

Enhancing Cure in Challenging UV Systems

Kenton Renkema, PhD, Kristy Wagner, Conner Sprik,*

Red Spot Paint and Varnish Co., Evansville, IN

Introduction

As the coatings world gets more and more comfortable with UV, the requests for application get more and more varied. A common and difficult theme of the requests is to replace thermal technology as carrier for all variations of effects i.e. pigment, matte, corrosion resistance, etc.. Most of these effects involve the suspension of particles of variable dimension and chemistry. Either or both of these qualities would be expected to reflect or absorb UV energy. Particle inclusion is expected to affect at least the nature of the UV cure, and very likely the extent of cure as well. This study hopes to begin to understand the relationship between filler, UV cure, and ultimate properties of the coating. And then begin the search for ways to counter the effects of fillers thereby expanding the utility of UV coatings.

Experimental

There were two major experiments run for this study. The first was a study of the transparency of various filled UV coatings to UV light. The second was a study how different photoinitiators affected the eventual properties of the final film formed. The general setup for those two experiments is below.

BASE COATING

All coatings used in this study were comprised of 33% of an acrylic acrylate, 17% TMPTA, and 1% BAPO with 49% butyl acetate comprising the rest of the base formula. This formula was chosen because it was relatively easy to perform a drawdown and it seemed to incorporate various particles easily. Particles mixed in various extents were red tints, black tints, red pearl, modified silica, zinc oxide (ZnO).

UV-VIS AND % CURE STUDY

Drawdowns of all coatings were done on 25 mm X 75 mm quartz slides with a 1.6 mil bar and produced coatings of 7 microns \pm 1 micron (via Olympus BX60 microscope using a Paxcam 5 setup). After draw down each slide was flashed in 150⁰ F oven for five minutes, and then immediately cured with three passes in a Fusion EpiQ line, H bulb¹, (UVA, UVB, UVC, UVV [E (mJ/cm²)/I (mW/cm²)] 2850/302, 2800/313, 600/68, 3050/337) and Q bulb¹ (UVA, UVB, UVC, UVV [E (mJ/cm²)/I (mW/cm²)] 4132/361, 3459/352, 276/35, 7204/701). UV-Vis was then run on the cured slides (Perkin-Elmer Lambda 850, 500-225 nm, 2mm slitwidth). ATR-FTIR was then run on the top surface of each coating and after a tape pull the bottom surface of each coating (thru Spectra-Tek microscope attachment to the Thermo 750 FTIR, with ZnSe).

PHOTOINITIATOR AND ULTIMATE PROPERTIES STUDY

Drawdowns of all coatings were done on 2 in X 5 in PC panels with the 1.6 mil drawdown bar. These were then flashed for five minutes at 150 °F and cured with either Fusion H-bulb or Q-bulb. Initial adhesion was checked by creating an 8 X 8 2mm crosshatch and then performing two Nichiban tape pulls. The panels were then cut in half. One half was submerged for 3h in boiling water. After a half hour cool down the panel's appearance was compared to the non-tested half and another adhesion test was administered. The photoinitiators were placed in the formula at 2% by weight. The effect of photoinitiators with absorption max at 250, 300, 440, and 450 nm were explored. A sensitizer and synergist were tried to mark their effect as well.

Results

The amounts of UV-Vis absorption by the base formula, a lightly pigmented red (~0.4% wt/wt), and heavy pigmented black (0.8%wt/wt) are shown in Figure 1. It can be seen with this data that the base resin system and photoinitiator already absorb some UV light but most of that is below 275 nm. The red coating actually shows the greatest difference in absorption in the visible end of the spectrum with 15-25% differences between the clear and red absorbances for 500 nm to 375nm. The lightly loaded red coating still has relatively good UV transparency. The more heavily loaded black causes greater difference from clear across the entire UV-Vis scan. The hashed lines in this figure represent the absorption just due from the pigments (the absorbances from the base have been subtracted).

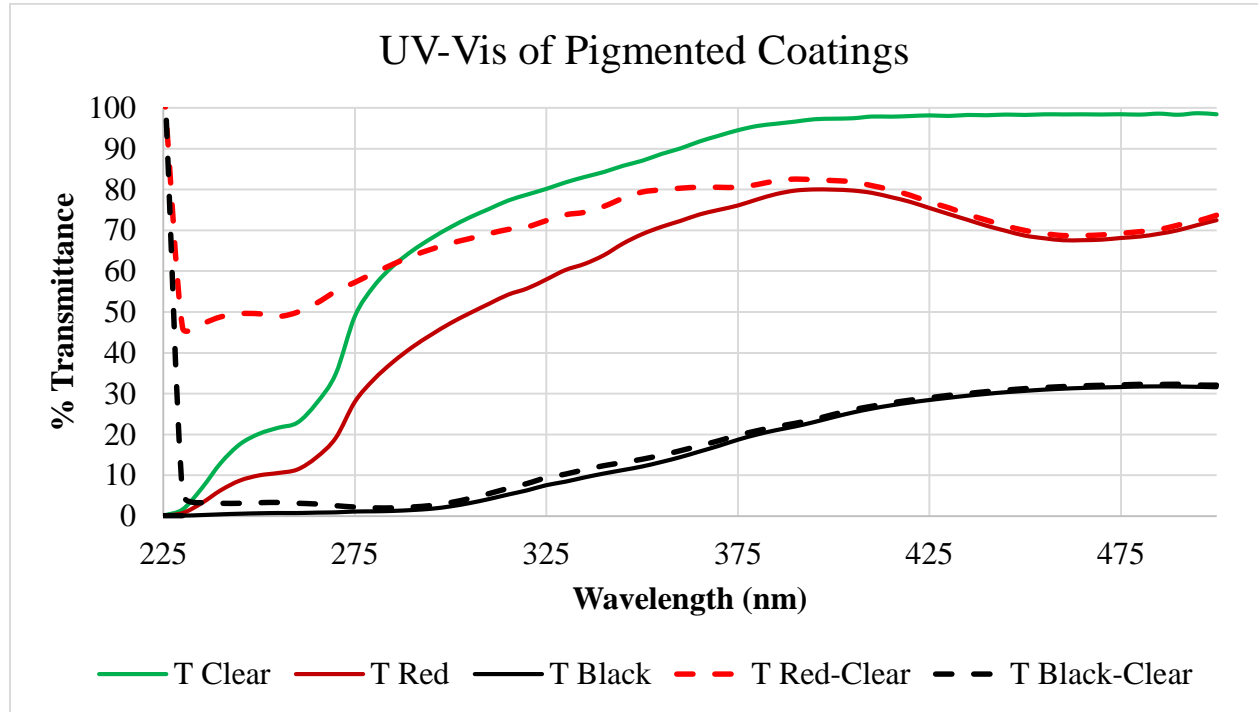


FIGURE 1: UV-Vis of pigmented coatings on quartz slide.

We also tried to look at the effect of particles on UV-Vis transmission. Figure 2 shows these collections again with coating cured on quartz slide. The red mica had similar light blocking to the pigments which is somewhat surprising given its relatively greater loading (3%) and particle size (9-47 μm). The matte silica with an 8% loading nearly cut off all light transmission through the sample at all wavelengths. The ZnO with 4% showed one of the more interesting curves with decent transmission from 500-390 nm but then precipitous drop to below 10% transmission by 375 nm. These results indicate that there are many factors which determine the light transmission through a sample, i.e material, loading, particle size, etc..

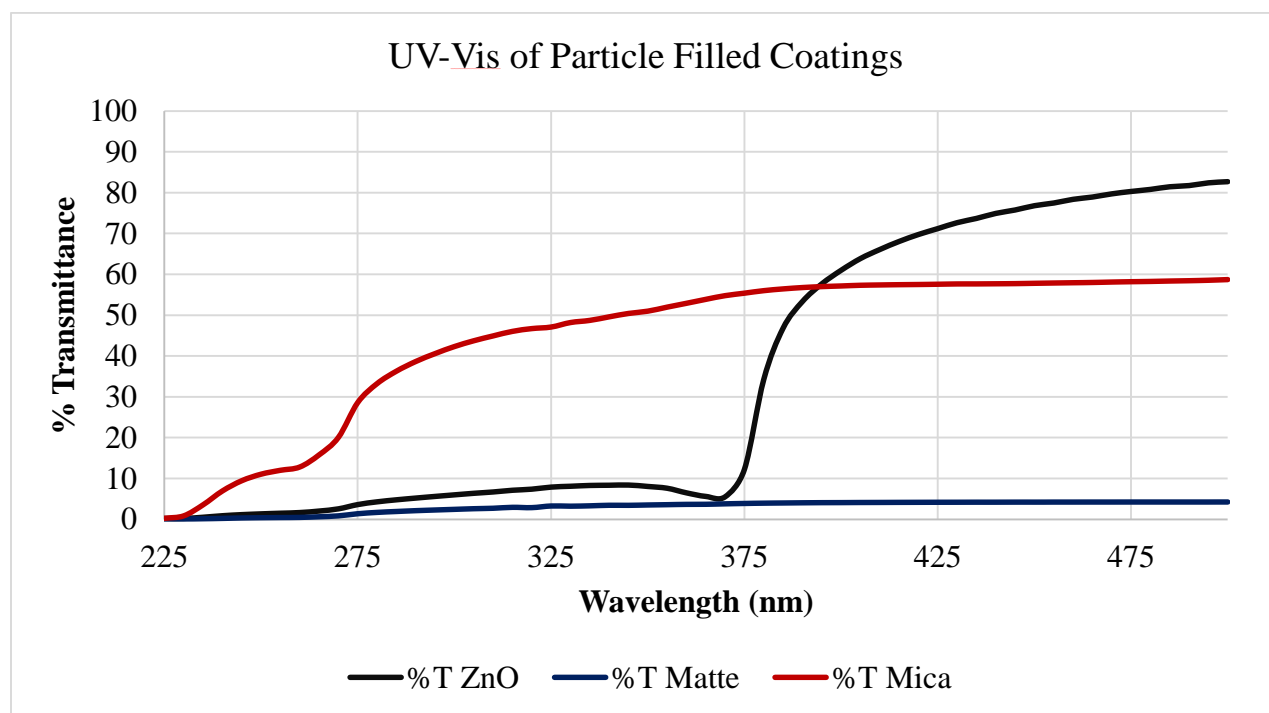


FIGURE 2: UV-Vis of coatings cured on quartz slides. Different materials and loadings applied.

The question then becomes how much does the amount of UV transmission affect the level of UV cure accomplished? We used ATR-FTIR on both the top surface of the coating and after a tape pull the bottom surface of the coating to try and address this question. Figures 3 and 4 show a sampling of the IR spectra collected. While this is an intriguing way of analyzing cure, close inspection of the area around the peaks will suggest that integration of the peaks is not entirely free of background signal. The best signal by this analysis tended to be the twist with the stretch being second best. Table 1 lists the integration of the different FTIR after cure. Scanning through the data the first thing that strikes the observer is that there is always less cure (~half as much) at the bottom surface than the top even with the clear base. The second thing that occurs when you compare all the different samples is that there is not that much difference in the % of acrylate left over. This is perhaps all the more interesting when considering the differences in UV absorption of the different samples and also the amount of error in the IR measurement. This data would suggest that placement of effects in UV coatings might not be as problematic as expected.

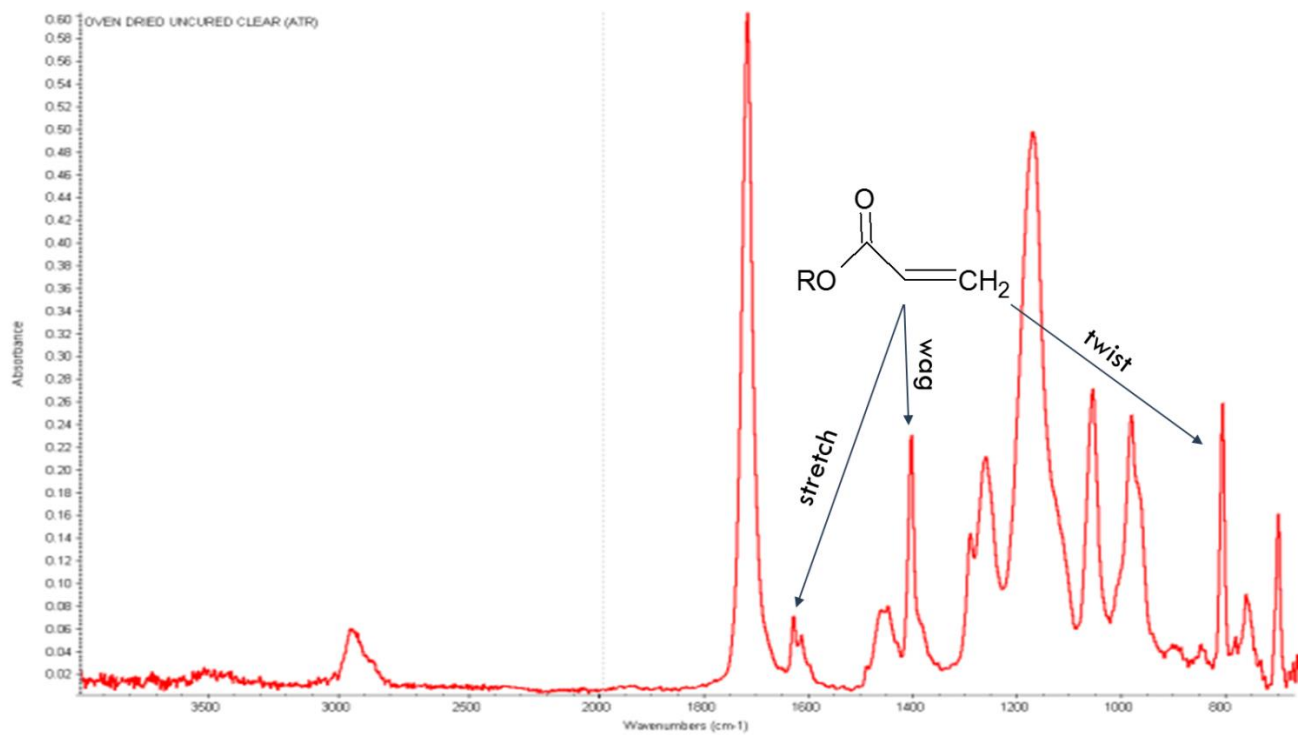


FIGURE 3. ATR-FTIR of uncured base coating.²

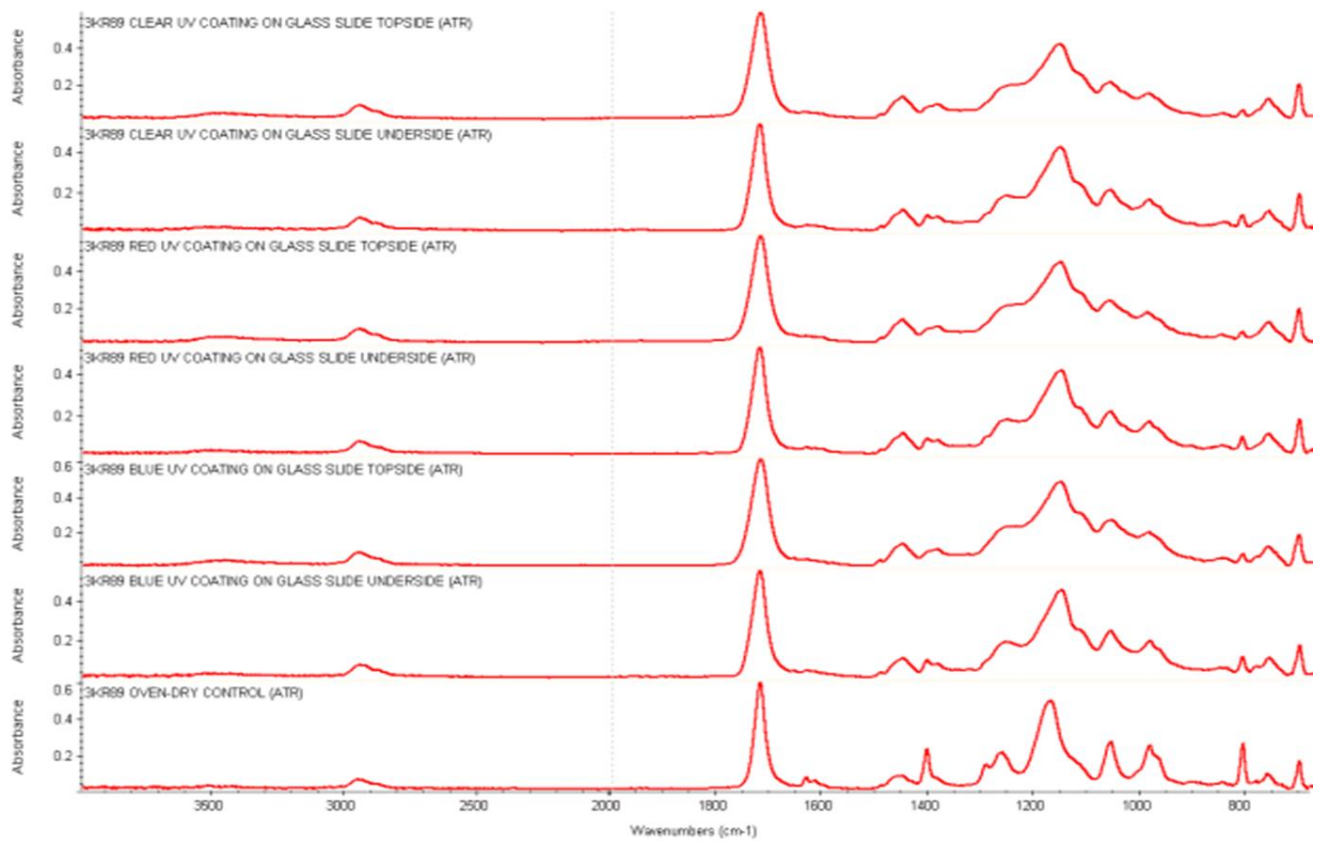


FIGURE 4. ATR-FTIR of pigmented coatings both top and bottom sides.

Coating	Surface	Integration			Integration		
		1646-1600	% cured	ratio	820-800	% cured	ratio
Uncured Clear		0.7419	0		1.86	0	
Clear	Top	0.0967	89.96	1.16	0.3385	85.99	1.16
	Bottom	0.1892	77.40		0.5366	74.43	
0.4-Red	Top	0.0547	94.40	1.16	0.3191	86.97	1.20
	Bottom	0.1517	81.21		0.5606	72.31	
0.8-Black	Top	0.1294	87.48	1.32	0.4224	83.70	1.19
	Bottom	0.2893	66.05		0.6334	70.36	
8-Matte	Top	0.0451	87.30	1.17	0.1777	80.04	1.07
	Bottom	0.1906	74.66		0.4741	74.86	
3-Red Pearl	Top	0.0988	89.87	1.15	0.3106	87.30	1.23
	Bottom	0.1735	78.00		0.5777	70.78	
4-ZnO	Top	0.1043	89.08	1.21	0.2944	87.70	1.19
	Bottom	0.2106	73.90		0.5336	73.62	

TABLE 1. Integration data from ATR-FTIR looking at the amount of double bond leftover.

While the differences in % uncured acrylate are smaller than expected, there is some increase with the bottom side % uncured that can be correlated with UV transmission, i.e. less transmission weakly correlates with greater % uncured acrylate bond. The question then becomes, is this amount difference enough to affect the final properties of the coating.

In attempt to learn about this question and to begin to see if cure can be enhanced with change of photoinitiator OR UV energy we ran an adhesion study to polycarbonate. We ran a clear version of base versus the 4% ZnO version. We kept the UV blocker constant for this part of the study so we can understand the effect of the other changes (PI and light source). We checked adhesion before and after a 3 hour submersion in boiling water. This could be an overly harsh test but should help us to distinguish greater cure. Table 2 tabulates our initial results of this study. We can see all of the different clears have 100% initial adhesion to PC no matter the bulb used. Only the ~450 nm PI clear lost adhesion during the 3 hour boiling water. Since the coating is the same, this result is either from poorer cure or the 2% photoinitiator presence.

Including the UV blocking ZnO (4%) in the clear formula now carries a fairly pronounced effect. 100% initial adhesion is only achieved for the ~300 nm PI, with partial adhesion formed for the 440nm, and 450 nm PI. We now find an enhancement by changing from an H bulb to a Q bulb. It is of note that the 250 nm PI did not even show initial adhesion. Three hours boiling water was very harsh on these partially UV blocked samples as only the 440 nm PI sample showed any adhesion and that with Q bulb. This now strongly suggests that differences in cure from clear to blocked are sufficient to cause changes in the coating's eventual properties. It is a little perplexing that the 440 nm PI was only able to give partial initial adhesion but then was the one sample that partially survived 3h BW.

Coating	PI Wavelength (nm)	Additive	H bulb		Q bulb		
			Adhesion	Adhesion after BW	Adhesion	Adhesion after BW	
Base	~250	None	100%	100%	100%	100%	
Base	~250	ZnO	0%	0%	0%	0%	
Base	~300, ~380	None	100%	100%	100%	100%	
Base	~300, ~380	ZnO	100%	0%	100%	0%	
Base	~450; cationic 250	None	100%	0%	100%	0%	
Base	~450; cationic 250	ZnO	44%	0%	90%	0%	
Base	~440	None	100%	100%	100%	100%	
Base	~440	ZnO	60%	0%	92%*	92%	

TABLE 2. Results of adhesion study versus photoinitiator employed.

We now see that the combination of UV blocking ZnO and 3 hour boiling water submersion were a severe combination. All photoinitiators struggled with this combination. We sought to learn if any other additives or combinations could affect the outcome when other factors were held constant. Table 3 shows our beginning work on this front.

All base data came from Table 2 for comparison sake. One of the most interesting enhancements was with the sensitizer and the 250 nm PI. Without the sensitizer not even initial adhesion was achieved. But with 0.5% photosensitizer the film now cured, and in the case of Q bulb, had 100% initial adhesion, which was partially maintained after boiling water. This was a pronounced effect of additive. All combinations of PI with the 300 nm PI including an amine synergist unfortunately led to no enhancement of the cure as evidence by this test. The amine synergist did have an effect on the 440 nm PI, which was predicted by some for this product. Strangely, here the initial adhesion was enhanced but that result did not always follow to the boiling water test. Given the narrow scope of our attempts it seems clear that effects of UV blockers can at least be partially offset.

Coating	PI Wavelength (nm)	Add.	Cured Observation	H bulb		Q bulb	
				Adhn	Adhesion after BW	Adhn	Adhesion after BW
Base	~250	ZnO	Hazy, Softer	0%	0%	0%	0%
	add sensitizer(380,400)	ZnO	Hazy, OK	48%	68%	100%	4%
Base	~300, ~380	ZnO	Hazy, OK	100%	0%	100%	0%
	add PI ~450	ZnO	Hazy, OK	100%	0%	100%	0%
	add synergist (300)	ZnO	Hazy, OK	100%	0%	100%	0%
	add PI ~250	ZnO	Hazy, OK	100%	0%	100%	0%
Base	~440	ZnO		60%	0%	92%*	92%
	add synergist (300)	ZnO	Hazy, OK	100%	34%	100%	0%

TABLE 3. Alternative additives ways to affect cure.

Conclusion

We began this study trying to validate the anticipation that fillers in UV coatings will affect the cure of the coating and thereby the eventual properties of the coating formed. Our work with UV-Vis does indeed show that filler does reduce the amount UV light available to accomplish cure. However, FTIR of the cured coatings with various fillers and levels versus clear showed a surprising similarity in percent cure. There was a weak correlation with greater UV blocking leading to lower cure. Further work showed that adhesion of the coating to polycarbonate was influenced by the presence of a UV blocker in the coating. Adhesion of the blocked coatings was affected by choice of photoinitiator. Photoinitiator that absorbed at longer wavelengths generally performed better. Other co-additives and alternative, wavelength cure-lights were also able to enhance cure. There seem to be many variables at play with filled UV coatings, but the responsiveness of the systems in this study to formulation and processing changes gives hope that this is an arena that UV will eventually tread without trepidation.

Acknowledgements

A thank you to Kristy Wagner for many discussions and organization of thoughts and to Conner Sprik, a summer intern, who performed many of the experiments. Also to Steve Gerst in analytical for helping with all of the IR and Chris Stofleth for discussions.

A thank you for all material support from BASF, Allnex, Estron, Doublebond, Spectra Group Limited, Esstech, Kawasaki Kasei Chemicals, SunChemical, Nanophase, and Evonik. Application support was given from Fusion and Milltech.

References

¹Fusion UV Systems, Lamp Output Report, 13mm Q bulb or 13mm H bulb.

²JCT Research, vol 3, No. 3, July 2006, 221-230/

