

# Formulating to Minimize Film Defects in Solventborne 2K Polyurethane Coatings

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Coatings formulators around the globe share the challenge of creating coatings with ever-decreasing volatile organic compound (VOC) levels. In the United States and Canada, this is frequently achieved through judicious use of solvents that are exempt from VOC regulation. Specifically within California's South Coast Air Quality Management District (SCAQMD), however, formulators need to create coatings as low as 100 g/L VOC, and are limited to a very select few VOC-exempt solvents. Unfortunately, those few VOC-exempt solvents have the tendency to cause defects in coatings during the drying and curing stage, such as solvent popping and low gloss. This formulation study examines the basic components in a 100 g/L VOC solventborne two-component polyurethane coating system, including polyols and solvents, to minimize film defects.

## INTRODUCTION

While VOC limits for coatings have continued to decrease over the years, the U.S. Environmental Protection Agency (EPA) has exempted several solvents from the calculation of VOC values based on the low maximum incremental reactivity (MIR) of these solvents. Ideally, use of VOC-exempt solvents can allow formulators to continue using conventional resin binders to maintain performance of their coatings, while also minimizing environmental impact.

Within California's SCAQMD, VOC limits are lower than those at the federal level for some types of coatings. For example, the VOC limit for industrial maintenance coatings is only 100 g/L.<sup>1</sup> Further impacting this is an even shorter list of VOC-exempt solvents that can be present in coatings used in this district.<sup>2,3</sup> With respect to two-component (2K) polyurethane coatings, the only practical VOC-exempt solvents for use within SCAQMD as of this writing are acetone, methyl acetate, and parachlorobenzotrifluoride (PCBTF).

One of the issues that is faced when formulating low-VOC coatings is the presence of inherent trade-offs that are exhibited by the aforementioned VOC-exempt solvents. Acetone<sup>4</sup> is exemplary at reducing the viscosity of most coatings resins, such as acrylic polyols. However, acetone also exhibits several traits that many would consider to be problematic: rapid evaporation rate, low flash

point, and hygroscopicity. In some situations, extensive use of acetone can also cause solvent popping in coatings. Methyl acetate has an evaporation rate similar to that of acetone and a slightly higher flash point, but it is generally more expensive.<sup>4</sup> Parachlorobenzotrifluoride (PCBTF) has a moderate evaporation rate and high flash point, but unfortunately offers poor solvency for most resin binders. This article focuses on the use of acetone/PCBTF blends as VOC-exempt solvents, in combination with various non-exempt tail solvents to formulate 2K polyurethane coatings at 100 g/L VOC.

Although the industrial maintenance coatings to which the SCAQMD's 100 g/L VOC limit applies are typically pigmented, it can be important for a formulator to first begin work with clear coatings to ensure the right combination of resins, solvents, and additives are being employed. This allows for easier visual inspection of coatings, and helps to ensure any issues such as compatibility, flow behavior, etc., are sorted out before adding pigmentation. Therefore, the work outlined in this article was performed with clear coatings.

## EXPERIMENTAL

Since a 100 g/L VOC limit does not allow for use of very much non-exempt solvent in a 2K polyurethane formula, it is important to utilize resin materials that are supplied at near 100% solids, or dissolved in VOC-exempt solvents or solvent blends. The primary polyol utilized in this study is a high solids acrylic polyol with low  $T_g$  and low molecular weight that is supplied in both n-butyl acetate (n-BA) at 80% solids and in PCBTF at 70% solids. For the work performed here, the n-BA version is used as a control, while the PCBTF version is used as the basis for the near-zero and 100 g/L VOC formulations.

When applying coatings that contain high amounts of PCBTF—with or without non-exempt tail solvents—it is not uncommon to observe low gloss and/or microfoam present within the coating film, such as that shown in *Figure 1*. Because it exhibits lower viscosity and better flow than many acrylic polyols, the high solids acrylic polyol used here did not exhibit as severe behavior as that shown in *Figure 1*. However, low gloss and microfoam were still present to some extent and became worse with increasing film builds.

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One strategy for improving this issue is to use low-viscosity resins or diluents that will remain fluid after application for a long enough period to allow the acetone, PCBTF, and any air that is entrained within the film to escape, and allow for adequate flow and leveling before significant crosslinking occurs. Such low-viscosity resins could be polyether, polyester, or natural oil-based polyols. An aliphatic polyester diol supplied at ~100% solids was used here for this purpose. The high solids acrylic polyol and the polyester diol were blended at a ratio of 80:20 for one set of formulas in this work.

When using a high solids acrylic polyol in combination with a low-viscosity polyester diol, the resulting coating does not exhibit any physical drying upon solvent loss, and may result in slower dry times than is desired by the end user. For this reason, it could be necessary to add some amount of a polyol of higher  $T_g$  and/or higher

**FIGURE 1—Low-VOC 2K polyurethane clearcoat over cold rolled steel substrate, exhibiting low gloss and microfoam.**



molecular weight that enables some physical drying behavior and faster molecular weight build upon crosslinking. A medium solids acrylic polyol, supplied at 65% solids in a blend of acetone/PCBTF, was employed for this purpose. It was found that only a small amount of this medium solids acrylic polyol could be utilized while maintaining an equal formulated viscosity to the other coatings. In these coatings, the ratio of high solids acrylic to polyester to medium solids acrylic is 65:25:10. *Table 1*

provides a comparison of properties of the polyols used in this article.

A simple control formula based on the HS acrylic was created, as shown in *Table 2*.

Based on the attributes of the control formula in *Table 2*, the following attributes were held as experimental constants for this study:

- *Total formula solids: 60% by weight*

- *Formulated polyol-component (Part A) viscosity: 22–24 cP (Brookfield viscosity, #21 spindle, small sample adapter, 100 RPM, 23°C)*
- *Formulated coating (Part A + Part B) viscosity: 48–52 cP (same conditions as above)*
- *Isocyanate type: standard grade hexamethylene diisocyanate (HDI) isocyanurate (~22% NCO, 191 g/eq NCO equivalent weight)*

**TABLE 1—Properties of Polyols**

	HIGH SOLIDS ACRYLIC POLYOL (HS ACRYLIC)		ALIPHATIC POLYESTER DIOL (POLYESTER)	MEDIUM SOLIDS ACRYLIC POLYOL (MS ACRYLIC)
HYDROXYL NUMBER OF SOLIDS (mg KOH/g)	140		230	110
HYDROXYL EQUIVALENT WEIGHT OF SOLIDS (g/eq)	400		244	510
NUMBER-AVERAGE MOLECULAR WEIGHT, MN (DALTONS)	< 1500			> 3500
WEIGHT AVERAGE MOLECULAR WEIGHT, MW (DALTONS)	< 2800			> 12000
GLASS TRANSITION TEMPERATURE (°C)	-7			27
NON-VOLATILE CONTENT (% BY WEIGHT)	80	70	100	65
SOLVENT	N-BUTYL ACETATE	PCBTF	NONE	ACETONE : PCBTF (3 : 1)
VISCOSITY AS SUPPLIED (cP)	5800	5500	9800	4500

**TABLE 2—Control Formula**

					FORMULA 1 (CONTROL)		
	MATERIAL	%NV	DENSITY (g/mL)	EQ. WT. AS SUPPLIED (g/eq)	MASS (g)	VOLUME (mL)	SOLIDS (g)
	HS ACRYLIC IN n-BA	80%	1.05	500	49.95	47.57	39.96
PART A	DBTDL (1% IN n-BA)	1%	0.883		0.30	0.34	0.00
	n-BA	0%	0.883		29.72	33.65	0.00
PART B	HDI ISOCYANURATE	100%	1.17	191	20.03	17.12	20.03
TOTAL MASS (g)					100.00		
TOTAL VOLUME (mL)					98.69		
DENSITY (g/mL)					1.013		
SOLIDS (%)					60.00		
VOC (g/L)					405.2		
DBTDL (% ON SOLIDS)					0.0050		
PART A VISCOSITY (cP)					22.5		
PART A + PART B VISCOSITY (cP)					48.5		

- *Isocyanate index*: 1.05:1 NCO:OH
- *Catalyst type*: dibutyltin dilaurate (DBTDL)
- *Catalyst level*: 0.005% on total formula solids

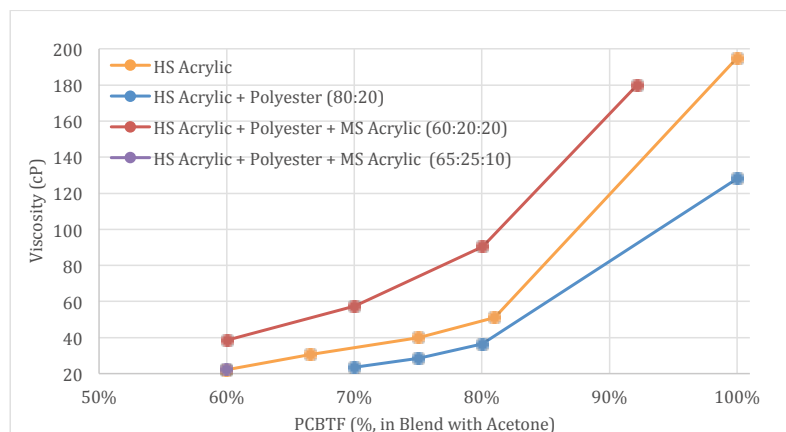
It is acknowledged that some of these constants, if varied, would also have an impact on the appearance of these coatings. They should be at least considered for investigation by a coatings formulator, and may be investigated further by the authors in future work.

Designing experimental formulas for this article first involved substituting the HS acrylic supplied in n-BA for the same polyol supplied in PCBTF. Creating a formula directly analogous to the control formula using PCBTF as the only solvent resulted in a Part A viscosity of 195 cP. Since the goal was to maintain an equivalent viscosity to that of the control formula while also maintaining the solids level for Part A at 49.96% to result in a total combined (Part A + Part B) viscosity of 60.0%, it was necessary to substitute some portion of the PCBTF with acetone to reduce the viscosity further. Several solutions of the HS acrylic at 49.96% solids in various acetone/PCBTF blend ratios were prepared, and their viscosities were measured (*Figure 2*, orange line). This same exercise was also performed for an 80:20 blend of the HS acrylic and the polyester (*Figure 2*, blue line), as well as for a 60:20:20 blend of the HS acrylic, the polyester, and the MS acrylic (*Figure 2*, red line). This three-way blend was found to be too viscous at a PCBTF:acetone blend ratio of 60:40, and it is generally preferred to use as little acetone as possible in these types of coatings. It was found, however, that a 65:25:10 ratio of this three-way blend of polyols at 60:40 PCBTF:acetone resulted in the proper viscosity of 22.5 cP.

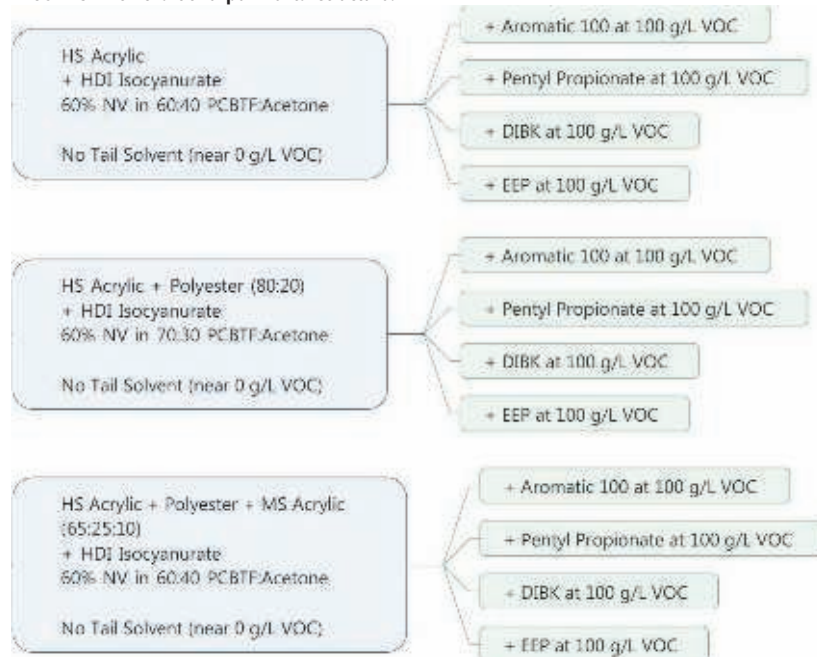
Once the proper PCBTF:acetone ratio was determined for each polyol combination to achieve the correct viscosity at 60% solids, the remaining experimental structure in this paper proceeded as follows:

- Prepare formulas with polyols in combination with HDI isocyanurate at “near zero” VOC with appropriate PCBTF/acetone blends as found above in *Figure 2*.

**FIGURE 2—Viscosity profiles of polyols in PCBTF/acetone blends at ~50% solids.**



**FIGURE 3—Flowchart of experimental structure.**



- Prepare 100 g/L VOC formulas using same polyols and HDI isocyanurate by replacing appropriate amount of PCBTF/acetone blend with various non-exempt tail solvents.
- Spray apply all coatings in a “wedge” from 1.5–4.5 mils dry film thickness (DFT) over panels that are pre-coated with a commercial black basecoat at 0.8–1.2 mils DFT.

- Evaluate 20° gloss at varying DFT, and distinctness of image (DOI) at 4.5 mils DFT.

An outline for these experiments is shown graphically in *Figure 3*.

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## RESULTS AND DISCUSSION

Visual inspection of the panels prepared as described in *Figure 3* showed that the control formula exhibits excellent appearance at DFT  $\geq 2$  mils, while the experimental formulas exhibit a reduction in appearance quality of varying extent. At 1.5 mils DFT and below, it is apparent that none of the coatings are able to flow properly due to the lack of flow and leveling additives. This may be acceptable for industrial maintenance coatings that are applied in thick films, but the use of flow and leveling additives

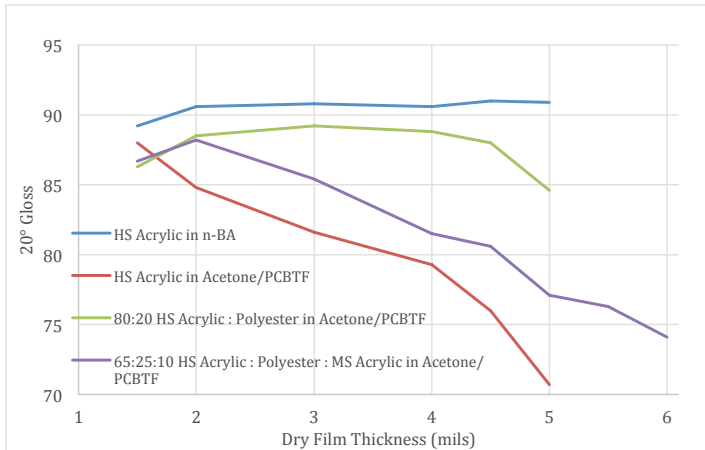
should be investigated to widen the application window for such a coating.

One of the metrics that was used for measurement of appearance was 20° gloss, and the control formula containing the HS acrylic was measured to be >90 gloss units across the range of film thicknesses at 2 mils DFT and above (*Figure 4*, blue line). The near-zero VOC formula containing the same HS acrylic exhibited acceptable gloss at 1.5 mils DFT, but the gloss drops steadily with increasing film thickness to only 70.7 gloss units at 5 mils DFT. Addition of the polyester polyol provided significant

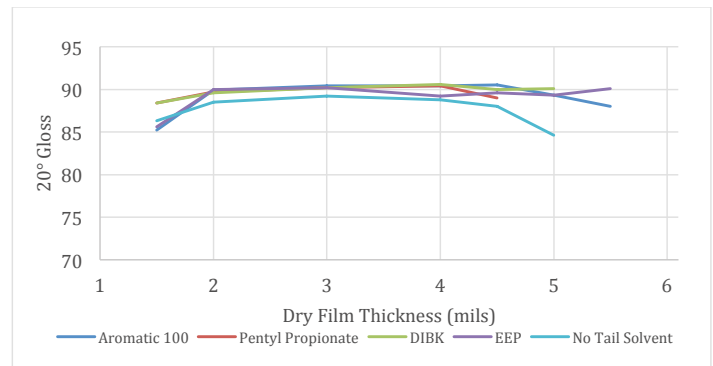
improvement in gloss (*Figure 4*, green line) but the gloss did not match that of the control formula, and dropped off at higher film builds as well. The gloss of the three-way blend of polyols (*Figure 4*, purple line) was found to be higher than that of the HS acrylic alone at 2 mils DFT and above, but shares the same inverse relationship with film thickness.

*Figures 5–7* demonstrate the improvement in gloss that is offered by the use of the various tail solvents at 100 g/L in each experimental formula. *Figure 5* displays the gloss of the coatings containing the HS acrylic in combination

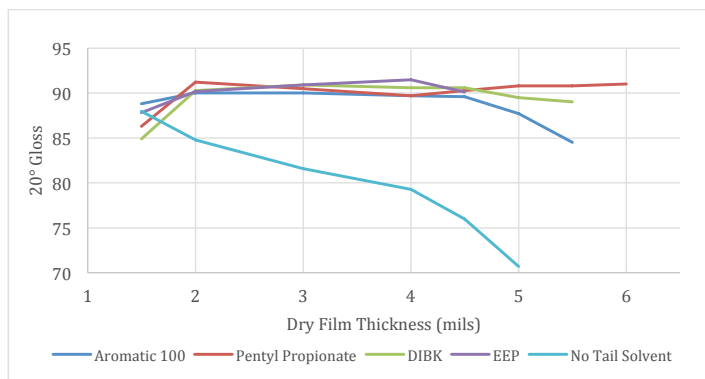
**FIGURE 4—20° Gloss of near-zero VOC 2K polyurethane clearcoats and control formula.**



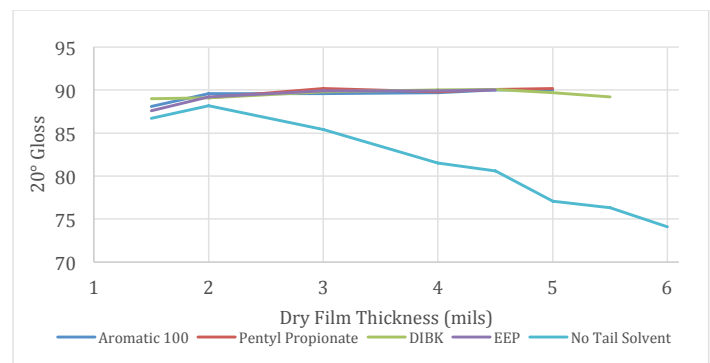
**FIGURE 6—20° Gloss of 100 g/L VOC 2K polyurethane clearcoats based on 80:20 HS acrylic : polyester blend (using various tail solvents) vs dry film thickness.**



**FIGURE 5—20° Gloss of 100 g/L VOC 2K polyurethane clearcoats based on HS acrylic (using various tail solvents) vs dry film thickness.**



**FIGURE 7—20° Gloss of 100 g/L VOC 2K polyurethane clearcoats based on 65:25:10 HS acrylic : polyester : MS acrylic blend (using various tail solvents) vs dry film thickness.**



with each tail solvent at 100 g/L VOC, and also shows gloss of the near-zero VOC HS acrylic coating for comparison. This is the only graph of the three that shows any notable differentiation of the tail solvents. All show a significant improvement over using no tail solvent at all, but aromatic 100 (Figure 5, dark blue line) did not enable as high of gloss above 4.5 mils DFT as compared with pentyl propionate or DIBK. Unfortunately, the coating containing EEP did not have any area greater than 4.5 mils DFT to measure.

Figure 6 shows the gloss of the coatings containing the 80:20 blend of HS acrylic and polyester polyol in combination with each tail solvent at 100 g/L VOC, and also shows gloss of the near-zero VOC coating with the same polyol for comparison. Each tail solvent offered a slight improvement across the range of film thicknesses and it is difficult to discern any real differences between them, although the gloss of the coating containing aromatic 100 (dark blue line) does decrease at 5.5 mils DFT vs that for EEP (purple line).

Figure 7 demonstrates the gloss improvement of tail solvents in the 65:25:10 blend of the HS acrylic, polyester, and MS acrylic, with the near-zero VOC coating for comparison. All four tail solvents offered a significant improvement at all measurable film thicknesses, and no discernable differences can be seen with this data.

A portable meter was used to evaluate distinctness of image (DOI) as a second metric for appearance quantification. DOI was measured at both 3 mils and 4.5 mils DFT to show the effect of film thickness. Figure 8 compares the DOI of all of the coatings based on the HS acrylic as compared to the control formula. The portable meter would not provide a measurement of the near-zero VOC coating due to its poor surface quality.

Just as it had improved the 20° gloss, the polyester polyol also provided a significant increase in DOI. This is especially apparent with the addition of tail solvents, and further at higher film builds as shown in Figure 9. It is seen that the use of pentyl propionate at 100 g/L VOC allows this polyol blend to achieve a DOI that is nearly equivalent to the control formula.

FIGURE 8—DOI of HS acrylic-based coatings.

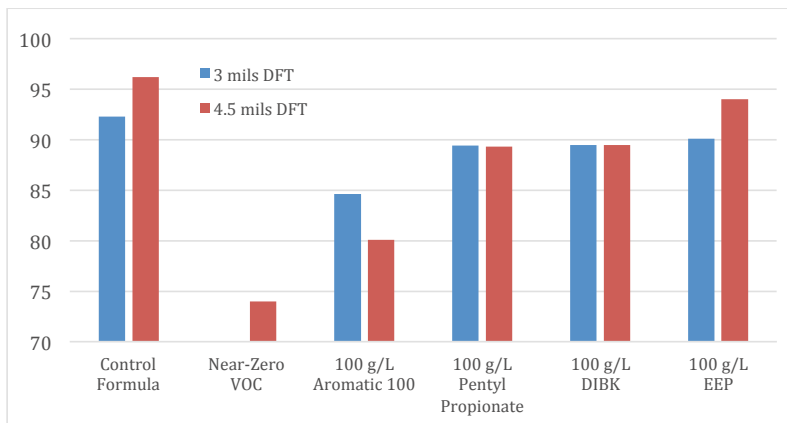


FIGURE 9—DOI of 2K polyurethane coatings based on 80:20 HS acrylic : polyester blend.

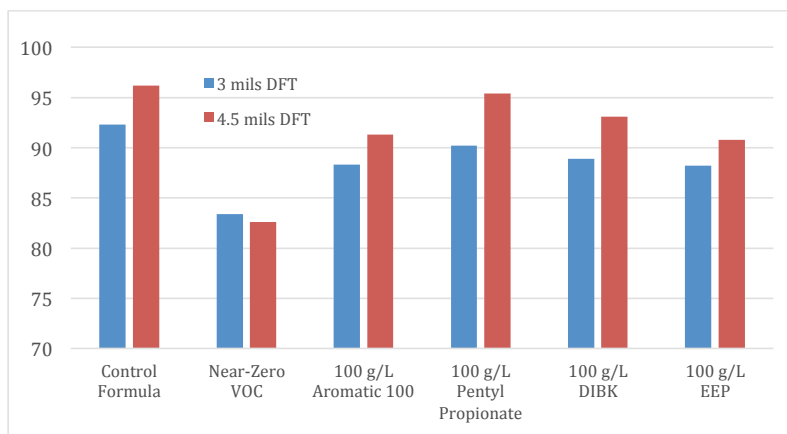
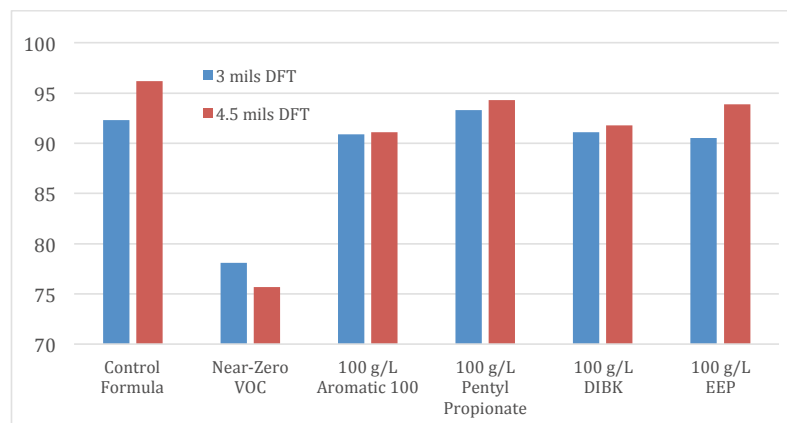


FIGURE 10—DOI of 2K polyurethane coatings based on 65:25:10 HS acrylic : polyester : MS acrylic blend.



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Coatings based on the 65:25:10 blend of the HS acrylic, polyester, and MS acrylic (*Figure 10*) do not achieve quite the same level of DOI as the 80:20 HS acrylic : polyester blend. Interestingly, however, DOI is more consistent between the two film thicknesses that were evaluated here. This type of behavior may be desirable to provide a more consistent finish across a wider range of application thicknesses, but the repeatability of this should be investigated further through additional work.

If 20° gloss or DOI were the only metrics used to evaluate the quality of coating appearance, it could be concluded that a 100 g/L VOC 2K polyurethane coating based on either 80:20 HS acrylic : polyester or 65:25:10 HS acrylic : polyester : MS acrylic, using pentyl propionate as a tail solvent provides equivalent film quality to that of the control formula. However, although 20° gloss and DOI are generally good metrics to use in evaluating surface quality, they were found to be insufficient for the overall quality of the coatings due to microfoam under the surface. While microfoam in the near-zero VOC coatings was easily evident by visual inspection, many of the 100 g/L VOC coatings exhibit excellent appearance upon casual observation. However, under closer inspection with a good light source present, it is revealed that all of the coatings contained at least some amount of microfoam beneath the surface.

*Figures 11–15* are photographs taken of the coatings based on the 65:25:10 HS acrylic : polyester : MS acrylic blend using a digital SLR camera with a macro lens under intense lighting. *Figure 11* shows the surface of the near-zero VOC coating and the severe microfoam that is at and under the surface.

*Figure 12* shows the 100 g/L coating using aromatic 100 as the tail solvent at 4.5 mils DFT. Dust and micro-scratches are present on the surface due to mishandling of the panel before photographing, but there is a great reduction in microfoam vs the near-zero VOC coating.

*Figure 13* shows the 100 g/L coating using pentyl propionate as the tail

solvent at 4.5 mils DFT. It is clear from this photograph that pentyl propionate provides even better reduction of microfoam than aromatic 100.

*Figure 14* shows the 100 g/L coating using DIBK as the tail solvent at 4.5 mils DFT. This panel also unfortunately experienced some micro-scratching before the photograph was taken. Reduction in microbubbles by DIBK is observed to be roughly equivalent to that of aromatic 100, and not as good as that of pentyl propionate.

*Figure 14* shows the 100 g/L coating using EEP as the tail solvent at 4.5 mils DFT. Although there are some minor micro-scratches present on the surface of this panel, it is clear that EEP provided the best reduction in microfoam compared to the other three tail solvents evaluated.

All of the aforementioned data was entered into a statistical software program to characterize the effect of polyol combination, tail solvent, and dry film thickness on 20° gloss, DOI, and nine-day pendulum hardness. This is displayed in *Figure 16*. With respect to 20° gloss, the 80:20 blend of HS acrylic and polyester display an overall advantage over the other two polyol systems, and all four tail solvents at 100 g/L VOC offer a vast improvement over the near-zero VOC coatings. DOI shows a very similar trend, although it is shown that the 65:25:10 blend of HS acrylic : polyester : MS acrylic results in equivalent DOI to the 80:20 HS acrylic : polyester blend.

Although performance characteristics have not been measured for the coatings in this article since the focus has been on appearance, it was desired to investigate the potential for solvent entrapment and its effect on the hardness development of the coatings. In looking at the polyol combinations, the polyester was found to reduce the pendulum hardness vs the HS acrylic alone, and the addition of the MS acrylic was found to offer limited, if any, improvement at the concentration used. Looking at the various tail solvents, all four resulted in at least some reduction in hardness vs the near-zero

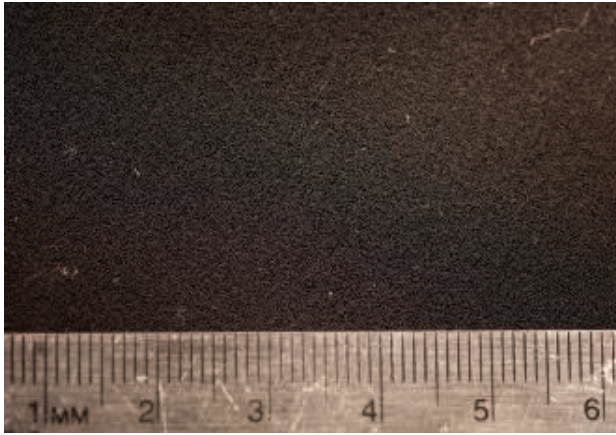
VOC coatings, which indicates there is likely some level of solvent entrapment in these films. EEP resulted in the greatest overall reduction in hardness, which could be due to its slower evaporation rate or some other factor.

## CONCLUSIONS AND NEXT STEPS

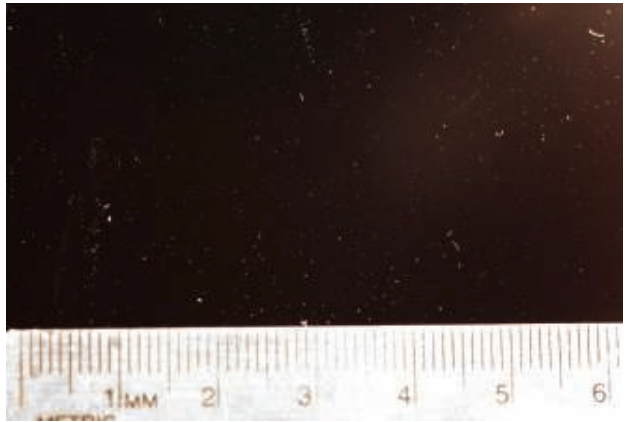
The high solids acrylic polyol utilized in this study has been shown to provide an appropriate basis for 100 g/L VOC coatings that are compliant with SCAQMD rules. When used as the sole polyol, however, this material did not provide ideal film appearance, regardless of the non-exempt tail solvent. Replacing 20% of the polyol solids with the polyester polyol resulted in much higher gloss and DOI, but also resulted in the side effect of reduced pendulum hardness after nine days at room temperature. Regardless of whether or not the coatings based on this 80:20 polyol blend reach equivalent end-hardness to the control formula, it would be prudent to increase the catalyst level to ensure that coating film properties are developed at a faster rate. Addition of the medium solids acrylic polyol as used at 10 parts in a 65:25:10 three-way polyol blend resulted in slightly lower gloss and equivalent DOI to the 80:20 HS acrylic : polyester blend; but it did not offer any discernable difference in hardness nine days after application. Other blend ratios should be evaluated to determine if a greater concentration of this medium solids acrylic polyol offers an advantage, assuming the resulting coating viscosity is acceptable.

It is clear from the results outlined here that the use of a tail solvent at 100 g/L is necessary to achieve good film quality versus acetone/PCBTF blends at near-zero VOC. While all of them offered some level of improvement, aromatic 100 and DIBK did not result in as good an appearance as pentyl propionate or EEP. It may actually prove difficult to choose between pentyl propionate and EEP based on the findings here. Pentyl propionate resulted in the best overall 20° gloss and DOI, as well

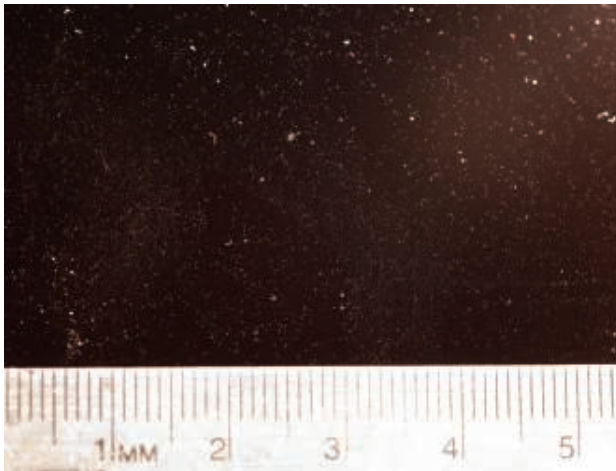
**FIGURE 11—** Photograph of near-zero VOC coating based on 65:25:10 HS acrylic : polyester : MS acrylic blend at 4.5 mils DFT.



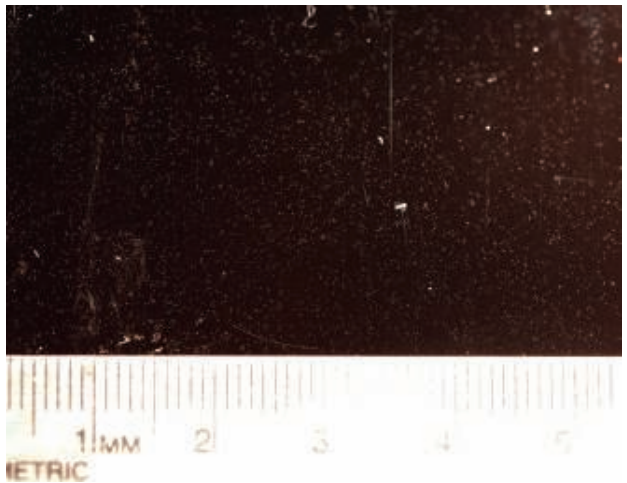
**FIGURE 13—** Photograph of 100 g/L coating based on 65:25:10 HS acrylic : polyester : MS acrylic blend and pentyl propionate at 4.5 mils DFT.



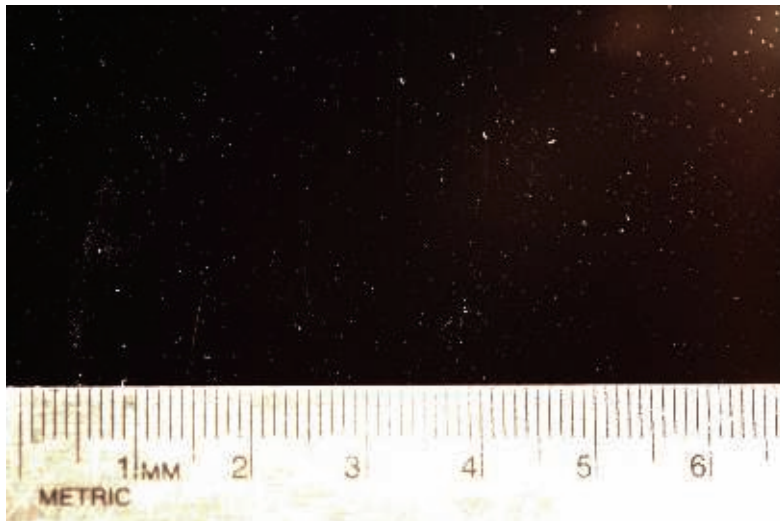
**FIGURE 12—** Photograph of 100 g/L coating based on 65:25:10 HS acrylic : polyester : MS acrylic blend and aromatic 100 at 4.5 mils DFT.



**FIGURE 14—** Photograph of 100 g/L coating based on 65:25:10 HS acrylic : polyester : MS acrylic blend and DIBK at 4.5 mils DFT.



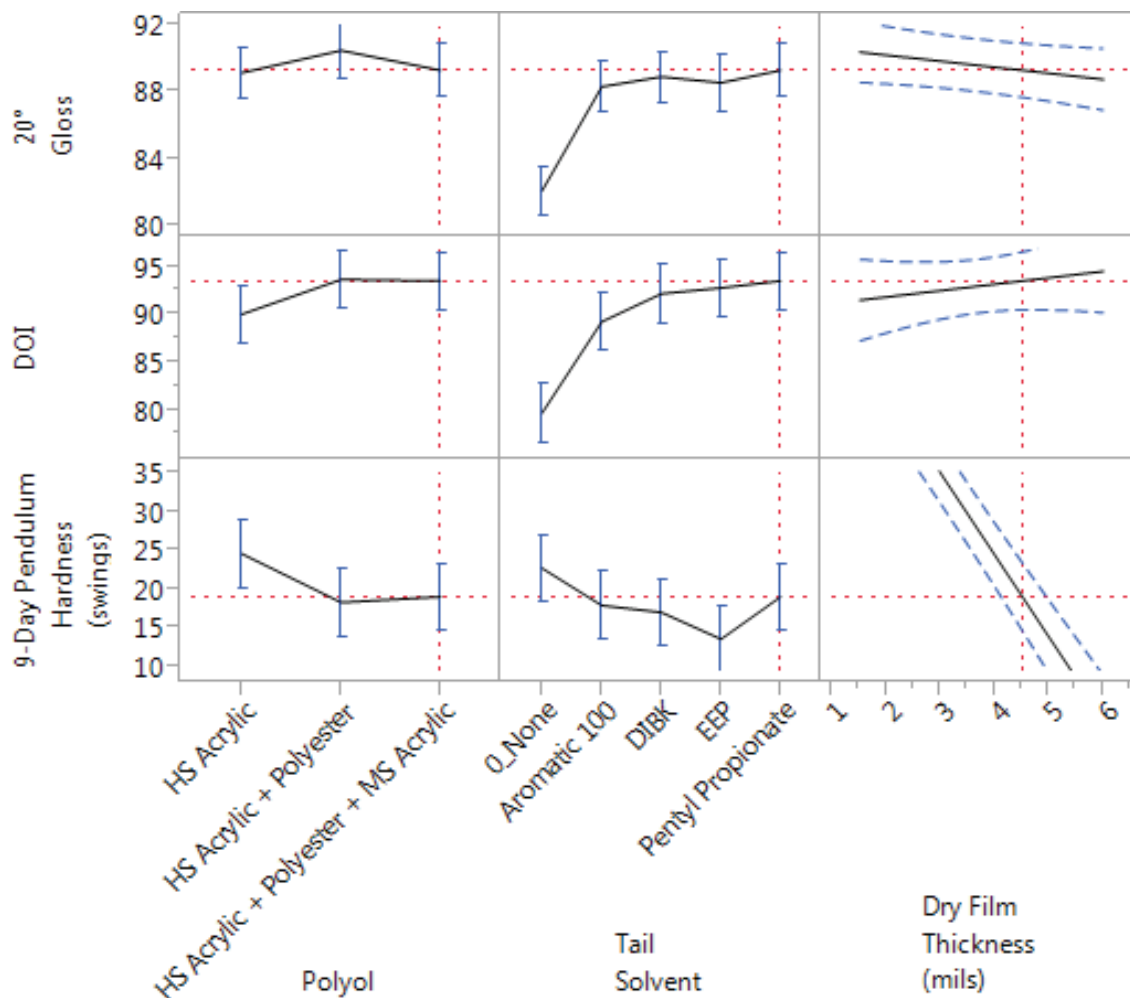
**FIGURE 15—** Photograph of 100 g/L coating based on 65:25:10 HS acrylic : polyester : MS acrylic blend and EEP at 4.5 mils DFT.





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FIGURE 16—Profile of gloss, DOI, and pendulum hardness as influenced by polyol, tail solvent, and dry film thickness in 100 g/L VOC coatings.



as the least reduction in nine-day pendulum hardness due to solvent entrapment. However, EEP exhibited the lowest tendency to promote microfoam within the coatings. It may be necessary to fully evaluate the performance of coatings that use both tail solvents to reach a proper conclusion as to which is better overall.

Lastly, all of the coatings here were formulated without the use of any formulation additives, such as defoamers or flow and leveling aids. Additional work should be performed using such additives to optimize coating film appearance even further. ❖

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