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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. These coatings are primarily used as stain-blocking primers over a variety of substrates. 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. This report describes the preliminary work performed in preparation of a more systematic and comprehensive study to evaluate the performance of paints sold for the SPSU market. Six primers, both water based and solvent based, were selected for testing and comparison. Basic primer characterization was completed, including sag, leveling, contrast ratio, and density, as was preliminary stain blocking testing, including stains by various markers and tannin.

B. Introduction

Currently the regulations in California allow SPSU paints to have a VOC content of up to 350 g/L. By January 2012, several air districts' rules will drop the allowed VOC limit to 100 g/L. The specialty primers under scrutiny in the tests presented in this report are stain blocking primers. There is currently no industry standard for what classifies a stain blocking primer as being of "acceptable" performance. For this project, it is necessary to create a set of guidelines to determine if a stain blocking primer shows "acceptable" performance. The best performing stain blocking primers currently on the market, as determined by industry recommendation, are shellac-based primers with a VOC limit of 550 g/L, and several oil based primers currently in the SPSU category with a VOC limit of 350 g/L. A number of water based products that are claimed to meet the 100 g/L VOC limit are also available in the market. A literature survey did not uncover any studies on whether any of the water based coatings perform at an "acceptable" level.

To begin the initial testing, several primers listed in the Materials and Methods section below were chosen, based on industry recommendations. A series of standard testing procedures such as sag, leveling, and density determination were performed on all paints selected. Common household marker stains described in the Materials and Methods section were used in preliminary testing, and the results are presented in later sections of this report.

Tannins were researched extensively, due to the persistent problem that they present when painting certain woods, such as redwood or cedar. Tannins are naturally occurring, plant-based polyphenolic compounds that are found in all wood species. They provide durability, stability, and aesthetic appeal to the wood. Knots in the wood usually contain a higher concentration of tannins.

Over time it is possible for tannins to leach out of the wood and into the coating, causing significant discoloration in the case of woods like redwood and cedar. Tannins form a water-soluble compound when exposed to the basic conditions typically associated with paints. Using 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 will not migrate. The conventional approach to this method is to use an anionic polymer dispersion with a reactive pigment, such as zinc oxide. Another approach to preventing tannin migration is the use of a chemical or actinic pre-treatment. 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.

Additional factors regarding tannins should be considered. For example, water based primers will most likely be more effective at preventing tannin bleed if they are formulated for fast drying, with a maximum amount of solids and a minimum amount of co-solvents. Primers that have a pH near neutral will also have a better chance of preventing tannin bleed, due to the need for a basic environment for the tannins to form water soluble compounds. The migration of water through the wood and coating should also be considered. A staining problem develops during the drying and film formation stage when tannins migrate outward, due to the water present in the painted wood. The driving force for this is the interfacial humidity exchange, where water acts in the way of an eluent, in a similar manner to the mechanism involved in thin layer chromatography. It is still not known for sure if the migration of tannins stops when hydric equilibrium is reached.

C. Materials and Methods

Substrate, Primer, and Topcoat Selection

Substrates were selected based on industry recommendations. Currently the substrates used in testing are cedar boards, redwood boards, and black and white BYK Byko-Charts. Future testing may include, but is not limited to, stained drywall and/or ceiling tiles.

Stain blocking primers were chosen based on industry 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 water based latex primers.

Six primers were chosen for initial testing: Zinsser Shellac-Based B-I-N, Zinsser High-Hide Cover Stain (oil based), KILZ Original Primer (oil based), Zinsser Waterborne Cover Stain, KILZ 2 Latex, and Behr Premium Plus Waterborne Primer and Sealer. From this list it can be seen that one primer was chosen in the shellac category (VOC content of 550 g/L or less), two oil based primers were chosen (VOC content of 350 g/L or less), and three water based primers (VOC content of 100 g/L or less) were chosen for testing.

The topcoat chosen for testing is a common interior latex paint: Behr Premium Plus Interior Latex Flat Paint.

Primer Characterization

Several basic tests were completed to characterize the six previously mentioned primers. The sections below give the specifics for each test as it was completed as well as the ASTM method.

Sag and Leveling. Three sag and leveling draw downs were made for each primer. Sag draw downs were done using the Leneta Anti-Sag Meter ASM-1 Standard Range. The sag draw downs were allowed to dry vertically, hanging from the left edge of the paper at room temperature. The values for sag were recorded from 0 – 10, with 10 being the best sag value, where none of the lines ran together. ASTM D4400-99 was followed for sag measurements.

Leveling draw downs were done 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 leveling value, where all leveling lines ran together. ASTM D4062-99 was followed for leveling measurements.

Contrast Ratio and Gloss. Three draw downs with a wet film thickness of 3 mil 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 value for the white portion of the chart. 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 taken with a Texas Instruments AR 2000 Rheometer using a cone-and-plate geometry. Each primer was run at least twice to obtain consistent results. Select primers were further tested using parallel plate geometry (40 mm diameter and 500 micron gap) with the Texas Instruments AR 2000 Rheometer. The Brookfield Model DV-II+ Viscometer with an LV3 spindle was also used with for testing on select primers.

VOC Determination. The volatile organic compound (VOC) levels in each paint were determined according to ASTM D6886-03. HPLC grade methanol was used as the solvent for sample preparation for water based 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. Karl Fischer titrations were used to determine the percent water in select samples.

Stain Blocking Testing

Common stains are important to include in testing to assess the blocking capabilities of each primer. The stains that have been tested so far are discussed below and include several types of marker stains and wood tannin stains.

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

Another test method was conducted using select staining agents from the previous test. Squares with side lengths of 4 cm were drawn and filled in on BYK Byko-Charts using the staining agents that proved difficult to block. The staining agents that were selected were red and black permanent marker, yellow highlighter, and blue pen. These staining agents were applied to the white portion of the charts, allowed to dry for 24 hours, and the color data was collected as an average of three readings using a DataColor Mercury spectrophotometer. Primer was applied with a 3 mil wet film thickness, allowed to dry for 24 hours, and color data was collected as an average of three readings. The topcoat was then applied, allowed to dry for 24 hours, and color data was collected as an average of three readings. For each primer, three charts were made.

Tannin Stains. Cedar and redwood boards were purchased and cut into boards approximately 1 foot by 7 inches. A section of the board was measured for accurate area measurements and painted. The board was weighed before and after painting and film thickness was determined. The primer was allowed to dry for at least 24 hours and the topcoat was 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 **Table 1**. From this table it can be seen that the sag and leveling values are in close agreement, meaning that generally the paints with the best sag resistance have poor leveling capabilities. Contrast ratio and gloss values at 60º were included in this study as another method of comparing the primers. Higher contrast ratios do not always lead to a higher stain blocking capacity. Several stain blocking primers block stains by preventing the staining agent from migrating into the topcoat applied on top of the primer. The solid weight fraction was determined for all paints, to be used in VOC calculation. The numbers presented are an average of two or more trials.

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

Primer Coating*	Sag	Leveling	Contrast Ratio	Gloss (60º)	Solids (wt. fraction)	Density (lbs/gal)
SB-A	10.0	0.0	0.89	2.5	0.780	12.4
SB-B	5.3	3.0	0.91	5.6	0.529	10.0
SB-C	10.0	0.0	0.94	2.9	0.775	12.5
WB-A	8.7	1.7	0.92	5.3	0.477	10.6
WB-B	8.7	3.0	0.94	6.9	0.548	10.6
WB-C	9.3	2.0	0.94	2.4	0.617	12.4
Flat TC	NA	NA	0.96	2.7	0.550	12.0

*SB – Solvent based; WB – Water based; Codes A, B, C are used in order to protect the identity of individual products

Density was determined and compared to the information provided on the technical data sheet (TDS) supplied by the manufacturer. All measured densities were reasonably close to the published values (where available).

Stain Blocking Testing

A method for categorizing the stain blocking abilities has not yet been agreed upon; however, the following provides some insight from basic visual observations. Marker stain testing showed that, in general, water based primers have difficulty blocking water based stains, such as highlighters, while solvent based primers have difficulty blocking solvent based stains, such as permanent marker. For each stain type, there is a noticeable difference in visibility between two colors of the same type of staining agent.

For the water based primers it was observed that WB-B did the best job of blocking the stain visibility through the topcoat, followed by WB-A and WB-C, respectively. Yellow highlighter was visible through all water based samples, although the green highlighter showed only through the WB-C samples. Bleeding, or thickening, of the stain line was seen with the yellow highlighter on these samples.

The solvent based primer testing with marker stains provided some interesting results. As previously mentioned, it was determined through industry recommendation that SB-B is seen as the most effective stain blocker available on the market. In fact, the testing that was conducted showed that SB-C was the most effective stain blocker, followed by SB-A, and finally SB-B. The permanent markers, both red and black, were visible through the topcoat of these samples.

Collecting color data from the marker stain square testing may allow for a quantitative measurement of the stain blocking ability of the primer and topcoat. The results of this test were in agreement with the marker stain line testing, as reflected in the obtained color data provided in the Appendix to this report. From the tables in the Appendix it can be seen that data from the two highlighters was only reported for latex paints. This was done because the highlighter stain was completely blocked by solvent based primers during previous testing.

Tannin bleed into the topcoat was not seen for many of the primers. Generally it was seen that the water based primers provided results that were very similar to the oil or shellac based primers. Ranking the samples is difficult due to variation between wood samples and variation in film thickness. Certain wood samples contain different amounts of tannins or knots, which contain a higher concentration and often times a different type of tannin. It may be necessary, in future testing, to base tannin blocking capabilities on a stain made from a concentrated tannin solution applied to a substrate.

For better comparison, film thickness was determined using the area of the section painted, the weight of paint applied, and the density of the paint. Wet film thickness for the painted boards can be found in **Table 2**. These values did not provide insight into the results due to the variation in wood samples and the acceptable stain blocking provided by the primers and topcoat.

Table 2. *Wet film thickness (micrometers) of primer applied.*

Primer Coating	Trial 1		Trial 2	
	Cedar	Redwood	Cedar	Redwood
SB-A	44	57	56	53
SB-B	33	62	58	47
SB-C	NA	NA	64	39
WB-A	38	30	72	44
WB-B	NA	NA	62	42
WB-C	NA	NA	51	46

Rheology

Viscosity versus shear rate was run for each primer at least two times. Representative plots for each primer are shown in Figures 1 and 2. In this plot it can be seen that there is not perfect agreement between the viscosity at a low shear rate and the values obtained for sag and leveling.

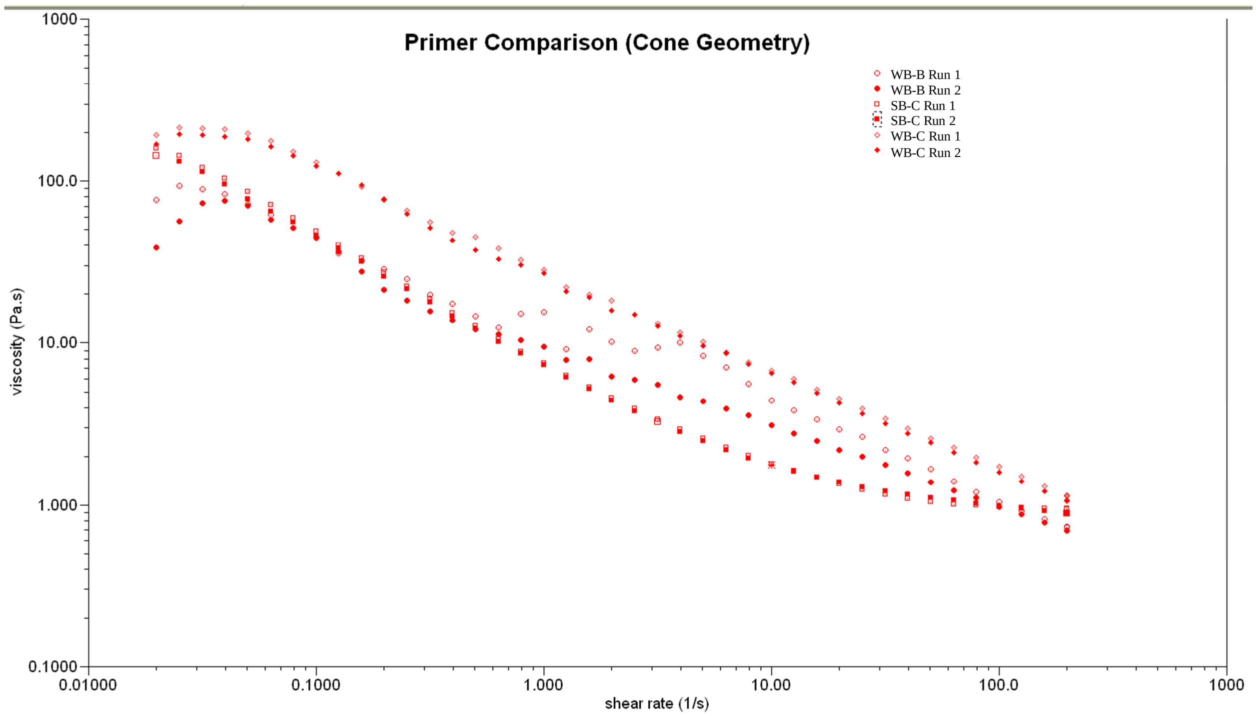

Figure 1. Viscosity dependence of shear rate for SPSU coating

SB-B gave especially surprising results. Rheology testing for this paint showed a very high viscosity at low shear rates. Low shear rate viscosity normally correlates to the sag and leveling properties of the paint. By this reasoning, SB-B should have showed a high value for sag and a low value for leveling. However, as seen in **Table 1**, the primer showed low sag and high leveling values. Visually, the paint appears as though it has a low viscosity at low shear rates, in agreement with the sag and leveling data. For this reason, further testing was done using both cone-and-plate and parallel plate geometries with the same rheometer as well as with a Brookfield Model DV-II+ Viscometer with an LV3 spindle. Further testing did not reveal an explanation for the behavior, and, as part of another study, testing may be done to determine the cause of test results showing apparently high viscosity at low shear rate for this primer.

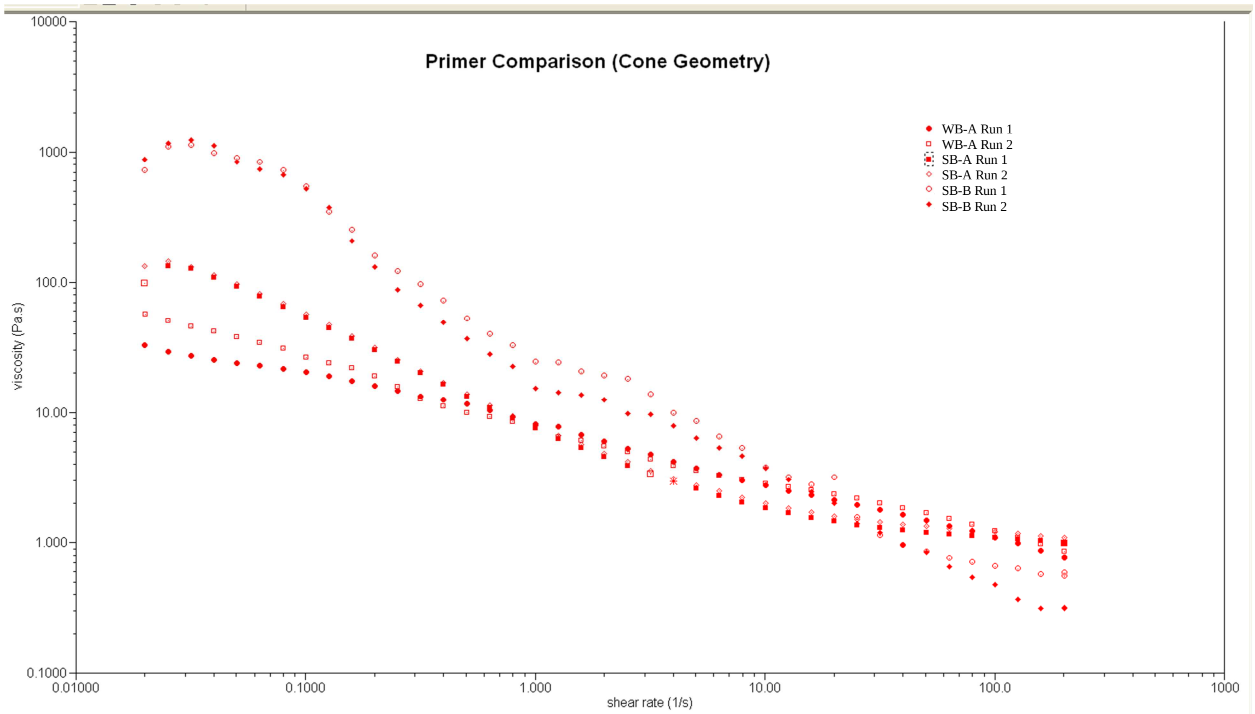

Figure 2. Viscosity dependence of shear rate for SPSU coating

<u>VOC Determination</u>

VOC determination for all primers is still in the preliminary stages. **Table 3** shows the VOC values that have been obtained for select primers as well as the expected VOC content as provided in the technical data sheet (TDS) from the manufacturer. As shown in the table, several of these values are consistent with the expected values, as provided by the TDS from the manufacturer. VOC values determined using Karl Fischer titration are not reported. There is a high potential for experimental error using this test method, due to interactions between the paint chemicals and both the water and the titrant. Therefore, all VOC tests were conducted with the GC method in accordance with ASTM D6886-03.

Table 3. *VOC content as determined experimentally and as provided by the manufacturer. Manufacturer values are coating VOC values. All values are in grams per liter.*

Primer Coating	Material VOC	Coating VOC	TDS VOC
SB-A	270	280	< 350
SB-B	370	460	< 550
SB-C	250	280	< 350
WB-A	20	57	90
WB-B	45	97	99
WB-C	32	69	< 100
Flat TC	28	74	96

E. Conclusion

The preliminary testing of the stain blocking primers selected has been very helpful in preparing for discussions with the industry panel ARB has gathered to coordinate the project. From the testing completed to date, it is clear there are many factors that come into play when categorizing the stain blocking capabilities of the primers. In order to accurately determine if stain blocking primers with a VOC content of less than 100 g/L have a performance that is “acceptable”, definite guidelines, standard procedures, and classification procedures must be developed and agreed upon. This is especially important for stain blocking test methods, which are currently based primarily on visual assessment. The next step is to consult with ARB and the industry group and determine which SPSU coatings will be included in the formal testing to insure results enabling ARB to guide the planned regulation of VOC content in this category.

F. References

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G. Appendix

Marker Stain Square Testing Results [Avg – Average; SD – Standard Deviation]

	L		a		b		E
	Avg	SD	Avg	SD	Avg	SD	
Red Permanent Marker	50.22	2.49	55.97	2.76	32.29	3.74	81.839
Primer Only							
SB-A	67.48	2.39	37.71	1.48	7.06	1.25	77.622
SB-B	68.03	0.78	42.14	0.77	0.39	0.37	80.030
SB-C	68.98	1.88	35.53	1.36	3.78	0.23	77.680
WB-A	91.21	0.26	3.86	0.41	-0.15	0.15	91.289
WB-B	62.71	53.21	7.16	0.29	-0.03	0.33	63.119
WB-C	91.95	0.22	8.78	0.24	-0.06	0.16	92.372
Primer & Topcoat							
SB-A	94.75	0.19	2.55	0.42	0.29	0.13	94.780
SB-B	93.93	0.30	10.33	1.44	-0.86	0.23	94.500
SB-C	94.66	0.35	2.02	0.18	0.38	0.08	94.682
WB-A	95.61	0.01	1.23	0.08	0.89	0.07	95.622
WB-B	96.17	0.04	1.07	0.28	1.17	0.14	96.183
WB-C	95.20	0.04	4.97	0.68	0.88	0.01	95.329

	L		a		b		E
	Avg	SD	Avg	SD	Avg	SD	
Black Permanent Marker	32.55	6.94	4.66	1.87	0.33	2.83	32.885
Primer Only							
SB-A	86.16	1.64	-0.63	0.33	1.67	0.31	86.182
SB-B	82.52	12.28	-0.83	0.29	-2.98	5.62	82.576
SB-C	82.46	1.80	0.56	0.05	1.52	0.06	82.476
WB-A	88.08	1.26	-1.05	0.12	-3.99	1.15	88.180
WB-B	92.18	1.26	-0.89	0.07	-2.02	1.38	92.206
WB-C	90.03	0.06	-1.36	0.40	-2.44	0.40	90.070
Primer & Topcoat							
SB-A	95.47	0.21	-0.85	0.01	0.67	0.01	95.476
SB-B	94.56	0.37	-1.04	0.06	-0.40	0.27	94.567
SB-C	95.18	0.07	-0.81	0.05	0.32	0.09	95.179
WB-A	95.35	0.14	-0.85	0.01	0.24	0.26	95.354
WB-B	96.17	0.36	-0.80	0.04	0.96	0.35	96.178
WB-C	95.20	0.06	-1.02	0.08	0.49	0.13	95.207

	L		a		b		E
	Avg	SD	Avg	SD	Avg	SD	
Blue Pen	51.64	3.40	2.53	1.28	-35.86	2.56	62.917
Primer Only							
SB-A	90.06	0.07	-1.82	0.03	1.37	0.22	90.085
SB-B	75.15	1.18	2.75	0.21	-18.17	1.11	77.361
SB-C	90.45	0.17	-1.58	0.04	1.60	0.25	90.475
WB-A	83.53	1.07	-9.05	0.85	-9.87	0.68	84.600
WB-B	84.94	1.64	-10.51	0.32	-10.99	1.29	86.294
WB-C	83.18	0.35	-7.95	0.11	-10.66	0.40	84.233
Primer & Topcoat							
SB-A	95.67	0.34	-0.93	0.03	0.80	0.04	95.678
SB-B	93.64	0.06	-1.57	0.16	-2.12	0.05	93.672
SB-C	95.87	0.35	-0.90	0.04	1.14	0.25	95.881
WB-A	93.16	0.49	-4.93	0.95	-2.15	0.97	93.315
WB-B	94.62	0.13	-2.82	0.18	-1.06	0.16	94.668
WB-C	86.89	0.15	-10.08	0.18	-9.33	0.45	87.963

	L		a		b		E
	Avg	SD	Avg	SD	Avg	SD	
Yellow Highlighter	87.69	1.16	-3.69	1.69	73.27	9.70	114.33
Primer Only							
WB-A	92.17	0.14	-1.78	0.13	12.62	0.97	93.05
WB-B	95.10	0.31	-1.84	0.27	14.41	2.56	96.20
WB-C	93.96	0.49	-2.19	0.22	20.54	3.77	96.21
Primer & Topcoat							
WB-A	94.76	0.42	-1.95	0.08	9.40	1.36	95.24
WB-B	96.17	0.18	-0.69	0.01	6.16	0.57	96.37
WB-C	95.17	0.06	-1.79	0.11	13.22	1.65	96.09

	L		a		b		E
	Avg	SD	Avg	SD	Avg	SD	
Green Highlighter	85.81	1.40	-43.71	3.06	76.51	2.60	123.00
Primer Only							
WB-A	90.42	0.03	-8.71	0.33	1.41	0.47	90.85
WB-B	92.92	0.31	-10.94	0.69	4.65	0.42	93.68
WB-C	90.56	0.67	-14.91	1.19	8.28	1.16	92.15
Primer & Topcoat							
WB-A	92.60	0.93	-6.25	0.74	0.36	0.04	92.81
WB-B	95.00	0.71	-4.44	1.16	1.48	0.08	95.12
WB-C	93.10	0.15	-8.92	0.11	2.24	0.07	93.55