

# Dominant Factors of Gloss Control in Radiation Curable Coatings

*Suresh K. Devisetti* \*, Loyd J. Burcham and Richard C. MacQueen  
Congoleum Corporation  
P.O.Box 3127  
Mercerville, NJ-08619  
USA

\* Corresponding Author

## Abstract

Gloss control is an important and complex process in radiation curable coatings. Prior work on gloss control extensively reviews various key parameters that affect the matting of UV coatings, but is not always clear or detailed enough in identifying the dominant factors over less significant variables. The current work investigates various process conditions and formulation parameters that influence gloss control in order to prioritize the key parameters. Parameters studied include UV energy dose, irradiance, photo initiator level, and curing temperature. These experimental findings are interpreted in the context of a dual-environment (air and inert) curing mechanism to provide a better framework for gloss control.

## Introduction

A low gloss surface is created by fine surface roughness which reflects incidental light in a diffusive manner. A low gloss finish is desirable in many industrial coating applications such as flooring coatings, coil coatings, wood coatings, over print varnishes and others. This low gloss surface provides an elegant and natural look to the product and camouflages any minor imperfections left by wear or the manufacturing process. Most of the time, the low gloss finish is produced/achieved by incorporating matting agents into the coating. These matting agents protrude above the coating mean surface and result in a micro-rough surface.

In conventional water and solvent based coating applications, low gloss is often achieved by selecting the matting agent particle size such that the particle diameter is slightly greater than the dry film thickness. Shrinkage of the wet film due to the aqueous evaporation during the drying process, combined with protruding particles at the surface, results in a lower gloss appearance. However, in high solids radiation curable coatings the wet and the dry film thicknesses are nominally very similar and usually much thicker than the diameter of the flattening agent. For example, a typical low gloss UV clear coat has a cured ("dry") film thickness on the order of 25 microns with a flattening agent particle diameter of 1 to 10 microns. It is difficult to achieve low gloss in such a situation because the small matting agent particles tend simply to be cured in place uniformly throughout the much thicker film and there is no mechanism by which a surface micro texture can be obtained. One method of overcoming this dilemma is to use a higher concentration of matting agent to obtain the desired micro roughness at the

coating surface by forcing an extremely high packing density of the matting agent particles. In this mechanism surface particles can not move downward as the film shrinks during cure, so instead the uppermost surface layer of the coating must shrink around the uppermost particles resulting in a surface micro texture. Unfortunately, the use of higher filler loading leads to a higher viscosity and results in application issues. This may also adversely affect the final film properties such as haze and mar resistance. Many matting agents with a variety of surface treatment technologies are designed to increase the mobility of particles towards the coating surface and thus increase the particle concentration at the surface, but high levels of matting agents are still usually required.

Because of the difficulties involved in obtaining lower gloss with radiation curable coatings, special techniques such as “Dual Cure” methods<sup>(1)</sup> (also referred to as “Gradient Cure”) are employed in the industry. As the name “Dual-Cure” implies, the process of obtaining low gloss involves a two-stage curing process where wet coating is partially cured in an air atmosphere and then totally cured in a nitrogen atmosphere. As the above cited reference describes, during the first stage, coating below the coating surface is polymerized and the coating surface is not cured due to oxygen inhibition at the surface. This leaves the matting agent exposed at the surface within a very thin film of uncured resin, resulting in lower gloss. In the next stage this uncured surface is fully cured under a nitrogen atmosphere for an improved degree of matting as the thin wet surface film shrinks around the exposed surface particles during inert curing. There are also examples (in particular, the PHOTOGLAZE™ method<sup>(2)</sup> developed by Lord Corp.) of dual cure mechanisms effective when both the pre-cure and final cure occur in an air environment, where the thickness of the uncured layer is controlled in the first stage by adjusting various spectral parameters during cure.

In addition to this overall dual environment curing cycle, the ability to achieve low gloss is also impacted by other parameters such as oxygen concentration, UV intensity, functionality, reactivity and viscosity of the formulation, coating thickness, temperature, matting agent size, and matting agent level. According to Hahn<sup>(3)</sup>, who studied the effect of oxygen concentration during the first stage of curing, for the same UV intensity, low oxygen concentration during the first stage results in a “full cure”, where a high oxygen concentration results in a “no cure”. These two scenarios are not favorable to obtain a low gloss finish. The optimum oxygen concentration, where the cure in the first stage is between full cure and no cure, is necessary to obtain low gloss values. This optimum oxygen concentration required to achieve low gloss also depends on the coating resin sensitivity to oxygen<sup>(3)</sup>. Additionally, the size of the matting agent has an influence on the final gloss. Smaller particle size and higher concentration result in a lower gloss. Hahn<sup>(3)</sup> also reported that the gloss decreases with increased UV intensity in air cure, and Christian<sup>(4)</sup> reported that gloss in the dual cure process decreases with increasing double bond content (moles of double bond per unit resin) of the formulation.

On the equipment side, Skinner<sup>(5)</sup> reported that UV spectral output and the spacing of UV lamps had an effect on gloss. According to Skinner, in the dual cure process, curing with a long wavelength bulb (V type lamp) in the first stage and then followed by short wavelength length (H bulb) in the second stage resulted in a lower gloss than curing with an H and H combination. Also, this author observed that in the particular system studied, the gloss could be further reduced by varying the coating thickness and dwell time between exposures. This

gloss variation with coating thickness was minimized <sup>(5)</sup> by using the V+H lamp combination. Finally, Ferner <sup>(6)</sup> reported that the temperature of the coating and type of the substrate can also have a significant impact on the gloss.

This past work on low gloss radiation curable coatings focused mostly on investigating the influence of various parameters on the gloss individually. In the real world all these parameters need to be controlled in combination. Thus, the objective of this work is to investigate the influence of various parameters as a group on the gloss and determine the dominant factors that influence the gloss control in radiation curable coatings.

## Experimental

### Coating and Application

The composition of the UV coating formulation used in the experiments is given in the following table.

NO	COMPONENT	WEIGHT %	PROPERTIES
1	Urethane Acrylate Oligomer	40.0	difunctional
2	Monomer	44.8	difunctional
3	Matting Agent	15.0	Polyamide; 5 micron
4	Photo Initiator (PI)	0.07%-0.60%	Type 1 (cleavage)

Coatings were applied using a laboratory air knife coater. The air knife pressure and the line speed were controlled such that the obtained coating film thickness was approximately 30 microns. The substrate used in our experiments was a plasticized PVC sheet. Coating application temperature was approximately 150°F.

### UV Curing Process

All samples of coated substrate were cured using the “Dual-Cure” process as explained in the Introduction section. Immediately after coating application onto the substrate, the coating was first irradiated in the air atmosphere using a Fusion UV Systems Inc. Light Hammer™ UV processor that was equipped with 2 rows of medium pressure mercury H-bulbs. This processor contained a conveyor belt with an adjustable speed from 10 fpm to 195 fpm. The lamp output could be varied and the distance between the lamps and the conveyor could be adjusted. Irradiance and energy values were measured using a PowerMap™ Radiometer (EIT, Inc.) Different values of irradiance ( $\text{mW}/\text{cm}^2$ ) and energy dose ( $\text{mJ}/\text{cm}^2$ ) were obtained using different lamp outputs and conveyor belt speeds. Unless otherwise specified, the temperature of the uncured coating entering the first stage UV processor was approximately 80°F.

After the coating was partially polymerized in the first stage under an air atmosphere, it was then polymerized completely under the nitrogen atmosphere using an Aetek Processor (American Ultraviolet Company). Throughout our experiments, the curing conditions in the nitrogen zone were kept the same – specifically  $350 \text{ mJ}/\text{cm}^2$  total nitrogen energy dose with a peak irradiance of  $950 \text{ mW}/\text{cm}^2$ . A BYK Gardener Glossmeter was used to measure the 60 degree gloss.

## Results

The results of the low gloss experiments are presented in Figures 1-3. Figure 1 shows the gloss as a function of UV irradiance during air cure for a coating with 0.07% photo initiator (PI) at an exposed UV energy dose of  $80 \text{ mJ/cm}^2$ . These results show significant gloss variation for different UV intensities in the air zone. As indicated in this figure, for a coating with 0.07% photo initiator, the change in UV irradiance from low to high causes the gloss to drop from a higher value to a lower value. This figure also compares the gloss after the first stage (only air) with the gloss after the second stage (air and nitrogen). The gloss after the second stage follows the same trend with irradiance as the gloss after the first stage, except that the final gloss is consistently lower than the gloss after UV air exposure only. This demonstrates that the final gloss is strongly dependent on the gloss obtained in the first stage.

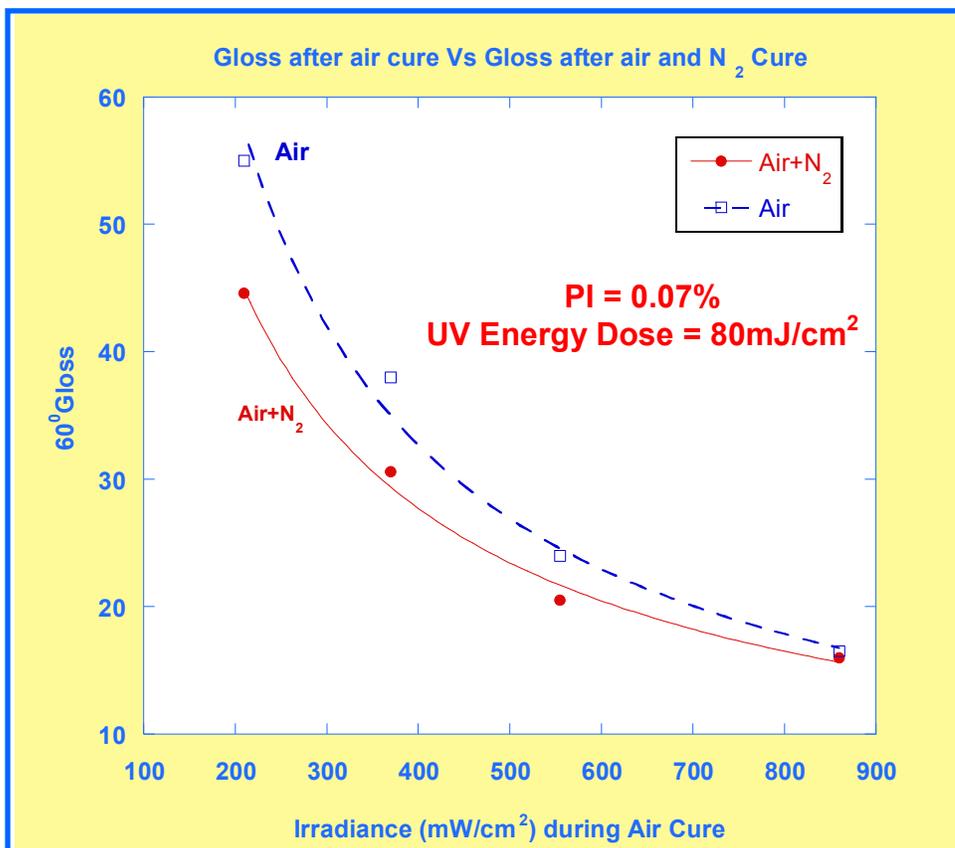


Figure 1: Gloss variation as a function of UV irradiance at low photo initiator level.

The influence of air-cure UV irradiance on the gloss can be readily identified by the above results for a coating with low photo initiator concentration. Interestingly, Fig. 2 shows that the behavior of gloss with irradiance changes dramatically when the photo initiator concentration is increased. At lower photo initiator concentrations, the gloss decreases as the irradiance increases (as in Fig. 1). When the photo initiator concentration is increased from 0.07% to 0.14%, the same trend of negative slope was observed but the irradiance effect on the gloss is reduced. When the photo initiator level in the formulation is increased to 0.2%, the influence of

UV irradiance on the gloss is negligible. It seems that this is the optimum photo initiator level to achieve a low gloss. At this optimum photo initiator level, the gloss is insensitive to UV irradiance while at the same time producing a minimum gloss. Beyond this optimum level, as shown in Fig. 2 for 0.4% and 0.6% photo initiator concentrations, the gloss increases as irradiance increases. This trend is completely opposite to the trend that is observed with lower photo initiator concentrations. More generally, Fig. 2 shows that this whole phenomenon of gloss change with UV irradiance can be divided into three different cases. If the photo initiator concentration is lower than the optimum concentration, then the gloss decreases as the irradiance increases. The slope of the curve is negative. If the photo-initiator concentration is more than the optimum level, then the gloss increases as the irradiance increases. At the optimum photo initiator concentration, the gloss does not change with irradiance.

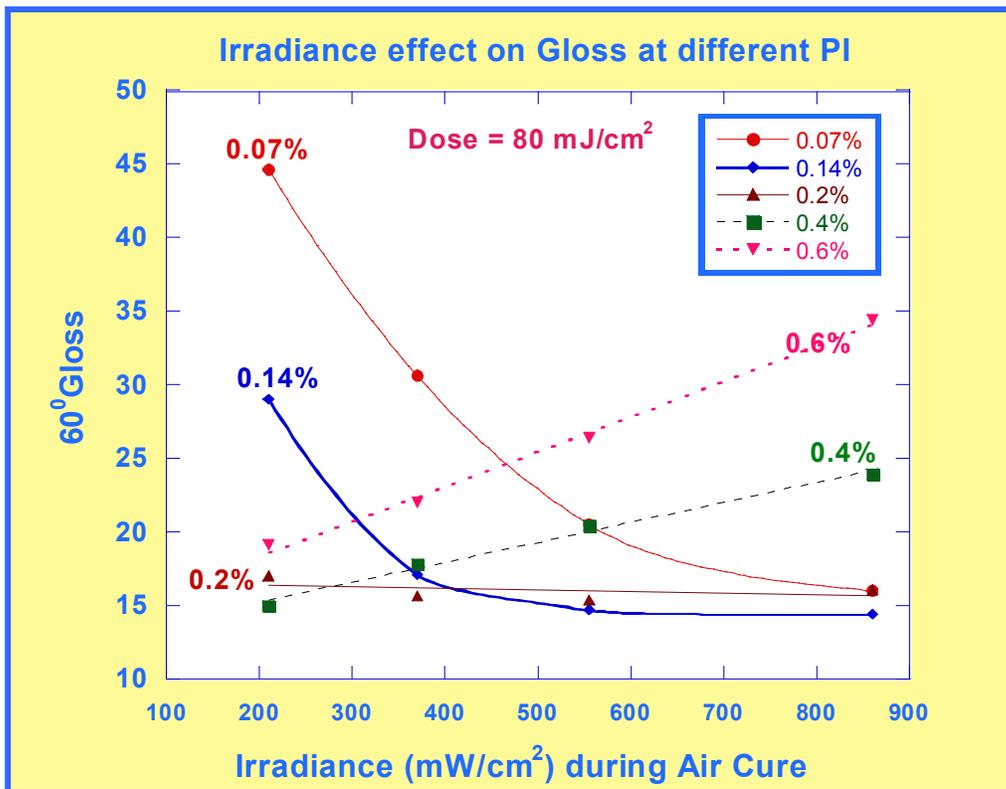


Figure 2: Gloss versus irradiance at different photo initiator concentrations.

Figure 3 (A-C) shows the influence of total air-cure UV energy dose on gloss as irradiance is varied for coatings with low, optimum and high photo initiator levels. As shown in these figures, the total UV energy dose does not affect the general trends of gloss variation with irradiance, but the gloss values drop to varying degrees as the total UV energy delivered to the UV coating increases. In the case of low photo initiator levels, as shown in Figure 3A, UV energy is more influential at lower irradiance than at high irradiance. In the case of high photo initiator levels, as shown in Figure 3C, UV energy is more influential at higher irradiance than at lower irradiance. When the photo initiator level is at optimum level (Fig. 3B), the drop in gloss with increased energy dose does not vary with irradiance.

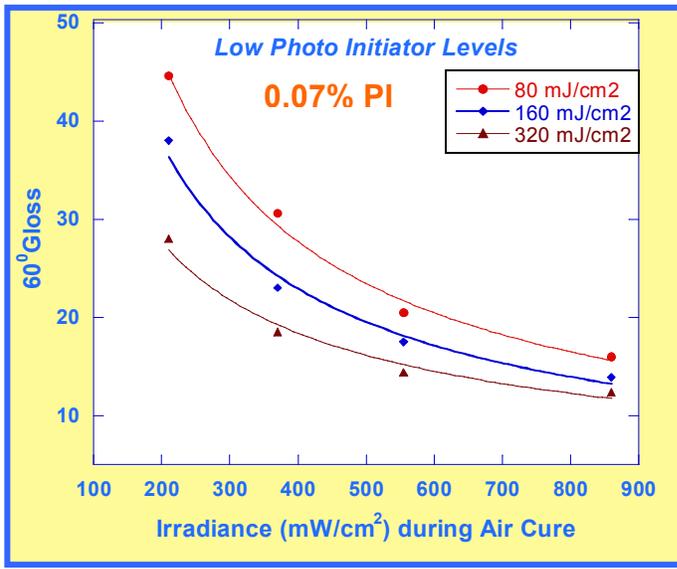


Figure 3A: Impact of UV energy on gloss vs. irradiance for coatings with low photo initiator.

Figure 3B: Impact of UV energy on gloss vs. irradiance for coatings with optimum photo initiator.

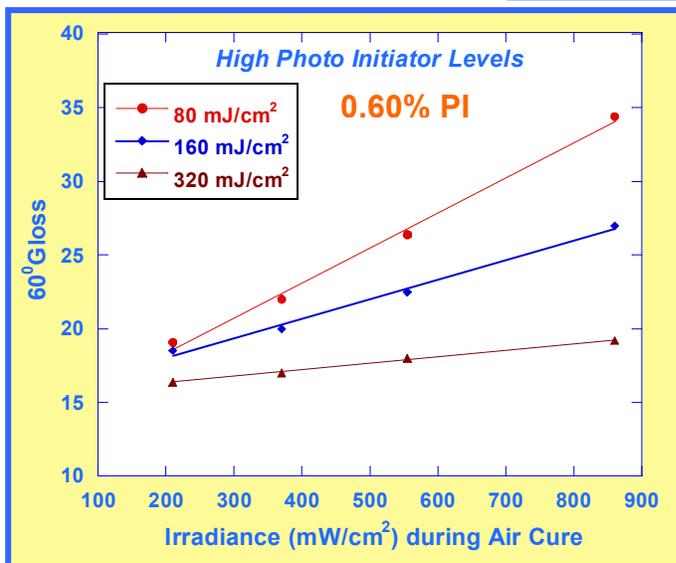
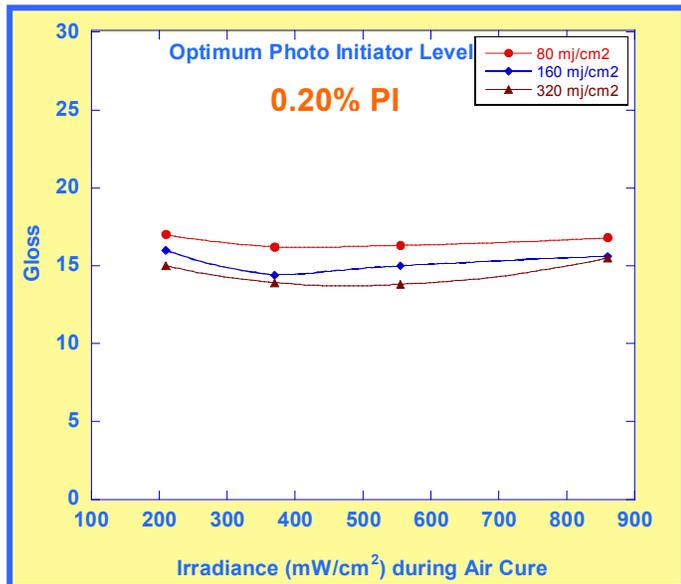


Figure 3C: Impact of UV energy on gloss vs. irradiance for coatings with High photo initiator.

As it is evident from the previous results, giving more energy (photon energy) during the first stage results in gloss reduction. It would be interesting to see the gloss response to UV irradiance at different thermal energies, instead of different photon energies. Figure 4 shows the impact of temperature on gloss variation with UV irradiance. As expected, increased thermal energy causes the gloss to decrease as the temperature of the coating entering the first stage increases. However, even though the gloss reduction is mainly due to the supply of more energy to the coating, the contribution of viscosity towards this gloss drop can not be disregarded. More work needs to be done to decouple this effect.

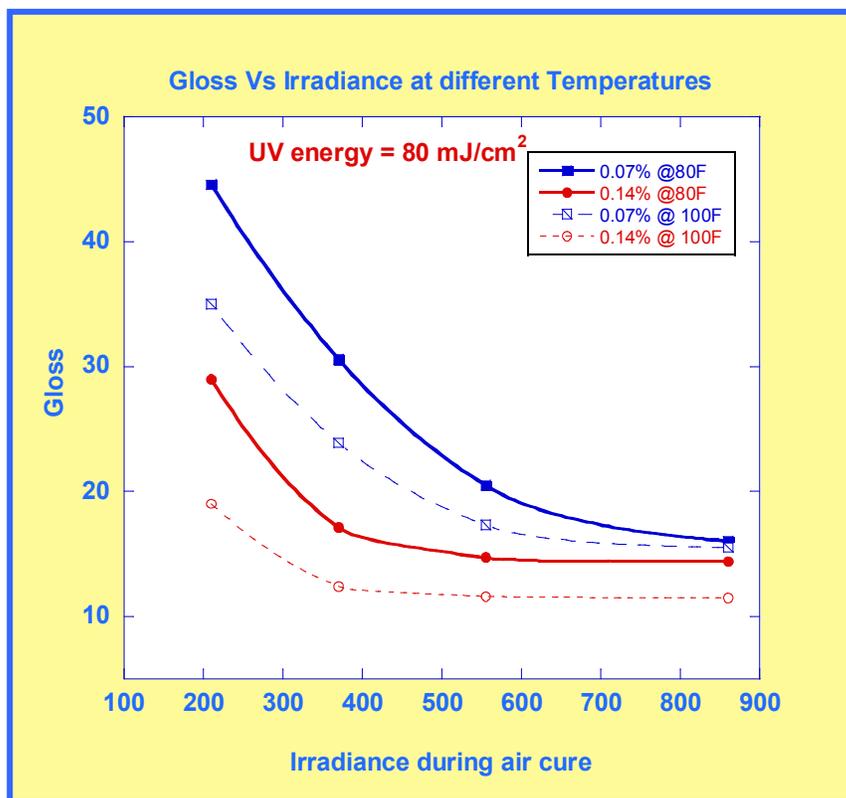


Figure 4: Impact of temperature on gloss variation with UV irradiance.

Finally, an important qualitative observation in our experiments, in general, is that the gloss can be related to tackiness of the coating surface after the first (air curing) stage. For the case of low PI coatings, the coating surface after the first stage is tackier for higher gloss values (lower irradiance) than for the lower gloss values. This indicates less air-stage surface cure at low irradiance, as would be expected for a low PI formulation, and therefore a deep uncured layer that cures to high gloss after UV exposure in a nitrogen atmosphere. Conversely, in the case of coating formulations with high photo initiator concentrations, the tack at high irradiance (where the gloss is high) is small. This suggests that there is excessive surface cure in this case, relative to the optimum amount, which is responsible for high gloss. These observations reiterate the fact that the level of curing at the coating surface after the first stage plays a significant role in achieving low gloss in radiation curable coatings.

## Discussion

The results presented above clearly indicate three general curing regimes, depending upon the level of photo initiator (PI). As was shown in Figures 2 and 3, in the low PI regime, gloss decreases with irradiance whereas in the high photo initiator regime, gloss increases with irradiance. Gloss does not change with irradiance when the level of photo initiator is at the optimum level. Changing UV energy does not change these trends, but offsets the gloss curves. Figure 5 shows how this whole phenomenon can be related back to the thickness of the uncured coating surface, which is determined by the effectiveness of oxygen inhibition during the first stage. It seems that low gloss is obtained when the uncured layer is at its optimum thickness for exposing the maximum amount of matting agent particles at the surface. These exposed particles hold the major contribution in creating a micro rough texture that results in a low gloss surface. If the uncured layer thickness is more or less than its optimum thickness, the resulting gloss will be high. For example, Figure 5 illustrates that when the photo initiator level and the irradiance are low, the bulk coating is not cured enough because of high oxygen inhibition and low intensity and results in a thick uncured coating layer at the surface, thus the gloss is high. This falls into the category of region 1. This occurrence of little cure in the bulk because of high oxygen inhibition can be overcome by increasing the starting concentrations of free radicals. This can be accomplished by high UV irradiances and high photo initiator concentrations. As UV intensities or photo initiator concentrations are increased, the oxygen inhibition is reduced and causes more cure in the coating bulk which in turn, results in a small uncured film thickness at the surface. Low gloss occurs in this case and is represented in region 2. As the photo initiator is increased further, too much cure occurs at the coating surface at high UV irradiance and leaves a very small or no uncured film at the top and causes gloss to increase. This is shown in region 3.

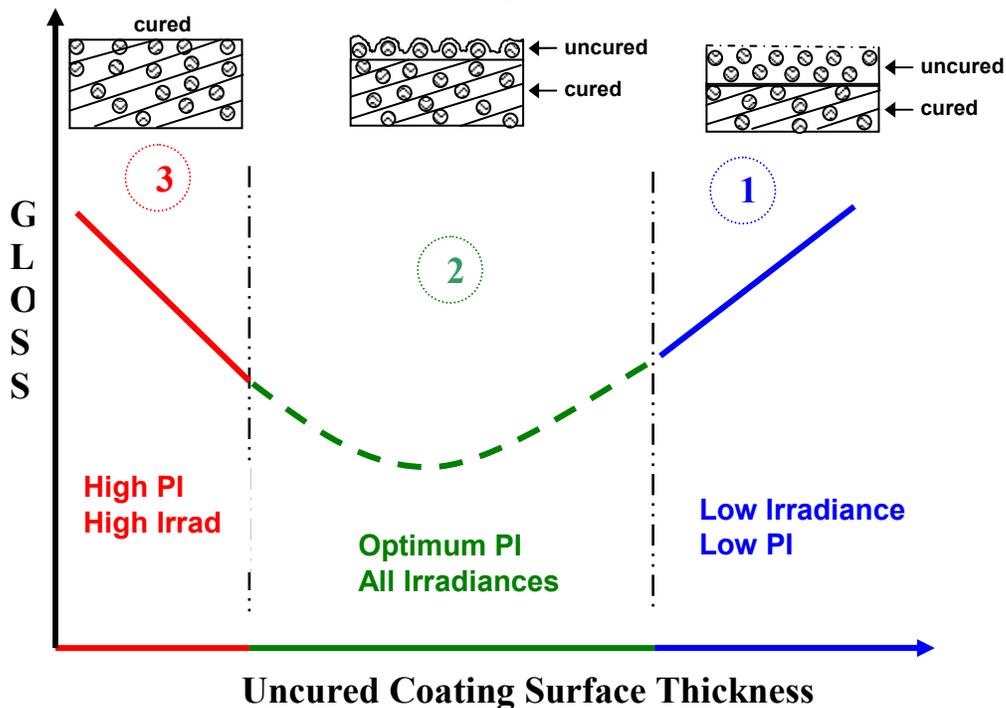


Figure 5: Impact of first stage uncured coating surface thickness on gloss.

Further simplification of this mechanism can be accomplished by introducing a parameter called “absorbed light intensity”. Bao and Jönsson <sup>(7)</sup> proposed “absorbed light intensity” in their study to investigate double bond conversion as a function of absorbed light intensity. The current study uses this concept of absorbed light intensity to simplify and explain the compounding effects of irradiance and photo initiator concentration impact on the gloss. The underlying premise is that the bulk absorbed light intensity ( $I_a$ ) in the coating subsurface will determine the depth to which oxygen inhibition will occur, and thus also control the thickness of the uncured surface layer after air-cure. The absorbed light intensity <sup>(7)</sup> is defined as

$$I_a = K \cdot I_0 \cdot [PI]$$

where  $I_a$  is the absorbed light intensity of the film,  $I_0$  is UV intensity at the surface of the film (measured by radiometry), [PI] is the known concentration of the photo initiator in the coating formulation, and K is a constant. The photo initiator concentration is represented in molarity (M). Absorbed light intensity is expressed as  $[M] \cdot W/cm^2$

Values for  $I_a$  in the present study have been calculated at different irradiances and photo initiator concentrations (values are relative since K is unknown). Figure 6 shows the gloss variation as a function of absorbed light intensity at constant UV energy.

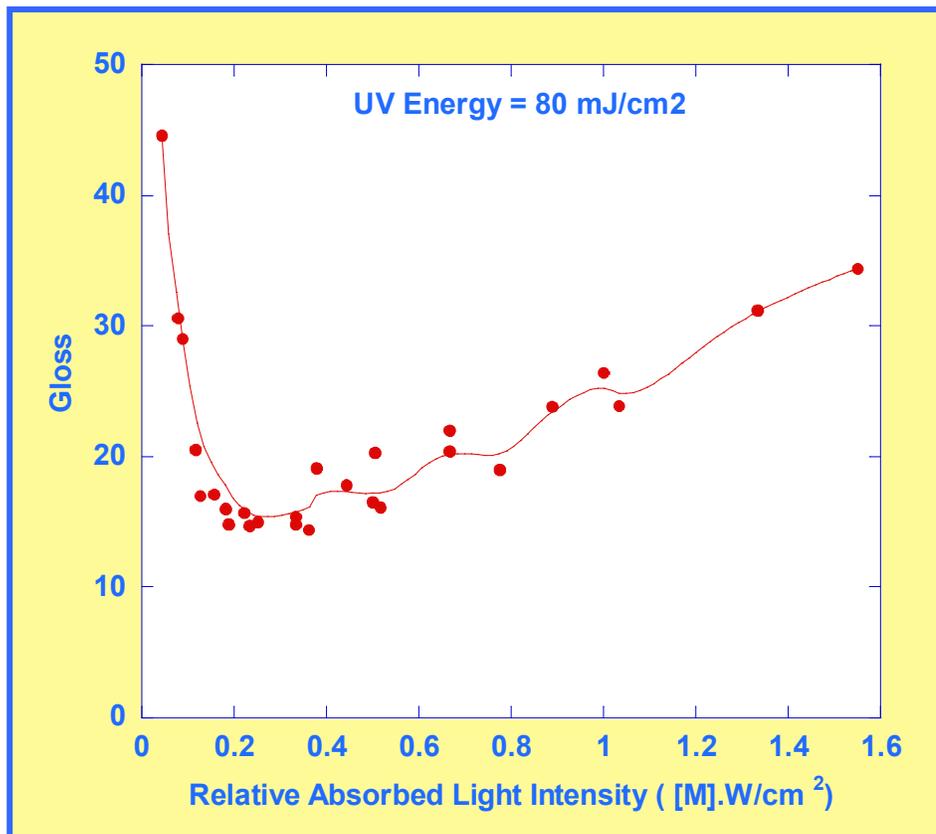


Figure 6: Gloss versus relative absorbed light Intensity after first- stage (air) cure.

As shown in the figure, gloss decreases as absorbed light intensity increases until a certain point and after that gloss increases as the absorbed light intensity of the formulation increases. Based on these results and the mechanism presented in Figure 5, the lowest gloss is obtained at a certain range of absorbed light intensity corresponding to the optimal amount of subsurface (bulk) cure, which in turn controls the thickness of the uncured surface layer for maximum exposure of the matting agent particles. Once the optimal  $I_a$  is known, the photo initiator level and irradiance can be balanced to maintain this optimal  $I_a$  and ensure the desired low gloss. The same trend would be expected to follow even at different total energies, although the gloss versus  $I_a$  relationship would be expected to be offset to lower gloss for higher total energy.

## Conclusions

This study illustrates the influence of UV irradiance, UV energy, photo initiator concentration, and curing temperature on radiation curable coating gloss. The most determining factor to achieve low gloss is the ability to obtain the optimum uncured coating thickness at the surface after the first stage pre-cure in air. Air-cure UV irradiance has an impact on the gloss, but this influence depends on the concentration of the photo initiator in the coating. At low photo initiator concentrations, low gloss is obtained at high irradiance. At high photo initiator concentrations, low gloss is achieved at low irradiance values. The gloss is somewhat insensitive to irradiance at optimum photo initiator concentrations. A parameter called "Absorbed Light Intensity" is proposed to explain the compounding effects of irradiance and photo initiator concentration on the gloss. Use of this parameter shows that the gloss is higher at low absorbed intensity values. As the absorbed light intensity is increased further, the gloss drops to a minimum before it starts increasing. The lowest gloss is obtained at a certain range of absorbed light intensity corresponding to the optimal amount of subsurface (bulk) cure, which in turn controls the thickness of the uncured surface layer for maximum exposure of the matting agent particles. This illustrates that the photo initiator concentration and UV irradiance need to be well balanced to achieve low gloss.

In this investigation it is further illustrated that UV energy has a significant influence on the gloss. For coatings with low photo initiator concentrations, UV energy is more dominant at lower irradiances. When photo initiator concentrations are high, UV energy is more dominant at higher irradiances. In these regimes where total energy and irradiance both significantly affect gloss, process control must include the measurement of both parameters. The universal dependency on UV energy dose also makes it unlikely that any regime exists where effective process control could be managed with irradiance alone (at least for thin UV clear coats). However, it appears that when the photo initiator level is optimized, the gloss is independent of irradiance. In this scenario, process control can be effectively managed with total energy dose alone.

## Acknowledgements

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