.3	9.8
WB7	9.0	9.9
WB8	8.8	9.6

Stain Characterization

Since the green highlighter and red Sharpie markers caused problems for water based and solvent based primers, respectively, a limited effort was spent on an attempt to characterize some of the markers by GC-MS and GC-FID. The results for the green highlighter show they contain glycerin and triethanolamine, as seen from the FID results of the green highlighter in Figure 12. Glycerin and triethanolamine are highly polar compounds indicating that colorant in green highlighter is also highly polar. Such compounds are highly miscible in water. As a result, the dried colorant can dissolve in the wet water based primer and diffuse to the surface. Ethylene glycol dimethyl

ether was included in this sample as the internal standard, and can also be seen in Figure A8 as the peak marked "EGDE". The results from the red Sharpie revealed small traces of several compounds, including: ethyl ether, 2-ethylhexanoic acid, 4-methyl-3-penten-2-one, and 4-hydroxy-4-methyl-2-pentanone (most abundant component). Polarity of 4-hydroxy-4-methyl-2-pentanone is comparable with solvents commonly used in solvent based coatings, indicating the colorant in red Sharpie has a polarity that matches the polarity of solvents in the solvent based primers. This would make it easier for the red colorant to diffuse through the primer layer.

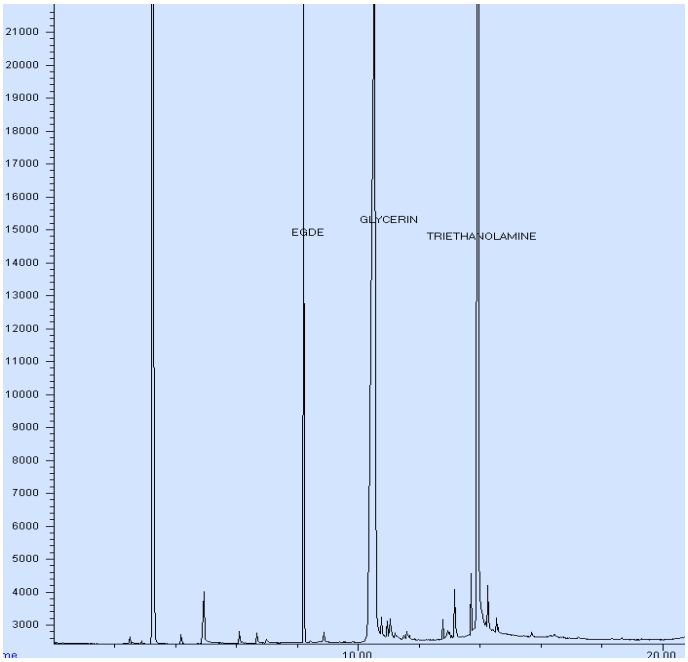


Figure 12. GC-FID Results for the Green Highlighter in Water

Drywall Stain-Blocking Results

Results of stain-blocking tests on drywall, conducted according to ASTM-D7514-09, are presented in Table 8. Average rankings of all stains for individual stain-blocking primers are presented in Figure 13 as a bar-chart. These results follow the same trends described earlier in this report for Byko-charts. In the case with Byko-charts, the average scores for solvent based coatings and the average scores for water based coatings (8.9 and 8.7, respectively), were virtually identical. Although the scores for painted drywall are lower, they are identical between solvent based primers and water based primers (Table 8). The average stain-blocking ranking of water based coatings for the green highlighter marker is significantly lower than that for the solvent based coatings. The same trend was observed with Byko-charts. However, on painted drywall, the WB1 water based coating performed well against green highlighter. Results of stain-blocking performance of two coats of water based primer on drywall are presented in Figure 14 and are compared with single coat primer results in Figure 15. It is clear that two coats of water based coatings perform better in all cases. Also, two coats of water based primers perform better than a single coat of solvent based primers.

Table 8 : Average Marker Stain Blocking Rankings for All Stains and Primers on Painted Drywall. (Best: 10)									
Primer	Blue pen	Red pen	Black Sharpie	Red Sharpie	Black Expo	Red Expo	Green Highlighter	Yellow Highlighter	Primer Average
SB1	7.0	7.7	6.7	6.3	6.7	6.7	6.0	10.0	7.3
SB2	7.7	8.7	6.7	6.7	6.7	6.7	7.0	10.0	7.7
SB3	7.0	7.0	6.0	6	6.0	6.0	6.0	9.0	6.9
SB4	7.0	7.0	5.7	5.7	7.0	7.0	5.0	10.0	7.0
SB5	9.0	9.0	7.0	7.0	7.0	7.0	7.0	10.0	8.1
SB6	9.0	9.0	6.7	6.7	6.7	7.0	7.0	10.0	7.9
SB7	9.0	9.0	7.3	7.0	7.0	7.3	7.7	10.0	8.1
Average SB	8.0	8.2	6.6	6.5	6.7	6.8	6.5	9.9	7.6
WB1	9.3	8.7	8.3	8.3	8.7	9.0	8.0	9.0	8.6
WB2	7.7	7.7	6.7	6.7	6.0	6.7	3.3	8.0	6.9
WB3	9.0	9.0	8.0	8.0	7.7	7.7	4.7	9.0	8.0
WB4	8.0	8.0	8.0	8.0	8.0	7.0	3.0	10.0	7.6
WB5	7.7	6.3	7.0	7.0	6.7	6.7	2.0	8.0	6.6
WB6	9.7	9.7	8.7	8.7	8.7	8.7	6.7	9.0	9.0
WB7	9.0	9.0	7.0	7.0	6.7	6.7	5.0	9.0	7.6
WB8	7.0	7.0	6.0	6.0	5.7	6.0	4.0	9.0	6.6
Average WB	8.4	8.2	7.5	7.5	7.3	7.3	4.6	8.9	7.6

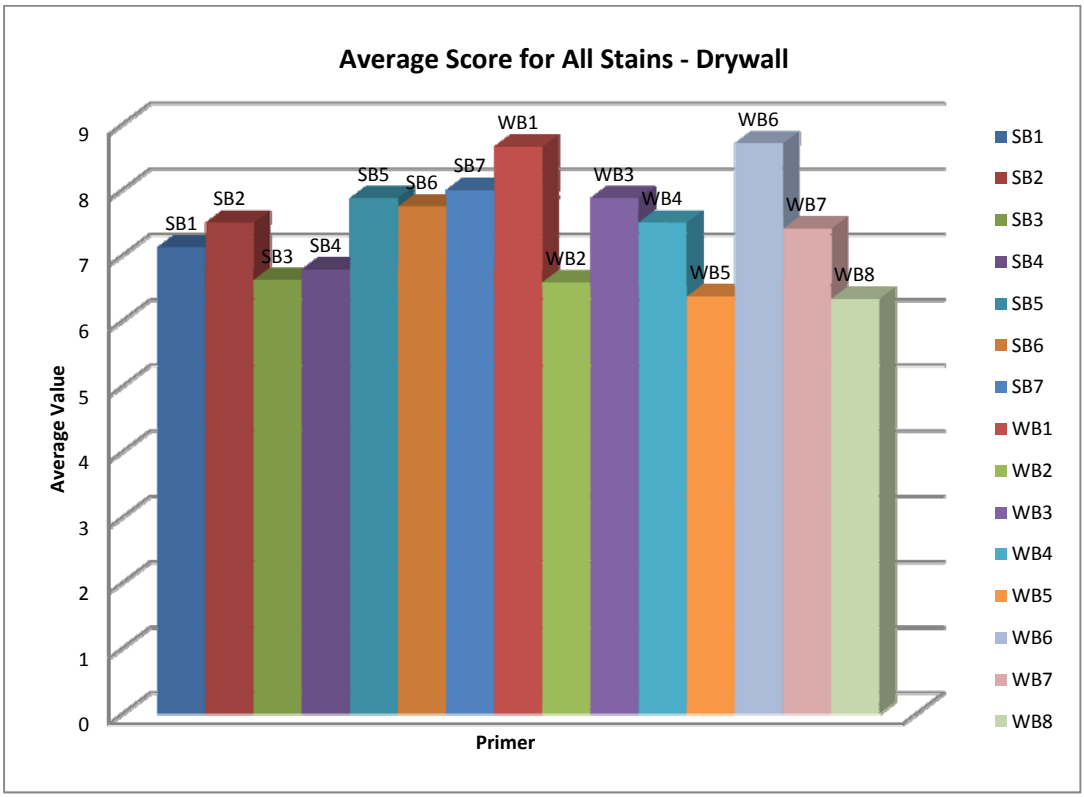


Figure 13. Average Marker Stain Test Rankings for all Primers and Stains (Best: 10).

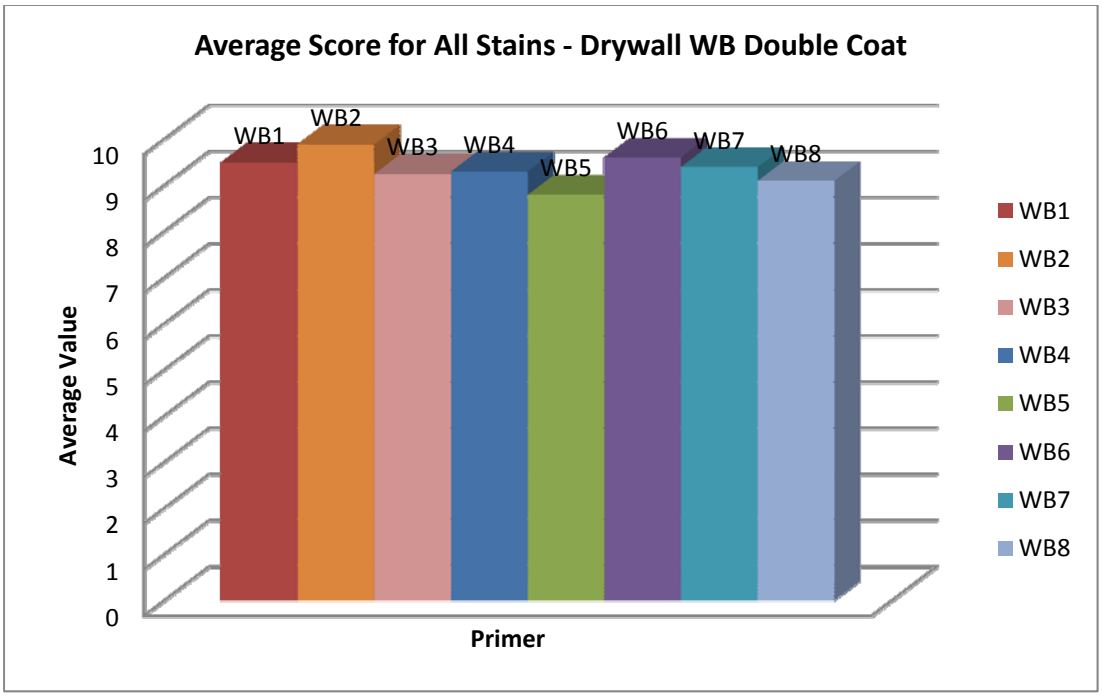
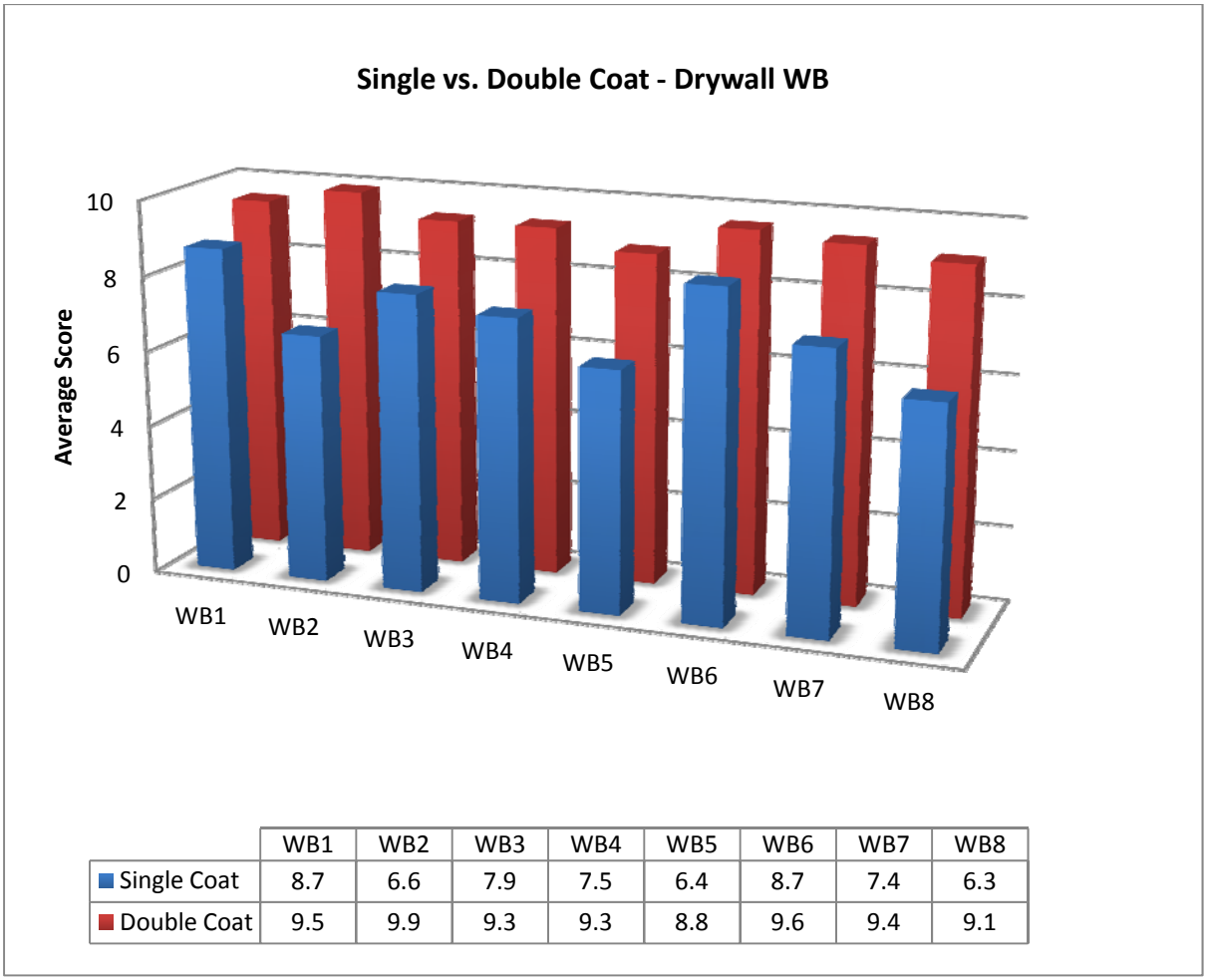


Figure 14. Average Marker Stain Test Rankings [All stains; Two Layers of Water Based Primers; Best -10].



	WB1	WB2	WB3	WB4	WB5	WB6	WB7	WB8
Single Coat	8.7	6.6	7.9	7.5	6.4	8.7	7.4	6.3
Double Coat	9.5	9.9	9.3	9.3	8.8	9.6	9.4	9.1

Figure 15. Comparison of Stain Blocking Rankings of Single versus Double Layers of Water Based Primers

Tannin Blocking Testing

The ability of each primer to block tannin bleeding into the topcoat was measured on a similar scale as before (1 to 10). The rankings (See page 11 for experimental details) for each primer coated with exterior topcoat were determined on both the cedar and redwood samples and the rankings can be seen in Figures 16 and 17, respectively. The values can also be seen in Table 9.

A few key statements can be made about the tannin blocking testing results. First, the ranking for the redwood samples are noticeably lower than the rankings for the cedar samples. Visual observation of uncoated samples shows that the redwood samples are significantly darker in color than the cedar samples, which is due to the inherently higher tannin content of redwood. Second, it can be seen that certain waterborne primers, namely WB2 and WB8, perform as well as the best solvent based primers on cedar. Finally, the redwood data shows a greater performance variation among the primers, and solvent based primers SB3 and SB6 demonstrate the best stain blocking performance. It was expected that solvent based primers would have superior tannin blocking

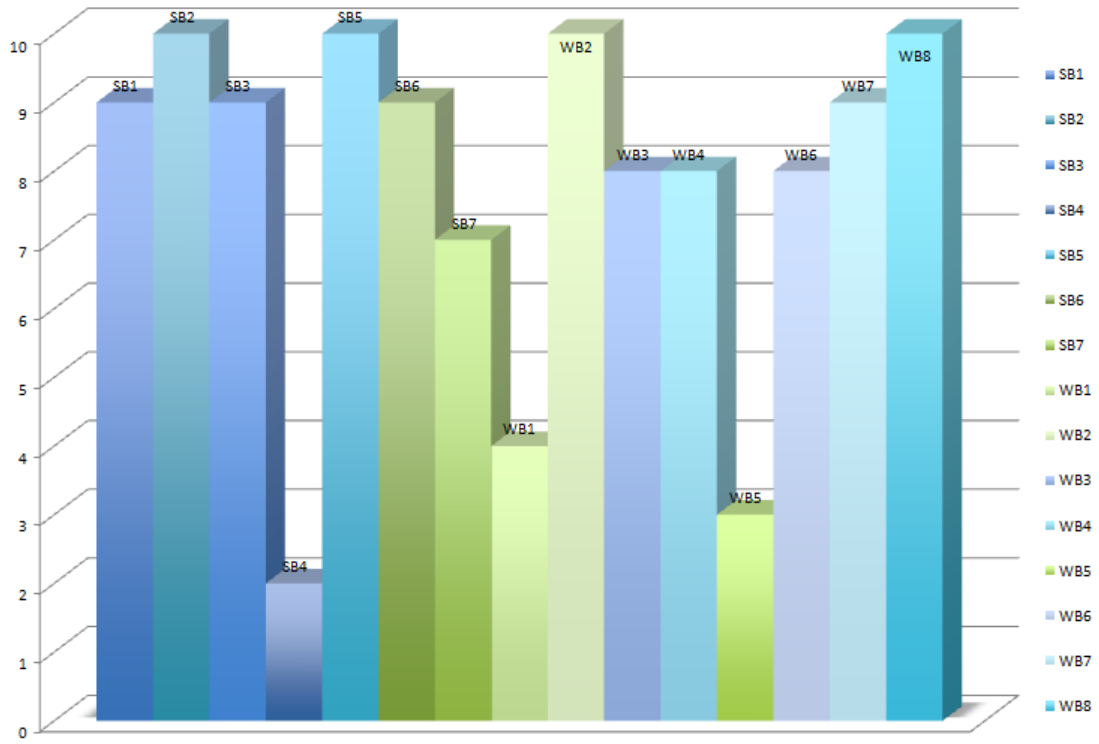


Figure 16: Tannin Blocking Test Rankings for all Primers on Cedar. (Best: 10)

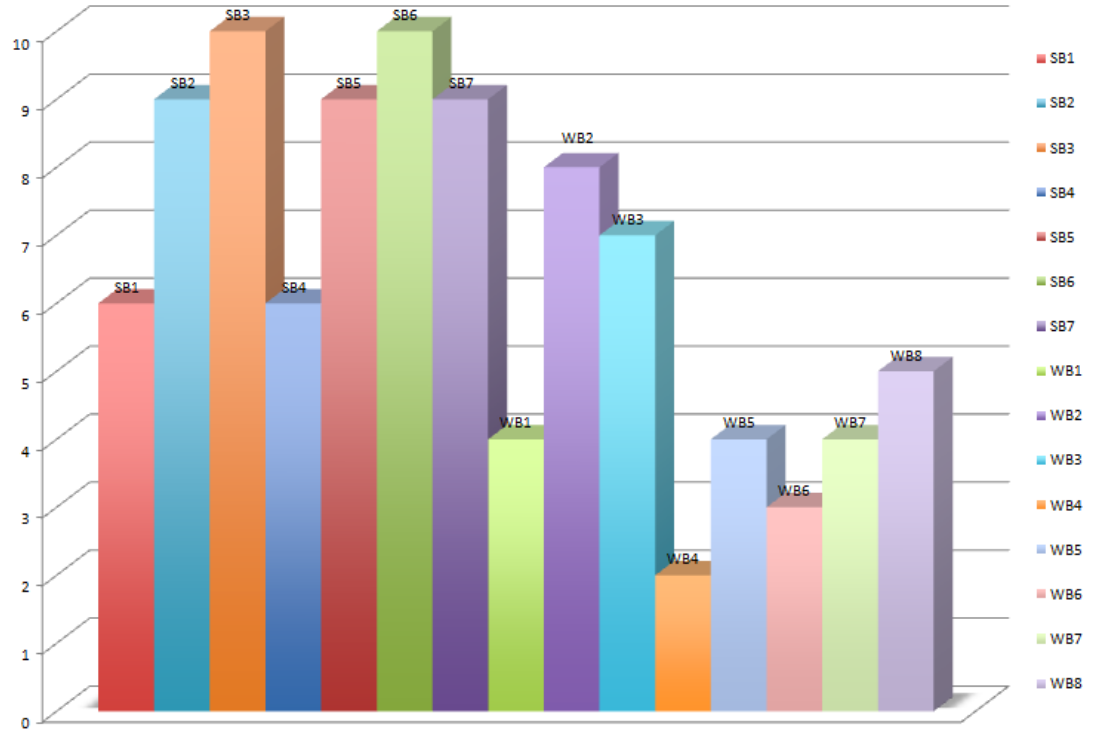


Figure 17: Tannin Blocking Test Rankings for all Primers on Redwood. (Best: 10)

Table 9: Tannin Stain Rankings for All Primers. (Best: 10)

Primers	Cedar	Redwood
SB1	9	6
SB2	10	9
SB3	9	10
SB4	2	6
SB5	10	9
SB6	9	10
SB7	7	9
WB1	4	4
WB2	10	8
WB3	8	7
WB4	8	2
WB5	3	4
WB6	8	3
WB7	9	4
WB8	10	5

capabilities. Tannins are water soluble and may migrate through a water based primer into the water based topcoat, while it is not likely for the tannins to migrate through a layer of hydrophobic solvent based primer.

Two Coat Tannin Blocking Test Results

Although water based coatings performed similarly to solvent based coatings on cedar, on redwood, performance of water based coatings was poor compared to solvent based coatings. Therefore, it was decided that the performance of two coats of water based primers should be tested on redwood. As indicated above, VOC emissions from two coats of the lower VOC category primers would be lower than emissions from one coat of the higher VOC primers. A new batch of redwood was purchased for this purpose. However, since properties of this batch of redwood were expected to be different from the batch that was used in previous tests, repeating the single coat tests was recognized as a necessity. The surface of the new batch of redwood was smoother than the surface of the redwood used in the previous test. Therefore, the new batch was used without sanding. Results of the repeated tests for both single-coat water based and solvent based primers are shown in Figure 18. The trends between these results and previous results (Figure 17) are consistent (i.e., as a class solvent based coatings perform significantly better than water based coatings). However, unlike the results from previous tests, the performance of WB3 coating is comparable to the best solvent based coating SB6. The effect of the difference between two batches of redwood is evident in the results shown in Figure 19.

A set of experiments were conducted with two coats of water based primers on the new batch of redwood. Results of the single and double coat water based primers on the new batch of redwood are compared in Figure 20. It is clear that two coats of the primers are more effective than one coat. A comparison of results for two coats of water based primers with one coat of solvent based primers is shown in Figure 21. Performance of two coats of WB2 and WB3 is similar to the performance of best solvent based coating, SB6. Also, the performance of two coats of WB6 is similar to the performance of single coats of SB1, SB5, and SB7.

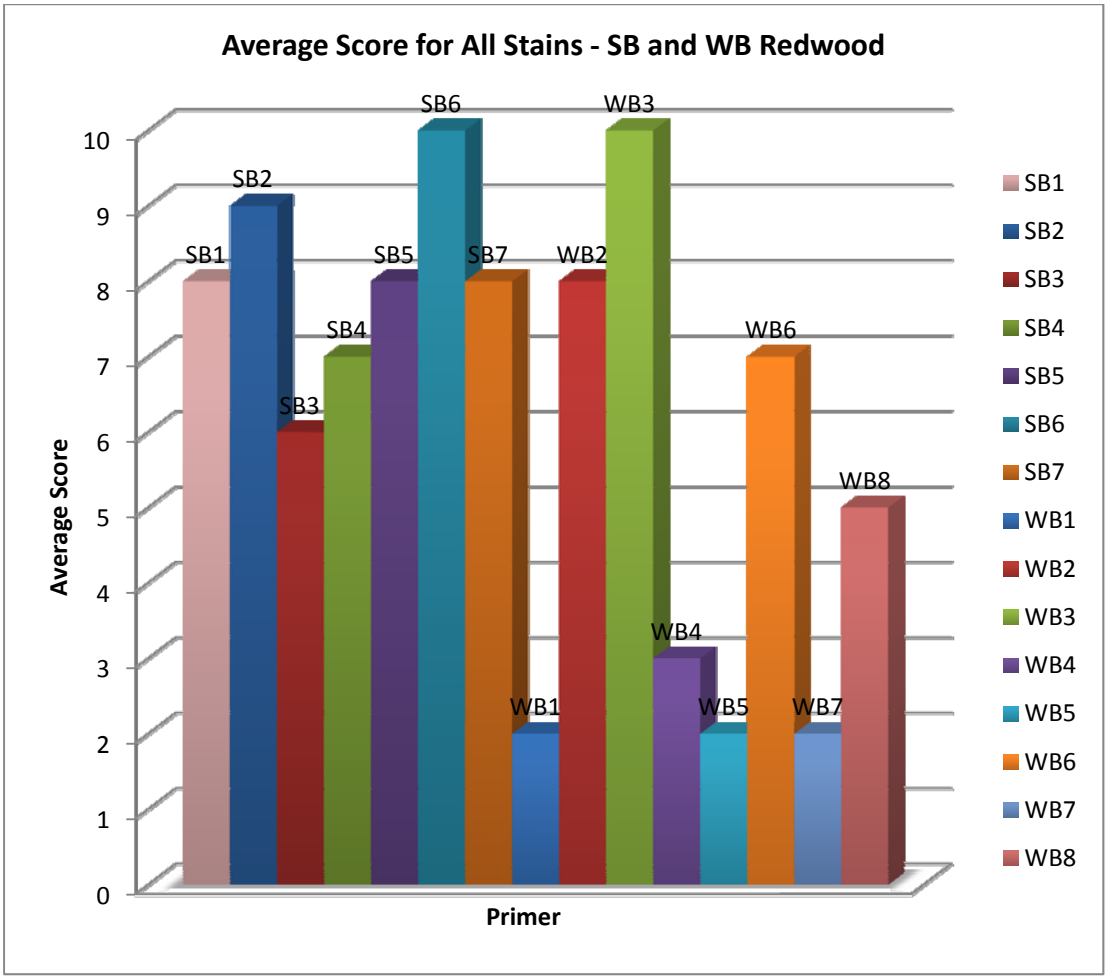
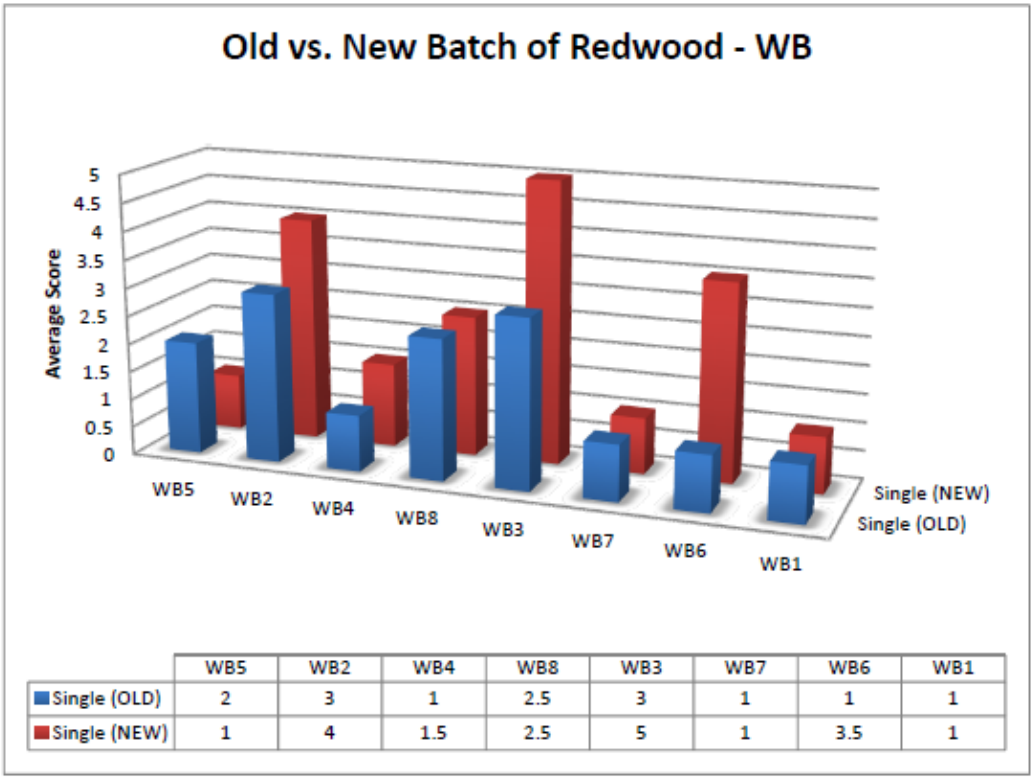
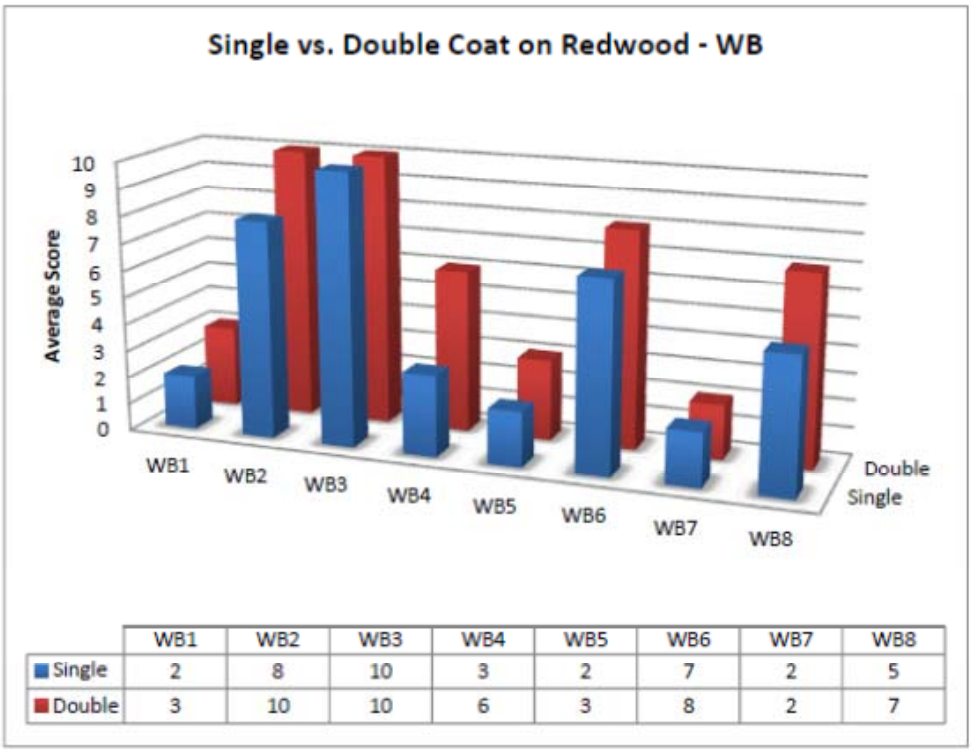


Figure 18. Tannin Blocking Test Rankings for all Primers on Redwood. (Best: 10)



	WB5	WB2	WB4	WB8	WB3	WB7	WB6	WB1
Single (OLD)	2	3	1	2.5	3	1	1	1
Single (NEW)	1	4	1.5	2.5	5	1	3.5	1

Figure 19. Tannin Blocking Test Ranking Comparison between Old and New Batches of Redwood



	WB1	WB2	WB3	WB4	WB5	WB6	WB7	WB8
Single	2	8	10	3	2	7	2	5
Double	3	10	10	6	3	8	2	7

Figure 20. Tannin Blocking Test Ranking Comparison between Single and Double Coats of Water Based Primers on New Batch of Redwood

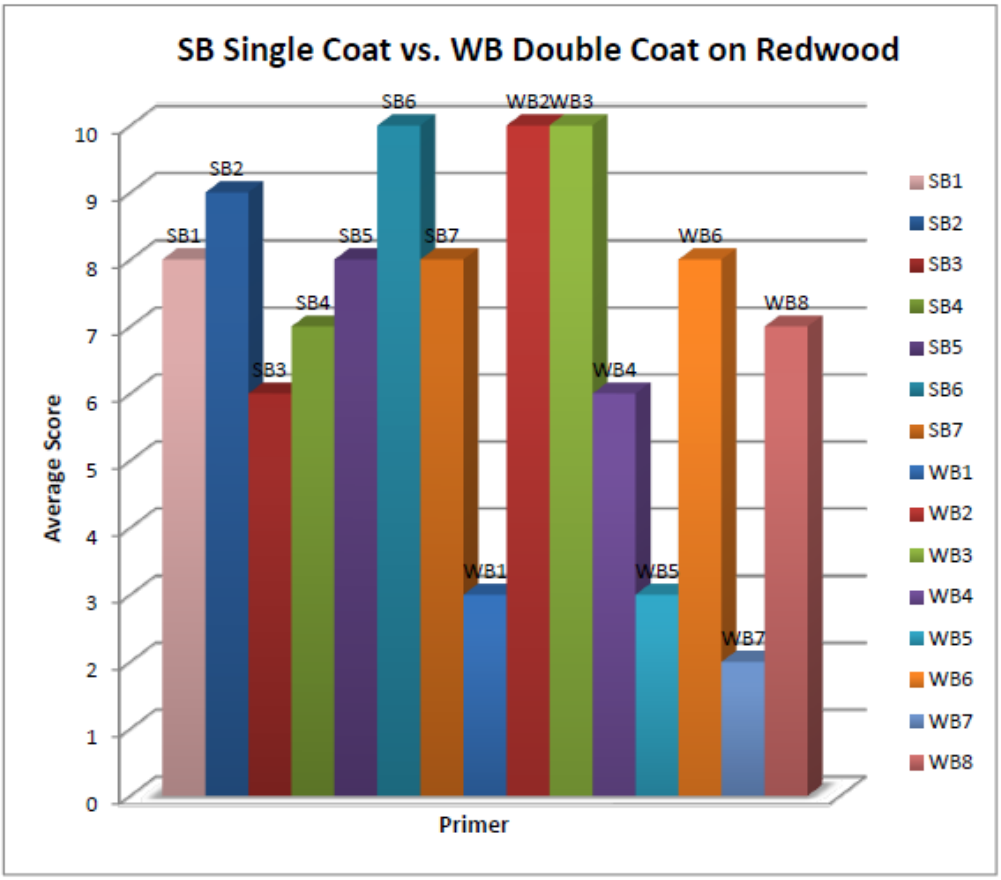


Figure 21. Tannin Blocking Test Ranking Comparison between Single Coats of Solvent Based and Double Coats of Water Based Primers on New Batch of Redwood

Laboratory Burned Redwood and Douglas Fir Test Results

Stain blocking rankings of all fifteen primers on redwood and Douglas fir that were burned under controlled laboratory conditions are shown in Table 10 and Figures 22 & 23. The rankings represent the averages of three data points per primer applied on three positions on each panel as described in the Materials and Methods Section of this report. The two classes of primers, solvent based and water based, show similar performance with at least one primer from each category exhibiting excellent performance. Results for water based primers were quite different when they were tested on unburned redwood. In those tests, single coats of the water based primers performed worse than the solvent based category. Results for Douglas fir indicate that solvent based primers perform better on Douglas fir than on redwood. As a class, water based coatings perform similarly on both types of wood. Water based primers WB2 and WB4 show excellent performance.

Table 10. Stain blocking rankings of primers applied on redwood and Doulas fir panels Burned under laboratory conditions

Primer Identification	Ranking on Redwood	Ranking on Douglas Fir
SB1	7.3	9.7
SB2	8.3	9.7
SB3	9.7	9.3
SB4	6.3	8.7
SB5	8.3	9.7
SB6	5.7	8.7
SB7	9.0	9.3
WB1	6.0	8.0
WB2	10.0	10.0
WB3	7.3	7.3
WB4	8.7	10.0
WB5	4.0	4.3
WB6	8.7	9.3
WB7	8.7	8.3
WB8	6.3	7.7

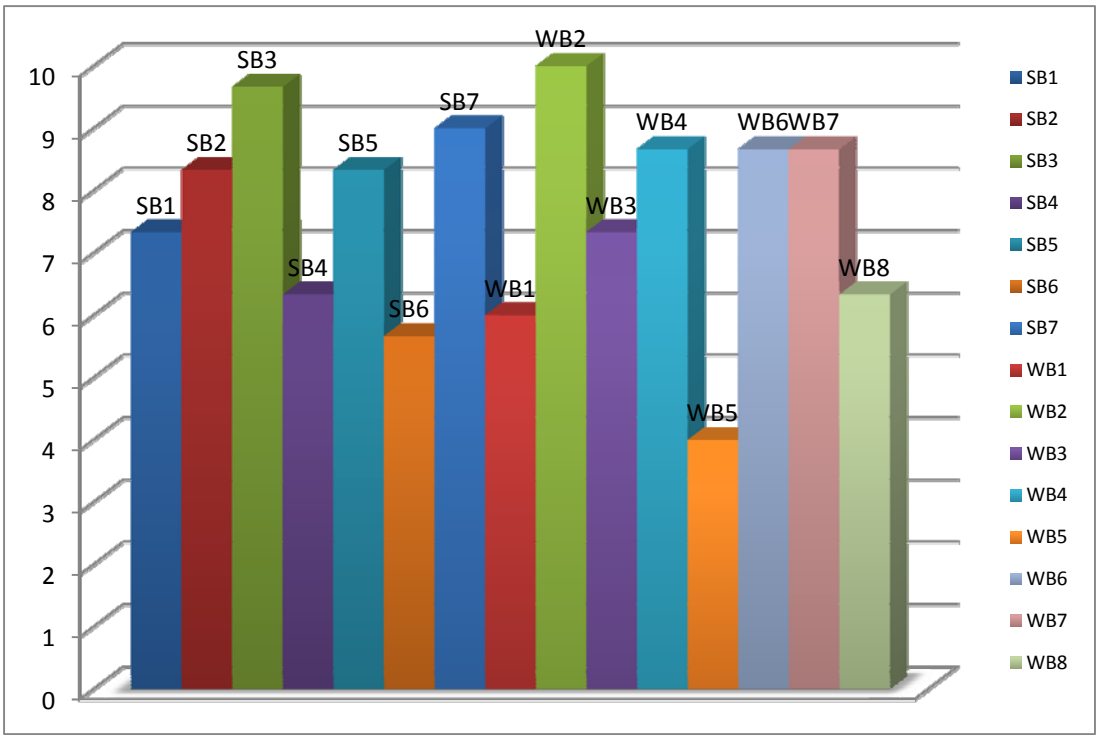


Figure 22. Stain blocking rankings of primers applied on redwood burned under laboratory conditions.

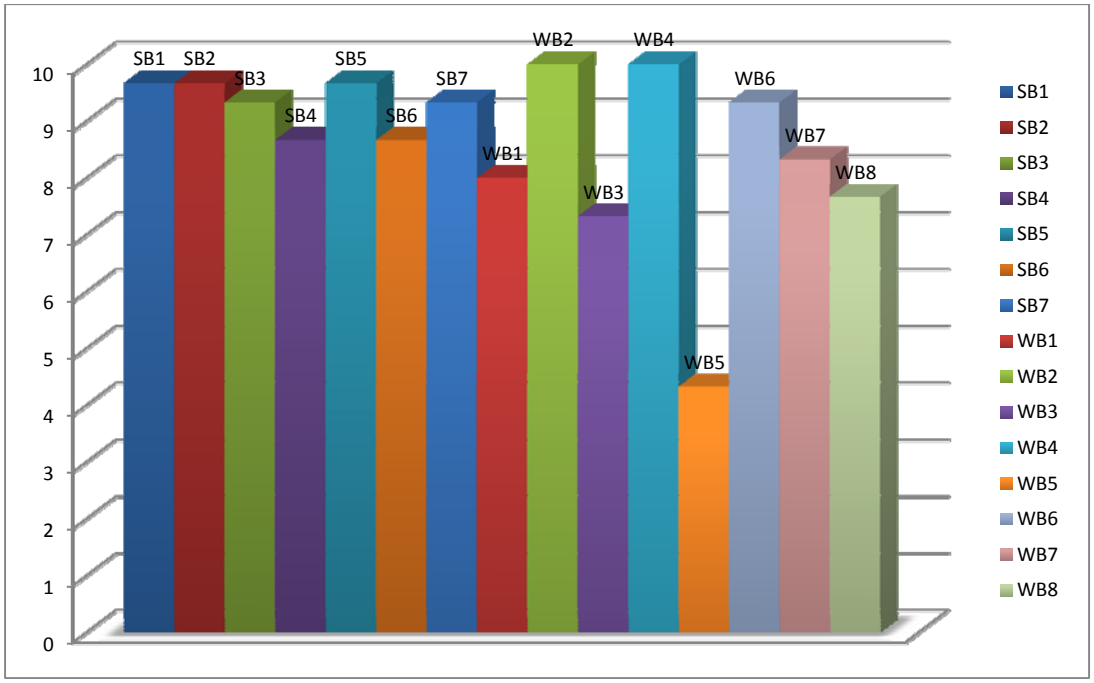


Figure 23. Stain blocking rankings of primers on Douglas fir burned under laboratory conditions.

Stain Blocking Results for Real Fire and Water Damaged Samples

Stain blocking rankings for the fifteen primers on the wood samples that were recovered from real fire and water-damage are shown in Table 11 and Figures 24 & 25. These rankings are not averages of three data points as in Table 10 and Figures 22 & 23 as there wasn't enough area on the panels to coat each primer more than once. They represent a single data point per each primer. Results on the fire damaged wood panel indicate similar performance by both solvent based and water based categories of primers. On the water damaged sample, solvent based primers outperform the water based primers; however, WB3 and WB6 primers' performance is similar to many solvent based primers, and WB8 matches the performance of the best solvent based primer.

Table 11. Stain blocking rankings on wood panels recovered from real fire and water damage sites

Primer Identification	Ranking on Fire Damaged Panel	Ranking on Water Damaged Panel
SB1	8	9
SB2	10	10
SB3	9	10
SB4	10	9
SB5	10	9
SB6	9	10
SB7	9	9
WB1	8	7
WB2	8	7
WB3	10	9
WB4	9	7
WB5	8	6
WB6	9	9
WB7	8	6
WB8	9	10

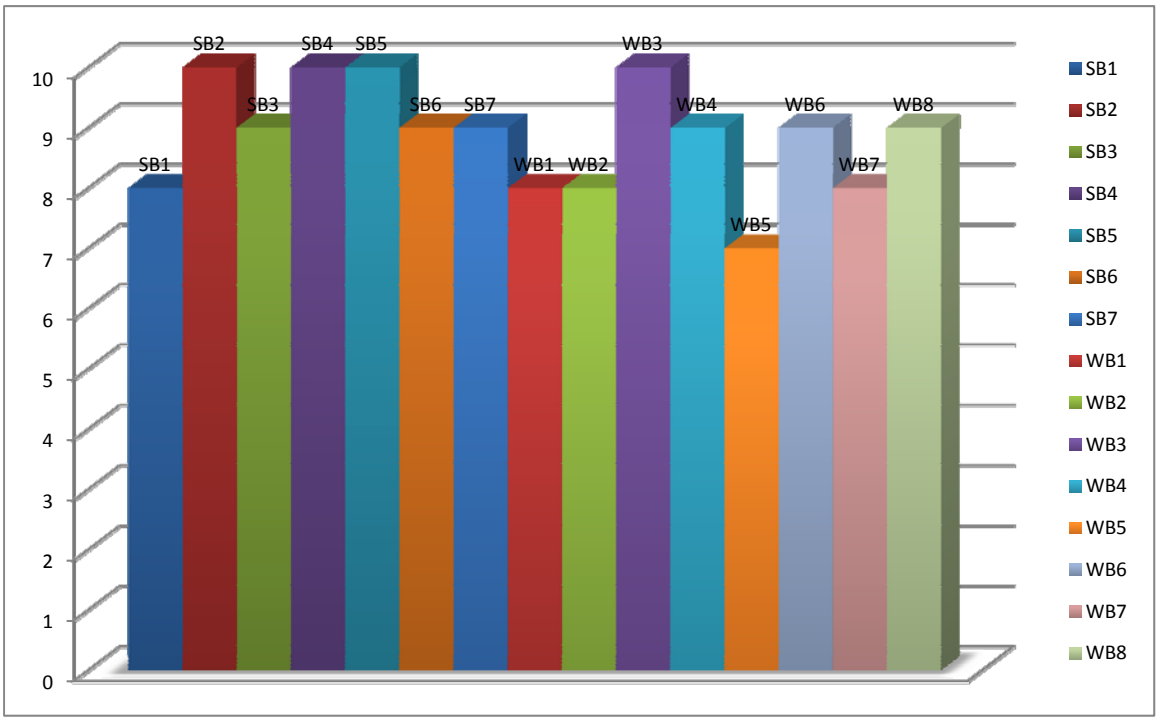


Figure 24. Stain blocking rankings of primers on real fire-damaged wood panel

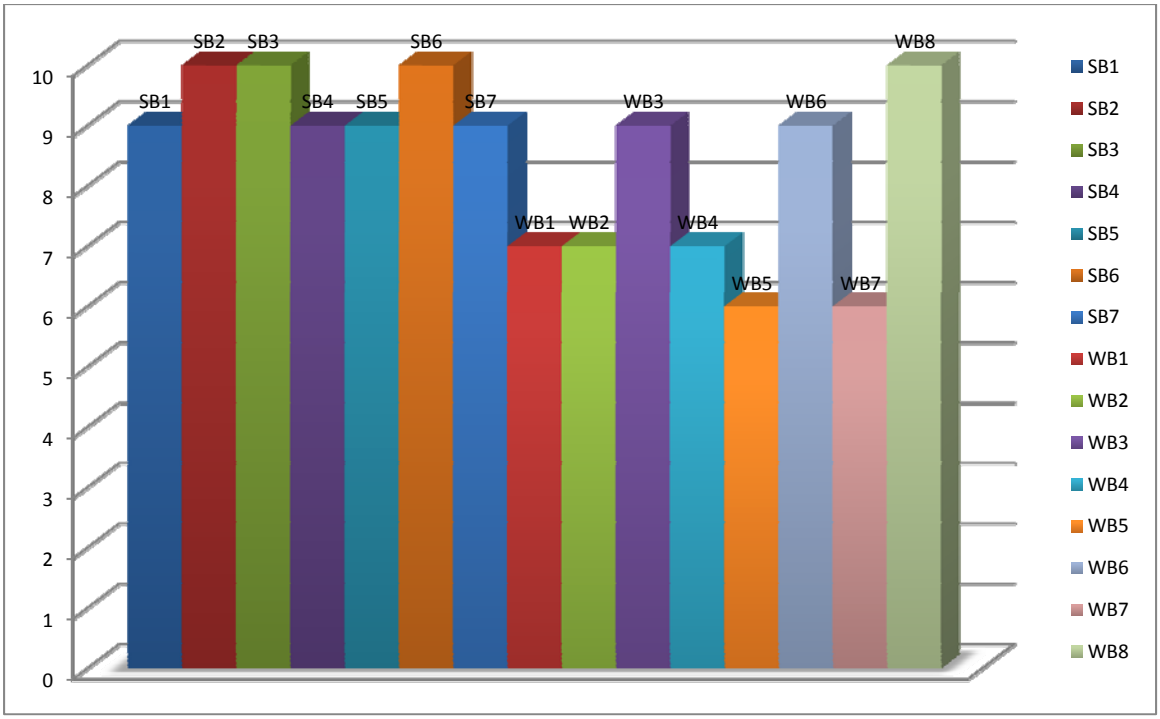


Figure 25. Stain blocking rankings of primers on real water-damaged wood panel

E. Conclusion

The ability of all fifteen primers in blocking household marker stains on draw-down charts and drywall was tested according to ASTM D7514-09. Results indicate that, when compared as a class, performance of water based primers (i.e., coatings containing less than 100 g/L VOC) is comparable to the performance of solvent based primers (i.e., coatings containing less than 350 g/L VOC) on both substrates. Solvent based primers clearly outperformed water based coatings in blocking green highlighter stains. However, water based primers outperformed solvent based category in blocking red Sharpie stains. Performance of two layers of water based primers was similar to the performance of a single layer of solvent based primers. Tannin blocking tests on cedar boards indicate there are water based coatings in the market that can match the performance of best solvent based coatings. However, solvent based coatings outperform water based coatings in blocking redwood stains. Several water-based primers, when applied as two coats on redwood, can match the best performing solvent based primers. The ability of the fifteen primers in blocking stains caused by fire and water damage on wood panels was also studied. Results indicate there are water based primers containing less than 100 g/L VOC that can match the best solvent based primers containing less than 350 g/L VOC on these substrates. Based on this work, ARB recommended to the local California air districts to keep their January 1, 2012, SPSU VOC limits of 100 g/L in place.

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