

## **HARDNESS OR FLEXIBILITY**

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### **ABSTRACT**

#### **Hardness or Flexibility...What Works?**

One of the most daunting challenges when developing a scratch resistant UV/E-Beam curable hard coat is balancing the properties of hardness and flexibility while maintaining good weathering properties. Too much hardness can lead to a coating that is brittle with limited substrate usage. Increasing the flexibility leads to a coating with greater substrate usage but with compromised scratch resistance. Due to this relationship of hardness and flexibility, significant increases in performance properties are very limited. The impediment for increasing weathering resistance while maintaining scratch resistance resides in the molecular structure of the oligomers and monomers used in the coatings. This paper will examine the hardness, flexibility, and weathering resistance of current technology along with their limiting factors. Further, a new performance product is characterized which addresses many of the current technologies short comings.

### **INTRODUCTION**

Typically, UV curable scratch resistant hardcoats are achieved by utilizing penta- and hexa- functional acrylate oligomers. Upon cure, these materials exhibit a coating that has exceptional hardness and scratch resistance. The major drawbacks to these materials are poor weathering properties, brittleness, and high shrinkage.

Poor weathering properties are a very significant area of concern because applications such as hardcoats for automotive forward lighting and window films typically require at least 5 years outdoor durability. The weathering properties of penta- and hexa- functional acrylate oligomers are not, by themselves, sufficient for most commercial applications. Failure can be seen early in accelerated testing in QUVA (<500 hours) and Florida exposure (<6 months). These failures tend to result from surface defects such as pinholes, mosaic patterns, cracks, and as well as a drop in gloss. Some of the weathering problems can be linked to hydrolysis of the polyester backbone, which makes up many of the multi-functional systems. Upon hydrolysis, molecular weight is decreased, and the coating becomes embrittled.

Also, highly functional systems are difficult to fully polymerize due to vitrification at low double bond conversion. When these systems are exposed to high sunlight weathering conditions, they can continue to convert and crosslink. However, this process is very slow. This additional crosslinking leads to additional shrinkage and a more brittle coating. Even under initial cure conditions, the brittleness of these coatings in conjunction with their significant shrinkage on cure can be problematic. Evidence of this can be seen in the fact that films made from highly functional acrylates are extremely difficult to prepare at over 10 microns thickness, as they tend to flake and crack upon cure.

One option the formulator has to mitigate these problems is to blend in more flexible and better weathering oligomers or monomers. The limiting factor in oligomer and monomer selection is due to performance needs. A number of oligomers are available that have better weathering properties than penta- and hexa- functional oligomers, but these materials tend to be di- and tri- functional in nature, and are known more for their toughness and flexibility than scratch resistance. Significant amounts of monomers, tri-functional and higher, would be needed to achieve hardness similar to penta- and hexa- functional oligomers. Monomer selection is limited due to hardness and weathering requirements. Certain di-functional monomers tend to weather well, but crosslink density is decreased thus lowering surface hardness. With tri-functional or higher monomers, hardness is maintained but weathering properties are compromised.

This paper describes the properties of a next generation performance product for hard coat applications. It is compared against highly functional urethane acrylate and polyester acrylate materials currently sold into this market. An excellent weathering urethane acrylate is also included for comparison.

## **MATERIALS AND FORMULATIONS**

The following commercially available materials are commonly used when formulating UV curable scratch resistant hardcoats. These materials will be used to compare and contrast a second generation performance product.

- Urethane Acrylate A is a di-functional aliphatic urethane characterized by its excellent weatherability and flexibility.
- Urethane Acrylate B is a hexa-functional aliphatic urethane characterized by excellent hardness and scratch resistance.
- Polyester Acrylate A is a penta-functional oligomer characterized by excellent hardness and scratch resistance.
- Performance Product A is an experimental performance product

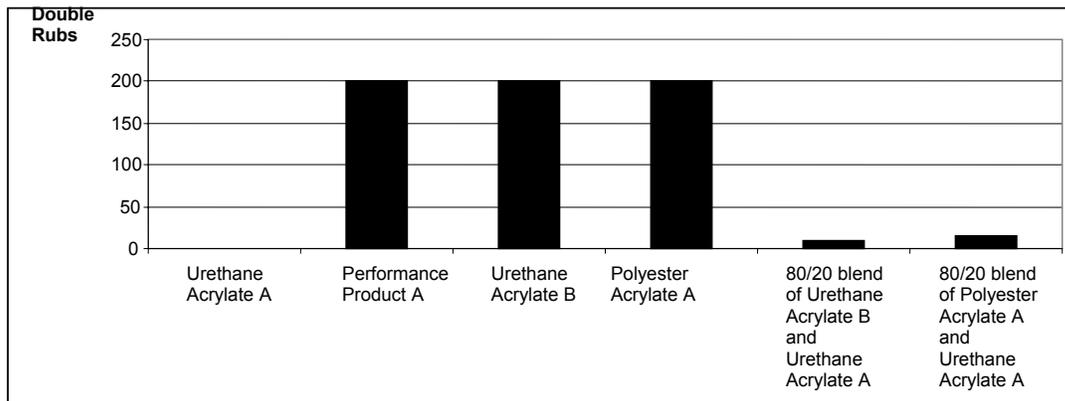
Each material was diluted in 50% Isopropyl Alcohol (IPA). Two percent by total weight of the photoinitiator 1-hydroxy-cyclohexylphenyl-ketone was added to each formulation. The formulations were applied to their respective substrates using the number six wire wound bar. After application, the substrate was placed in an oven at 50°C for 5 minutes. After flashing off the solvent, the substrate was allowed to cool for 2 minutes before cure. Curing was performed on a 600 watt/in Fusion UV unit equipped with two “H” bulbs at 100% power. Each formulation was exposed to a total energy density of 800 mJ/cm<sup>2</sup>.

## **TESTING**

The bulk of the testing performed in this study focused on scratch resistance and haze development as a result of abrasion. Steel wool scratch resistance was measured using 0000 steel wool wrapped around a 2-lb ball peen hammer. Failure was recorded as the number of double rubs required to scratch the coating. Haze development was measured after abrading the coating with a Taber ® Industry 5150

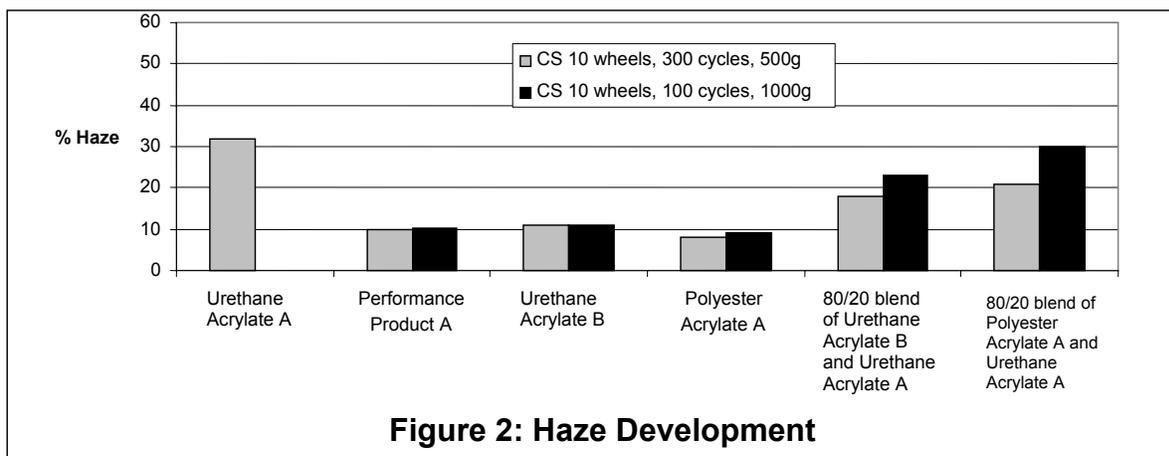
equipped with CS 10 wheels and 500g or 1000g weights. Haze was measured using a BYK haze meter after 300 cycles for 500g weights and 100 cycles for the 1000g weights. Scratch resistance and haze measurements were measurements on Mylar® film, a 2-mil polyester film, and polycarbonate. Accelerated weathering was measured using a QUV/basic equipped with UVA-340nm bulbs. Each formulation for weathering was applied as a topcoat over white super durable powder coated aluminum panels. The cycle times were 8 hours for the light at 60°C and 4 hours for the dark/condensation at 55°C. Impact was measured on B-1000 steel panels using a BYK Gardner impact test equipped with a 2-lb weight. Gloss measurements were made with a BYK Gardner micro-TRI-gloss, and color measurements were made with a BYK Gardner color guide.

## RESULTS



**Figure 1: Steel Wool Scratch Resistance**

In Figure 1, no difference in #0000 steel wool scratch resistance could be seen when comparing Performance Product A, Urethane Acrylate B and Polyester Acrylate A. However, measurements were very difficult on substrates coated with Urethane Acrylate B and Polyester Acrylate A as the coatings easily cracked when handled and during testing. In addition, curl was significantly increased when coating thickness increased for Urethane Acrylate B and Polyester Acrylate A. These problems were not seen when using Performance Product A. In work not shown, it was determined that blending of Urethane Acrylate A with either Urethane Acrylate B or Polyester Acrylate A can produce a material that has good steel wool scratch (100-150 steel wool double rubs), but only about 10-15% of di-functional material can be added. When the di-functional oligomer content reaches 20%, steel wool scratch resistance drops significantly. Due to the low cross-link density of Urethane Acrylate A, steel wool scratch resistance was zero. The coatings based mainly on Urethane Acrylate A were scratched by simply placing the 2-lb hammer, wrapped with steel wool, on the substrate.



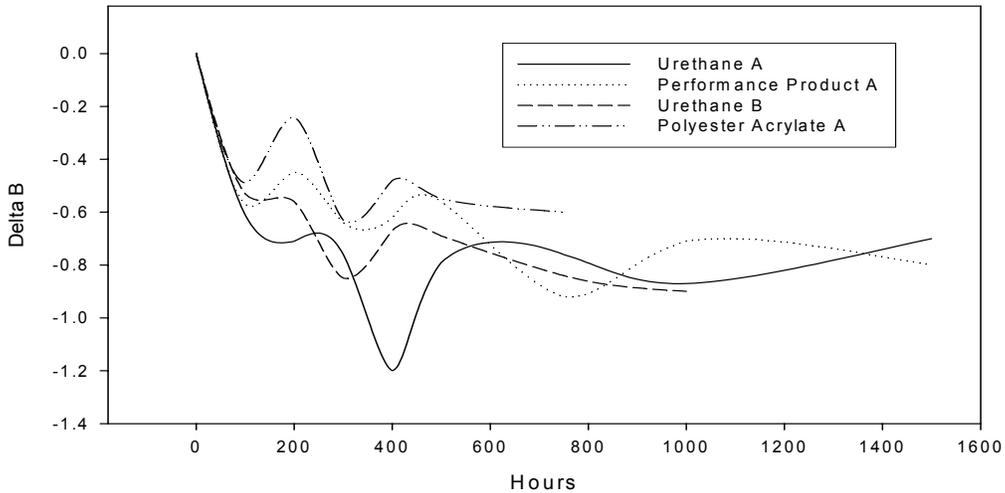
**Figure 2: Haze Development**

Figure 2 examines haze development under two test conditions after 300 cycles with 500 gram weights and after 100 cycles with 1000g weights. Haze numbers were

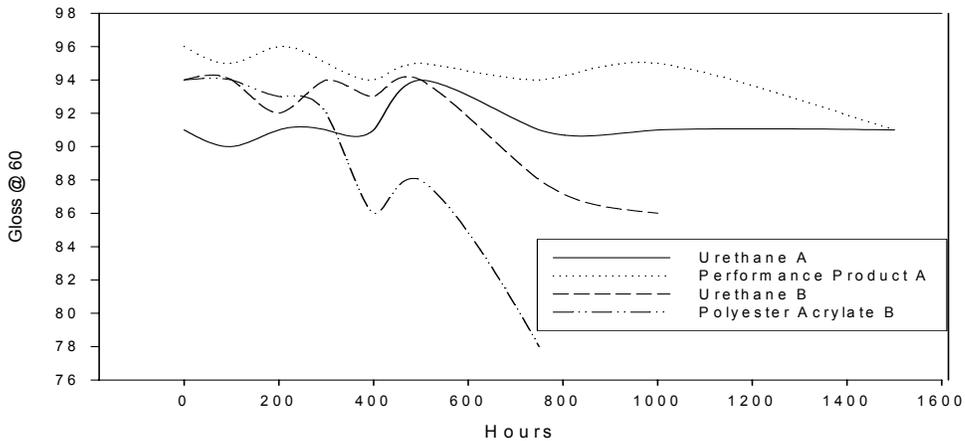
very consistent for all the substrates tested under both test conditions. The standard deviation was less than 0.5% (based on 20 reading per sample). Blending of di-functional (Urethane Acrylate A) materials with penta- (Polyester Acrylate A) and hexa- (Urethane Acrylate B) functional oligomers produced haze numbers between 15 - 20% when the di-functional oligomer makes up only about 10-20% of the formulation after 300 cycles and 20-30% haze after 100 cycles. Formulation blends based mainly on Urethane Acrylate A have haze numbers that range from 30-60% due to its low cross-link density (haze numbers over 30% were not listed for Urethane A blends due to the lack of coating remaining on the substrate). Haze development, for 1000g and 100 cycles, could not be measured for any coatings based mainly on Urethane Acrylate A as the coating was removed completely by the completion of the 100 cycles. Performance Product A, Urethane Acrylate B and Polyester Acrylate A showed only a slight difference in haze development between the two test conditions.

Penta-functional Polyester Acrylate A shows the least haze development under either condition. However, Performance Product A still meets met commercial specifications (<10% haze development under conditions tested). Hexa-functional Urethane B also performed well, but did not quite meet the maximum 10% haze specification. Urethane Acrylate A did not compare well to penta- and hexa-functional oligomers due to its low crosslink density. Blending of Urethane Acrylate A with other penta- or hexa- functional materials such as Urethane Acrylate B or Polyester Acrylate A did reduce haze development, but those numbers were only to twice that of Polyester Acrylate A. In data not shown here, it was determined that to achieve haze numbers below 20%, only 5-10% of di-functional oligomers can be used. At 5% levels or less, haze development was very similar to Urethane Acrylate B, and between 5 and 10% levels, haze development increased to between 12-20%.

Figures 3 and 4 examine the color and gloss changes of the coating during accelerated weathering exposure in QUV A.



**Figure 3: QUVA Exposure (Delta B)**



**Figure 4: QUVA Exposure (Change in Gloss)**

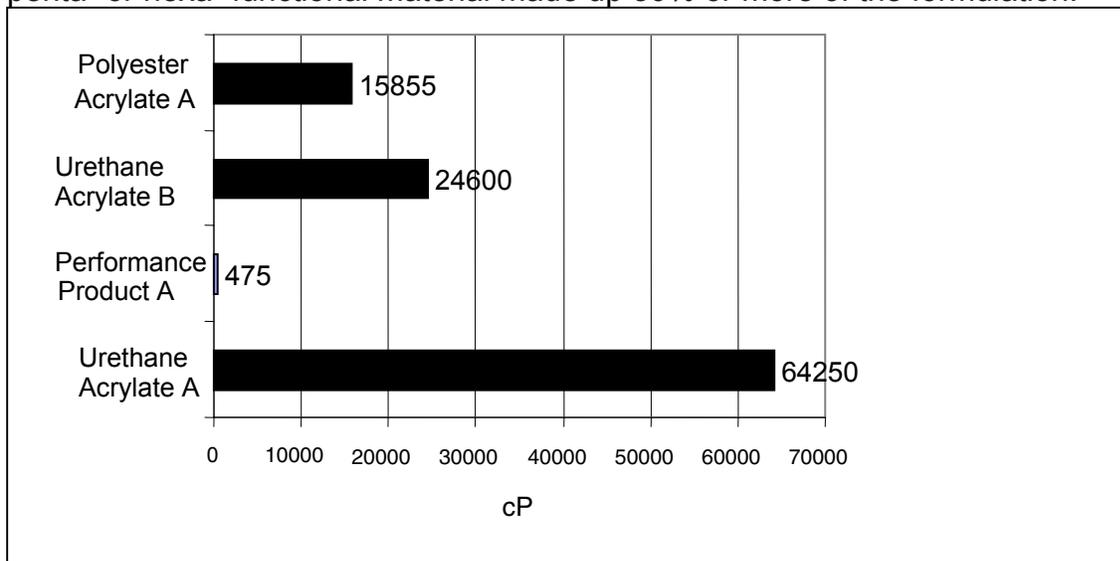
A significant change in color was observed during exposure. After reviewing the data, the color change seen in Delta E (not shown) was dominated by changes in Delta B (Figure 3). Delta B showed a bleaching effect between 200 and 600 hours of exposure. During exposure, the bleaching effect did not show any correlations with performance of the coating (visual defects). However, large and/or drastic changes in gloss (Figure 4) did correlate with the coating performance.

Polyester Acrylate A had a significant drop in gloss after 200 hours. During that time, surface defects started to form (pinholes, cracks, and mosaic patterns). This was also observed at the 500 hours mark for Urethane Acrylate B. Performance Product A shows its largest drop in gloss around 1200 hours, around the same time surface defects started to form. Urethane Acrylate A gloss remained very consistent throughout exposure and no visual defects were observed during exposure. When comparing all the weathering data, none of the coatings based on penta- or hexa-functional oligomers survived more than 700 hours in QUV-A. Blends of di-functional oligomers with Urethane Acrylate B, Polyester Acrylate A and other penta- and hexa-functional materials performed identically to the penta- and hexa-functional oligomers.

**Table 1: Impact Resistance**

	Urethane Acrylate A	Performance Product A	Urethane Acrylate B	Polyester Acrylate A	90/10 and 80/20 blends of Urethane Acrylate B and Urethane Acrylate A
Direct Impact (in*lbs)	>80	14 30	<2	<2	<2
Failure Mode	none	14 – whitening 30 – cracking	cracking	cracking	cracking

In Table 1, impact resistance, as measured by direct impact, was poor for penta- and hexa-functional oligomers. Any impact, as low as 2-in\*-lb, caused the coating to crack and flake-off when testing Urethane Acrylate B and Polyester Acrylate A. With Performance Product A those effects were not seen until the coating was exposed to 30-in\*lbs of force. The failure at 14-in\*-lb was due to whitening of the coating. Urethane Acrylate A had outstanding impact resistance due to its low cross-link density. Blends of di-functional oligomers with penta- and hexa-functional materials had similar properties as Urethane Acrylate B and Polyester Acrylate A when the penta- or hexa-functional material made up 80% or more of the formulation.



**Figure 5: Viscosity of Neat Acrylated Oligomers**

Low viscosity is a desirable attribute for a product as it allows greater formulation and application latitude. Formulating with undiluted oligomers such as Urethane Acrylate B and Polyester Acrylate A, require significant amounts of solvents or monomers to achieve a workable application viscosity. Solvents are most often used due to the limited number of monomers available for use. Monomer selection is limited by the weathering and hardness requirements for hardcoats. Monomers that impart hardness tend to have poor weatherability, and monomers that weather well tend to impart lower crosslink density. These problems are not associated with solvents because they are removed through drying ovens before cure. However, most solvents increase the coating's VOC content.

From Figure 5, it can be seen that Performance Product A 's viscosity at 25°C is much lower than that of Urethane Acrylate A, Urethane Acrylate B, and Polyester Acrylate A. The viscosities of blends of Urethane Acrylate B and Polyester Acrylate A with Urethane Acrylate A were intermediate between the viscosities of Polyester Acrylate A and Urethane Acrylate A. The lower viscosity of Performance Product A translates into a coating less influenced by monomer content, or lower VOCs due to lower dependency on solvent for viscosity reduction.

## **CONCLUSION**

Commercial products used for hard coat applications perform well in scratch resistance but have poor weathering properties, are brittle and are high in viscosity. A second generation product has been developed that addresses all the shortcomings of typical materials. Performance Product A offers: significantly lower haze development in abrasion tests, better long-term weathering, higher impact resistance, and lower viscosity than the current offering of commercial products. Performance Product A is a new product that overcomes the limitations associated with the common penta- and hexa- functional oligomers. Performance Product A represents an opportunity to unify flexibility with hardness.