

Innovative Waterborne UV Polyurethane Dispersions for Wood Coatings

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UV-curable technology has received widespread attention in industrial research for many years. The earliest developments were introduced in the graphic arts industry. This market still continues to have the highest usage of UV/EB formulations in North America, where overprint varnishes are the largest single application. However, other markets are experiencing rapid growth as the performance and productivity benefits of UV technology become more apparent. According to RadTech's biennial UV/EB market

As legislation for solvent emissions becomes more stringent, waterborne materials are an excellent choice because it is possible to formulate zero-VOC lacquers, including spraying applications. Along with this benefit and cleanup advantages, these materials can also provide low viscosity without the addition of low-molecular weight monomers, which can be detrimental to performance.

Waterborne UV-curable coatings require drying for the evaporation of water; thus, a two-step process is needed. This drying step can be in either a forced air infrared oven or microwave oven for industrial applications or under ambient conditions for floor coating applications. For wood coatings, waterborne UV-curable resins offer excellent adhesion, open pore wood finishing and a low build appearance. Grain raising is possible (as with other water-based wood coatings), but this can be minimized with sanding between coats. Pigmented systems are also available that use many universal-type colorants for custom color matching.

Waterborne (WB) UV Polyurethane Dispersions (PUDs) are a viable resin choice for coatings for several end-use markets, including wood floors, kitchen cabinets and furniture. They offer high-end performance with minimal process issues and nearly zero volatile organic compounds (VOCs). Since UV-PUDs are high molecular weight

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survey, applications such as 3-D inkjet, plastic and metal coatings, electronics, UV for fingernails and water-based formulations are expected to grow at seven percent or more per year over the next several years.¹ Thus, formulators and manufacturers have new opportunities for innovation and high potential to increase efficiency.

UV-curable coatings are mainly classified by three primary types—water-reduced, 100% UV and solvent-reduced. The latter two have been the primary available technologies. However, waterborne UV chemistry is becoming a viable and growing alternative with several advantages.

TABLE 1

Basic properties of UV-PUDs

	% Solids (wt)	pH	Viscosity (cps) 23°C	Koenig Hardness before UV (sec)	Koenig Hardness after UV (sec)	MFFT (°C)
UV-PUD 1	35	8.0	200	50	155	0
UV-PUD 2	40	7.0	200	20	145	0
UV-PUD 3	40	7.5	200	10	125	0

polymers, the crosslink density of the cured networks compared to 100% solids is lower, but this limits shrinkage after cure resulting in excellent adhesion to most substrates. UV-PUDs also inherently yield good mechanical performance due to having hard urethane and urea domains which can have hydrogen bonding, coupled with softer domains which come from the choice of raw material building blocks such as the polyols.

Excellent hardness can be achieved as well, partly arising from acrylate crosslinking. A study has been conducted evaluating the performance of WB-UV-PUDs as coatings on wood substrates, including flooring and furniture. These resins have been designed to fulfill the range of requirements needed for adequate protection of the substrates, minimizing formulation issues and ease of processing. Table 1 provides basic properties of the resins used to formulate these coatings. This investigation will further detail the comparison of these resins to traditional resin types used in these markets.

Experimental

The UV resins were formulated for industrial wood applications according to the Kitchen Cabinet Manufacturers Association (KCMA)², Architectural Woodwork Standards (AWS)³ and individual furniture manufacturer's specifications. Similarly, the formulations for wood flooring were

suitable to meet the Maple Flooring Manufacturers Association (MFMA) testing requirements.⁴ All formulations were adjusted to be equal in solids and included standard additives such as defoamer, surfactant, matting agent, rheology modifier and photoinitiator.

Coated wood panels were prepared following the four steps:

1. Sprayed approximately 3 wet mils of coating over 18x18 stained maple panel.
2. Air dried for 10 minutes.
3. Force dried for 10 minutes at 50°C.
4. Cured with a mercury bulb at 500 mJ/cm².

After sanding with a 3M superfine sanding sponge, a second coat was applied at approximately 3 wet mils. Repeated steps 2-4. A wait period of 14 days followed before testing unless otherwise indicated in the test method.

Furniture Test Methods

Chemical/Stain Resistance

Applied enough chemical/stain to create a 0.25 to 0.5 inch diameter spot on the test panel. Covered with watch glass. Waited 16-20 hours. Removed chemical/stain and washed the surface of the panel with water. Rated each chemical/stain on a scale of 0 to 5 (0 being complete destruction of the film and 5 being no effect on the film).

Chemicals Used

Vinegar, lemon juice, orange juice, grape juice, ketchup, coffee, olive oil,

1% detergent solution, mustard, water, nail polish remover (acetone-based), ammonia, VM&P Naphtha, isopropyl alcohol (70%), red wine, Windex, 409 cleaner, Lysol, gasoline, Murphy's Oil Soap, 10% TSP, Betadine, Kiwi black shoe polish, sunscreen (90 spf) and plasticizer.

Scrape Adhesion

Cut 4x7 inch piece from each test panel. Tested adhesion with a BYK balanced beam scrape adhesion and mar tester with 5,000 grams of weight using the loop stylus. Rated on a scale of 0 to 5 (0 being complete removal of the film and 5 being no effect on the film).

Ballpoint Pen Indentation

Cut 4x7 inch piece from each test panel. Tested for ballpoint pen indentation with a BYK balanced beam scrape adhesion and mar tester with 300 grams of weight using the small pen #5785. Waited one hour before evaluating the panel. Rated on a pass/fail scale. Any indentation that could be seen from a distance of 24 inches was considered a failure.

Plasticizer Resistance

Applied a two-inch square piece of red vinyl to the test panel. Applied a force of ½ lb/in². Placed the specimen in an oven at 50°C for 72 hours. After cooling at room temperature for one hour, removed the vinyl square. Evaluated for softening and blistering.

Green Print Resistance

After curing test panel, waited one hour then applied a two-inch square

piece of #10 cotton duck cloth to the finish. Applied a force of 2 lb/in² directly to the duck cloth. Waited 24 hours then removed cotton duck cloth. Evaluated for printing.

Hot Print Resistance

After curing the test panel, waited 14 days then applied a two-inch square piece of #10 cotton duck cloth to the finish. Applied a force of 1 lb/in² directly to the duck cloth. Placed the specimen in an oven at 60°C for 24 hours. Removed the duck cloth and allowed the specimen to cool for one hour. Evaluated for printing.

Boiling Water Resistance

Applied 10 mL boiling water to the test panel. Placed a ceramic coffee cup full of boiling water on top of the 10 mL of water. Waited one hour. Removed the cup and wiped with paper towel. Waited 24 hours. Evaluated for whitening.

Scotch Brite Scratch Resistance

Made a 3 mil drawdown on a Form 3B-H Leneta card. Air dried for 10 minutes then force dried for 10 minutes at 50°C. Cured with mercury bulb at 500 mJ/cm². Waited 14 days before testing. Recorded the gloss (60°C) of the coating. Applied a two-inch square from a green Scotch Brite scrub pad. Placed a 200 gram weight on the pad. Slid the pad back and forth across the surface of the coating for 10 double rubs. Removed the pad and recorded the gloss. Reported % gloss lost.

Koenig Pendulum Hardness

Made a 150 micron drawdown on a glass panel. Air dried for 10 minutes, then force dried for 10 minutes at 50°C. Measured Koenig hardness before cure. Cured with mercury bulb at 500 mJ/cm². Measured Koenig hardness one hour and 7 days after cure.

Flooring Test Methods

Stain Resistance (ASTM D 1308)

Materials included deionized water, 1.5% Pine Sol solution, vegetable oil

(four-hour dwell); 50% alcohol/water solution, Naphtha, beer (Yuengling) and Coca-Cola (one-hour dwell)

On a Leneta card, a 3 mil wet film was cast and allowed to dry and cure. A one- to two-inch diameter pool of the staining liquid was applied and allowed to stand on the surface at 25°C for one or four hours under a watch glass. The watch glass was removed and the coating rinsed with water and allowed to dry for 60 minutes. Evaluation for any objectionable alteration of the surface such as discoloration, change in gloss, blistering, softening, swelling or loss of adhesion indicated failure.

Heat Stability

Samples were placed into a 50°C oven for 48 hours and examined for freedom from sediment and suspended solid matter.

Sanding

All samples were subjected to sanding with a 100-grit sanding disk and observed for “gumming” or rolling.

Adhesion

Cross-hatch adhesion.

Fingernail Mar

On a Leneta card, a 3 mil wet film was cast and allowed to dry and cure. Samples were rubbed with a fingernail and noted for any marring.

Coefficient of Friction (CoF)

On a Leneta card, a 3 mil wet film was cast and allowed to dry and cure. Used a spring balance connected to a 100 gram weight with a leather shoe, slowly increased the force until the weight began to slide. Made sure the spring balance was parallel to the surface. The reading on the spring balance scale when the load begins to slide is a measure for the static friction. The coefficient of friction $\mu = F_f / F_n$. The finish must achieve a CoF reading between 0.50 and 0.70.

Black Heel Mark Resistance (BHMR)

On a Leneta card, a 3 mil wet film was cast and allowed to dry and cure. Using a hockey puck to simulate a

FIGURE 1

Chemical resistance

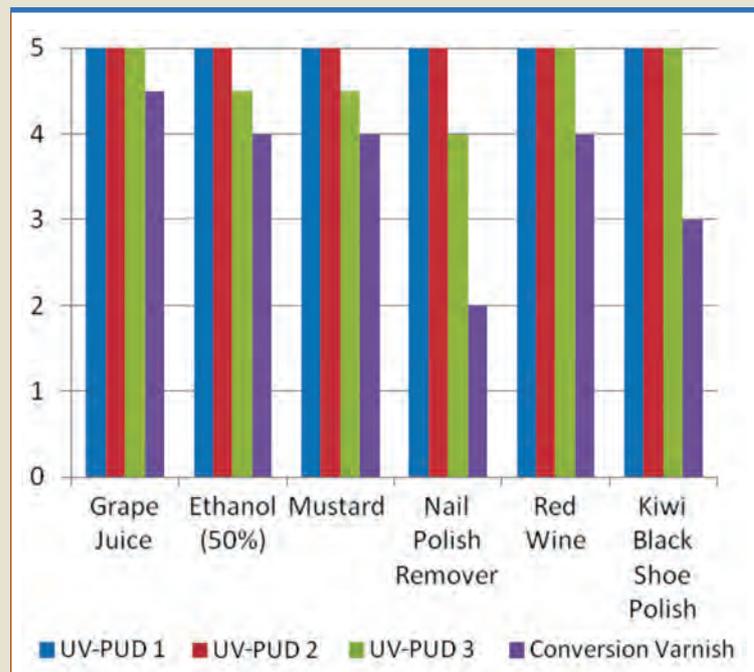
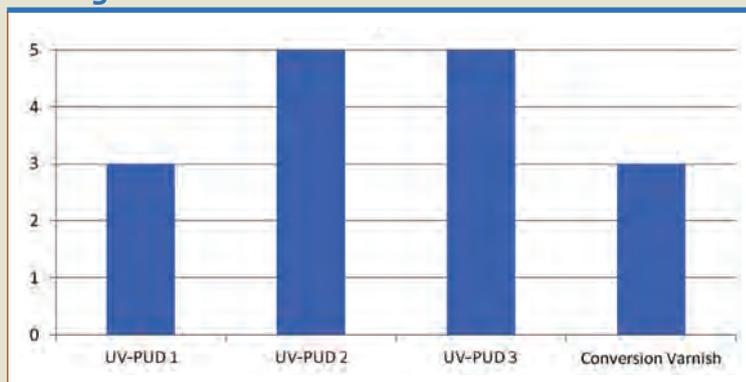


FIGURE 2

Boiling water resistance



black heel, the film was struck to produce a black mark.

Results and Discussion

One of the predominant choices for solvent-based coatings for industrial wood applications is conversion varnishes. Conversion varnishes are blends of oil-based alkyds, urea formaldehyde and melamine. They use a strong acid catalyst such as p-toluene sulfonic acid. They have a pot life of 24 to 48 hours. Conversion varnishes show very good performance on industrial wood. However, they have very high VOCs and formaldehyde emissions and are not considered environmentally friendly. A traditional conversion varnish has been evaluated in comparison to the UV-PUDs.

Among the 25 chemicals tested, six showed differentiation as indicated in Figure 1. The conversion varnish was particularly weak for nail polish remover and shoe polish, but all UV coatings showed excellent resistance. Specifically, UV-PUD 1 and UV-PUD 2 showed the best performance amongst the group.

The boiling water resistance was tested and the results are given in Figure 2. The conversion varnish and UV-PUD 1 showed only mediocre performance, while the other UV coatings showed far superior performance. All of the coatings showed very good scrape adhesion, hot and green print resistance, and plasticizer resistance. Koenig hardness was also measured after cure (Figure 3). While all of the coatings produced hard surfaces (>100 seconds), the conversion varnish and UV-PUD 1 were the hardest (>140 seconds).

UV-PUD 1 also has moderate hardness prior to UV cure. This provides some benefit, especially for blocking properties where coated parts may have some contact prior to curing and surface scuffing is not desired.

FIGURE 3

Koenig pendulum hardness

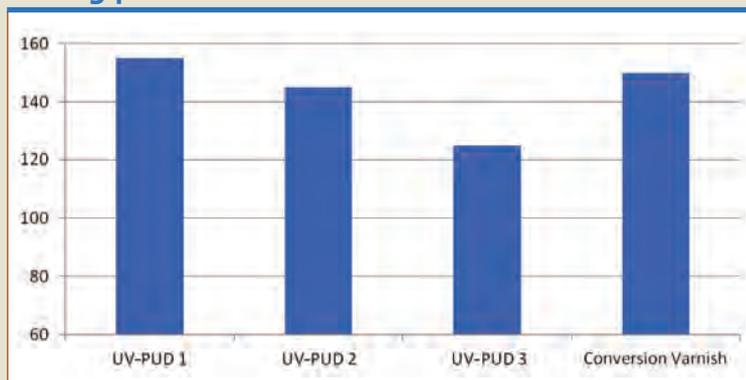


FIGURE 4

Scotch Brite scratch resistance

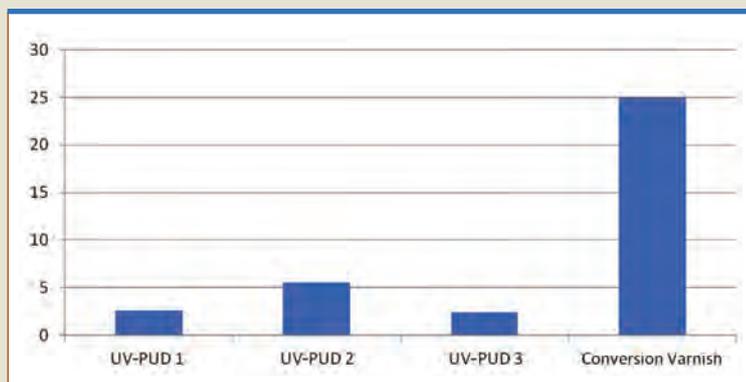


TABLE 2

IPA resistance test results

	UV-PUD 1	UV-PUD 1	UV-PUD 1	UV-PUD 2	UV-PUD 2	UV-PUD 2	Comm NCO	Comm Az
	1% PI	2% PI	3% PI	1% PI	2% PI	3% PI	N/A	N/A
10 FPM	Pass	Pass	Pass	Pass	Pass	Pass	N/A	N/A
20 FPM	Pass	Pass	Pass	Fail	Pass	Pass	N/A	N/A
30 FPM	Fail	Pass	Pass	Fail	Fail	Pass	N/A	N/A
2K after 1 week	N/A	N/A	N/A	N/A	N/A	N/A	Fail	Pass

Figure 4 presents the scratch resistance of the coatings and clearly indicates the robustness of UV resins compared to the conversion varnish. The cured coatings are scratched with a green Scotch Brite scrub pad that contains a 200-gram weight. The gloss is recorded before and after the rubs and a % gloss loss is calculated. The lower the number, the better the performance. All of the UV resins performed very well for this test, while the gloss for the conversion varnish was reduced by 25%. The high molar mass of these materials, a dense crosslinked network and the unique morphology of polyurethanes (hard and soft domains) results in a superior balance of chemical and mechanical properties. Ballpoint pen indentation was also tested and, as expected, the UV coatings performed very well with only slight inferior performance from the conversion varnish.

In the flooring evaluation, two commercial two-component (2K) WB floor finishes based on PUDs were included for comparison. The first is a widely used, standard product on the market that requires isocyanate to crosslink (Comm NCO). This finish is often noted as the best floor finish available. The other is a polyfunctional aziridine crosslinked finish that is still among the top sellers in this market and is promoted as a very hard finish

(Comm Az). Due to the lower hardness of UV-PUD 3 prior to cure, this resin was not included in the flooring evaluation since a high surface tack would not be practical in the application of this coating and would cause significant surface defects to the floor.

A commercial, portable UV-curing unit was used to cure the UV finishes. Since many variables can impact the degree of cure of the finish, it was the goal of this study to investigate the impact of changing the photoinitiator level (1 to 3 %) and the speed of the curing machine (10 to 30 ft/min).

All of the samples passed a majority of the chemicals with exception of the isopropyl alcohol/water test (50:50). Table 2 indicates which samples showed failures after one-hour exposure. For the UV-cure coatings, it is clear that optimal performance can be achieved by either increasing the photoinitiator level or by decreasing the speed of the machine. This result emphasizes the need to balance the speed of the machine with the photoinitiator level to achieve the desired properties. It is not clear why the isocyanate crosslinked finish failed this test.

FIGURE 5

Koenig hardness in seconds

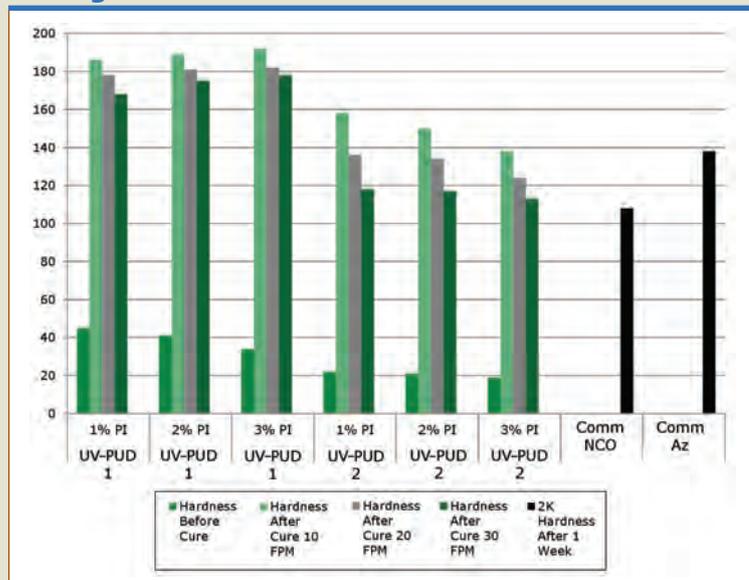
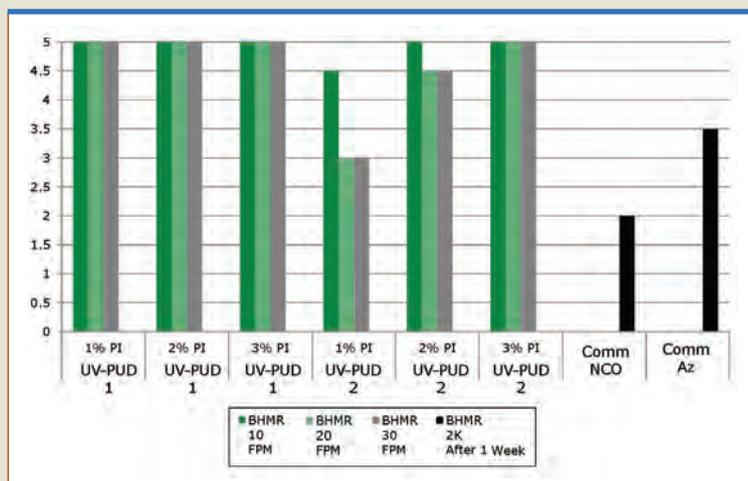


FIGURE 6

Black heel mark resistance



All of the finishes passed testing for heat stability, sanding, adhesion, fingernail mar and CoF. Figure 5 shows the hardnesses of the finishes as measured in Koenig seconds. UV-PUD 1 is significantly harder than UV-PUD 2 prior to UV cure. High hardness is essential to allow walking on a coated floor before curing. It also allows the application of two coats before the final cure. Walking on UV-PUD 2 will leave undesirable footprints on the floor surface. The hardness data shows us the immediacy of the UV cure. While the 2K systems took one week to reach their final hardness, the UV-cured finishes achieved their hardness within seconds and most of the UV formulations were significantly harder than the 2K coatings. It was also noted that the photoinitiator can have a plasticizing effect on the uncured finish. This effect can be seen in the hardnesses of UV-PUD 2 at equal speed. The hardness goes down slightly as the photoinitiator level is increased. As expected, as the curing speed is increased, the hardness decreases as well. Thus, it would be critical for contractors to understand the speed/performance balance during application.

The BHMR was evaluated by striking the coating with a hockey puck. Figure 6 shows that both UV finishes have better BHMR than the isocyanate-crosslinked finish. With the proper combination of machine speed and photoinitiator level, they both outperform the 2K finishes. The taber wear was measured in milligrams lost after 1,000 cycles with 1,000 grams load using the CS-17 wheel. Figure 7

shows that the aziridine-crosslinked 2K finish had the poorest results, while the UV-cured finishes performed as well or better than the isocyanate-crosslinked finish. The UV polymers have been custom-designed to give hard elastic features that make these materials less brittle. As seen in the industrial wood study, the UV-PUDs have significantly better scratch resistance than the 2K finishes as well. While all of the finishes are based on polyurethane chemistry and have densely crosslinked networks, the higher hardnesses of the UV-cured surfaces contribute to lower gloss losses (Figure 8).

Conclusion

Waterborne UV technology will continue to penetrate industrial sectors as raw material suppliers and coatings manufacturers better understand the value proposition of this technology. The UV coatings in this study performed very well in all tests as specified by KCMA and some furniture manufacturer standards. As well, WB-UV finishes have been compared to WB-2K finishes according to specifications

FIGURE 7

Taber abrasion

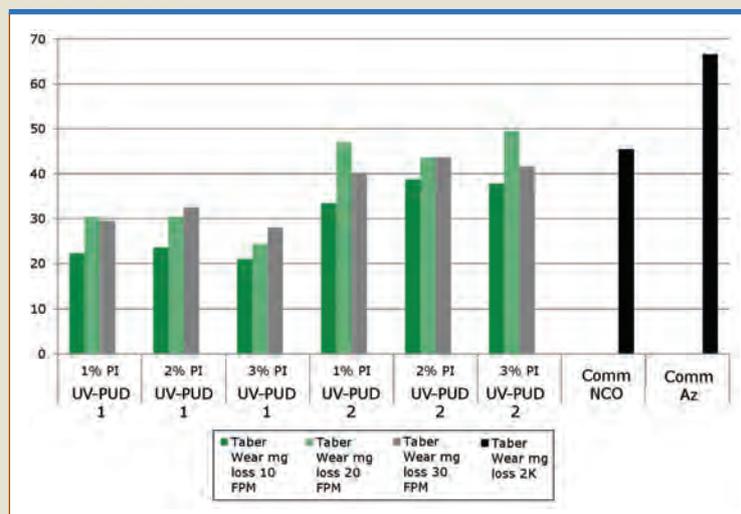
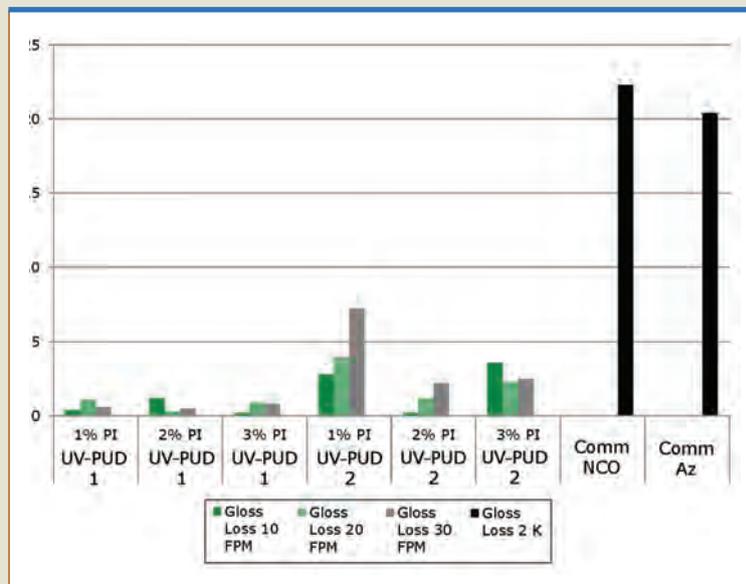


FIGURE 8

Gloss loss



outlined by MFMA. They show clear performance advantages for flooring compared to traditional 2K PUDs. The UV formulations are also significantly lower in VOCs, have a longer pot life and remove the need to handle any crosslinking chemicals on the job site, thus increasing worker safety. These benefits have already been recognized in the industry and have recently led to the creation of a new group of materials recognized by the MFMA, “Group 6—High Gloss UV Finishes.” Additionally, this is evident in the high-volume cabinet and wood furniture markets where WB-UV coatings are becoming the standard technology. Further developments are in progress investigating the application of UV finishes on substrates other than wood such as vinyl composite tile. ▀

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