

# The Next Generation of Weatherable Hardcoats

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## **Abstract**

Plastic substrates such as polycarbonate and acrylic often have been considered or used in a variety of applications as replacements for glass. Plastics can offer excellent impact resistance and clarity and most attractively, they allow for design freedom and thus allow for some very aesthetically appealing appearances that were once inconceivable. Despite the many benefits that plastic offers, they have a major drawback in that they don't always provide the desired degree of chemical, scratch, mar and abrasion resistance and in the case of polycarbonate, weatherability.

## **Introduction**

One of the revolutionary markets where plastic has favorably replaced glass is automotive lighting, where polycarbonate has a stranglehold. To meet the demands of the polycarbonate headlamp industry, in the early 1980's, thermally cured silicone abrasion resistant hardcoats were developed. These coatings are still in existence today because they continue to provide some excellent performance properties, but they often require a primer layer in order to gain adhesion to the polycarbonate. This can be a major drawback not only because it adds a second step to the coating application process, but it also adds extra drying time to an already long cure cycle. As coating technologies evolved, UV technology quickly broke into the headlamp market with direct adhesion systems that not only eliminated this extra coating step, but also increased throughput by shortening cycle time. These UV systems have been a dominate mainstay for over 15 years with both spray and flowcoat technologies available.

In recent years, OEM standards have changed greatly, and the envelope of design and performance capabilities continues to be pushed. Among these revolutionary designs are large lenses that wrap up on top of the vehicle (Figure 1). This model creates more direct exposure areas which promotes more rapid deterioration of the hardcoat. A second design is decorative or functional two shot molding that gives a two tone effect (Figure 2). This two shot design can impart more stress in the molded part and also, it demands the hardcoat to be more thermally stable. These innovations affect both plastic and coating, but many feel that plastic technology has evolved much faster than coating technology to meet these performance criteria, and thus, there is a need to take hardcoat performance to the next level. Furthermore, rising fuel costs, weight reduction initiatives and other safety requirements have made plastic substrates attractive for applications outside of lighting including pillar posts, sun roofs, and windows. Most all of these applications require a protective hardcoat for long term performance.

Figure 1: Horizontal Lens Design



Figure 2: Two Shot Mold Process



## History of UV Hardcoat Technology

As a quick synopsis, current UV hardcoat technology evolved based on the principle that hardness is best achieved through the use of high functionality oligomers and monomers. However, due to their base structure and the structural strain and immobility incurred when they react during UV cure, these materials are more susceptible to UV degradation, eventually microcracking, hazing, or delaminating upon prolonged exposure. Thus, with these hardcoat systems, it is difficult to achieve long term weatherability especially in extreme exposure conditions. Therefore, improving the weatherability aspect of UV hardcoats while still maintaining the required high scratch and abrasion resistance properties is a continual challenge. Traditionally this challenge has been met through techniques such as blending in small amounts of more durable oligomers, monomers, conventional acrylic resins, or inorganic components. Adding higher than recommended levels of stabilizers can also prolong hardcoat failures. However, these techniques also have performance limitations or more often, application limitations, and thus, taking UV hardcoat technology to the next level requires a change at the most basic structural level – resin technology.

## New Product Design

### Establishing an Objective

As with any new product development, the first step is to determine what the final product must look like, and a key to this is determining the critical characteristics as defined by a very knowledgeable base of global customers and OEMs. Features of current hardcoat systems that cannot be sacrificed are not only performance related – clarity, chemical, scratch & abrasion resistance – but maybe more importantly, handling & application related – long term stability, ease of application by spray or flowcoat and recyclability.

Apart from these key requirements, the emphasis is on the need to improve weatherability. The new performance target must significantly exceed the current standard of 3 years, which is typically evaluated in a hot, humid environment like Florida and a hot, arid environment like Arizona – both of which have very different effects on coating and plastic. The desired performance standard is a minimum of 5 years with an ultimate target of 10 years at exposures of both the current standard of 45° and 5° south; this would more closely simulate wrapping lens designs or roof top applications. In order

to determine improved performance in a more timely fashion, accelerated test methods such as xenon arc and carbon arc were used as critical test criteria (Table 1).

Test	Method	Target
Florida Exposure	5° south facing	> 5 years
Arizona Exposure	5° south facing	> 5 years
Xenon Arc	SAE J1960 (borosilicate)	> 5000 hours
Sunshine Carbon Arc	Continuous Method	> 3000 hours

Table 1 - Weathering Targets for Next Generation Hardcoat

## Experimental

### Resin Screening Experiments

To achieve the objectives for the next generation UV hardcoat, initially, all technical avenues were considered. However, the strengths of current systems and knowledge gained during its lifecycle were also kept at the forefront. The first step of this hardcoat product development was at the most basic level and involved numerous DOE studies with the primary aim to baseline current hardcoat resin materials vs. other standard and novel resin chemistries. Through this technique, urethane technology proved to be a leader in performance, but one phenomenal finding was that several novel acrylate resins and blends, minus any stabilization additives, exhibited durability equal to or better than current technology that had been fortified with protective stabilizers. Plus, these next generation materials still maintained a high level of scratch and abrasion resistance (Figure 3 & 4).

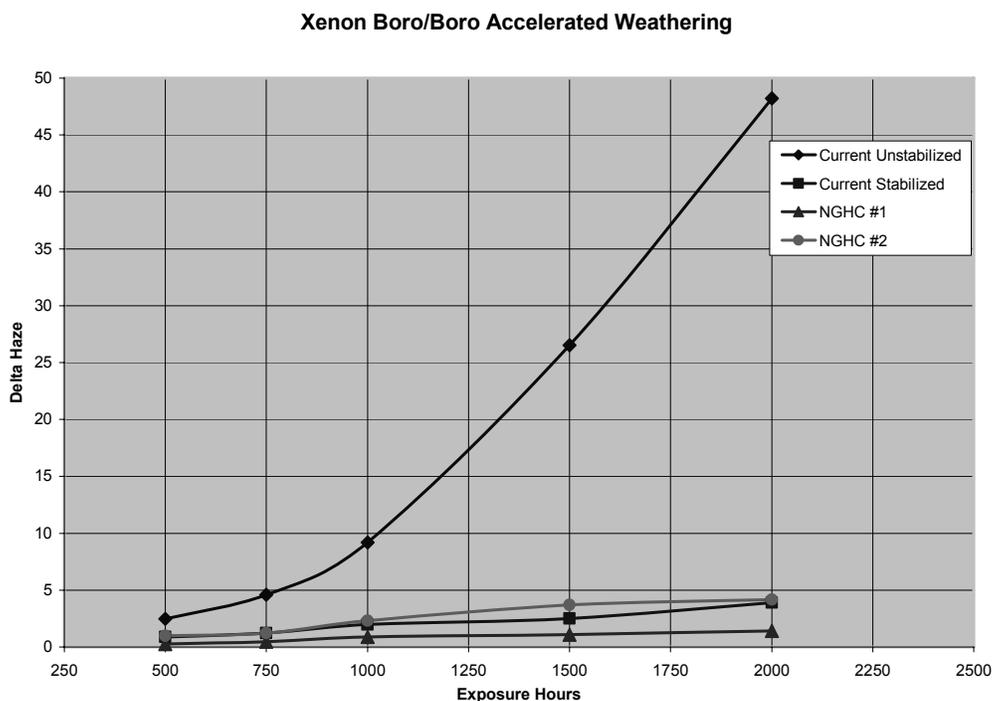


Figure 3: Xenon Arc Performance of Current Hardcoat Technology (Unstabilized & Stabilized) vs. Next Generation Hardcoat Technologies (Unstabilized)

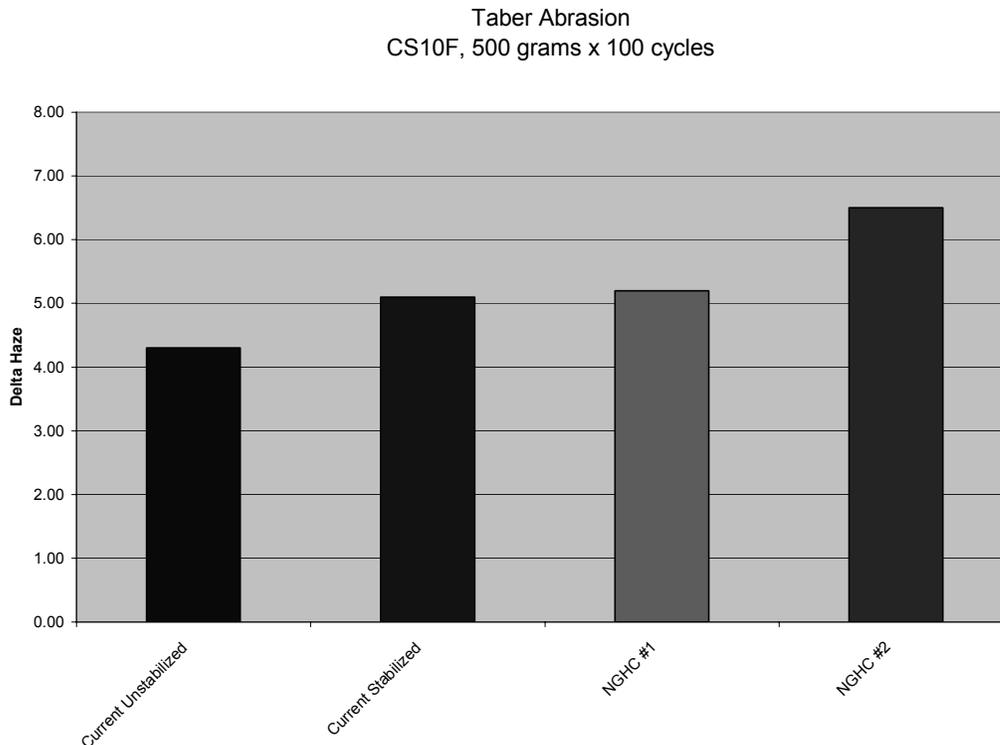


Figure 4: Abrasion Performance of Current Hardcoat Technology (Unstabilized & Stabilized) vs. Next Generation Hardcoat Technologies (Unstabilized)

Additional DOE screenings with these technologies focused on identifying the effect of variations to the starting materials on end performance. Some of the variations that were considered – such as backbone type and molecular weight – had fairly predictable results. However, other variations – such as polyol branching – proved more interesting.

### ***Photoinitiator and Stabilizer Experiments***

The second step in product development focused on the photoinitiator and stabilizer packages. Although these components make up only a small portion of the formulation, they have a considerable impact on overall performance. In any UV formulation, it is critical to choose photoinitiators that match the requirements of cure speed, optimal cure throughout the film, part geometry, and equipment capabilities. However, in exterior applications, this becomes a bit more complex for several reasons.

Foremost, extended UV light exposure leads to photo-oxidation of the base polymer structure. Stabilizing the coating and thus slowing the onset of this phenomenon can be done by using UV absorbers which filter out certain wavelengths of UV light and hindered light amines which act as free radical scavengers. A combination of both is necessary for optimal performance. However, because photoinitiators trigger the cure cycle by absorbing UV light, overlap of UV absorbers and photoinitiator absorbance spectra must be minimized or else overall performance – namely surface hardness, adhesion and extended durability – may be sacrificed primarily due to cure retardation. Thus in the screening process both photoinitiator and stabilizer package must be evaluated concurrently.

### Photoinitiator and UVA Absorbance vs. UV Bulb Output

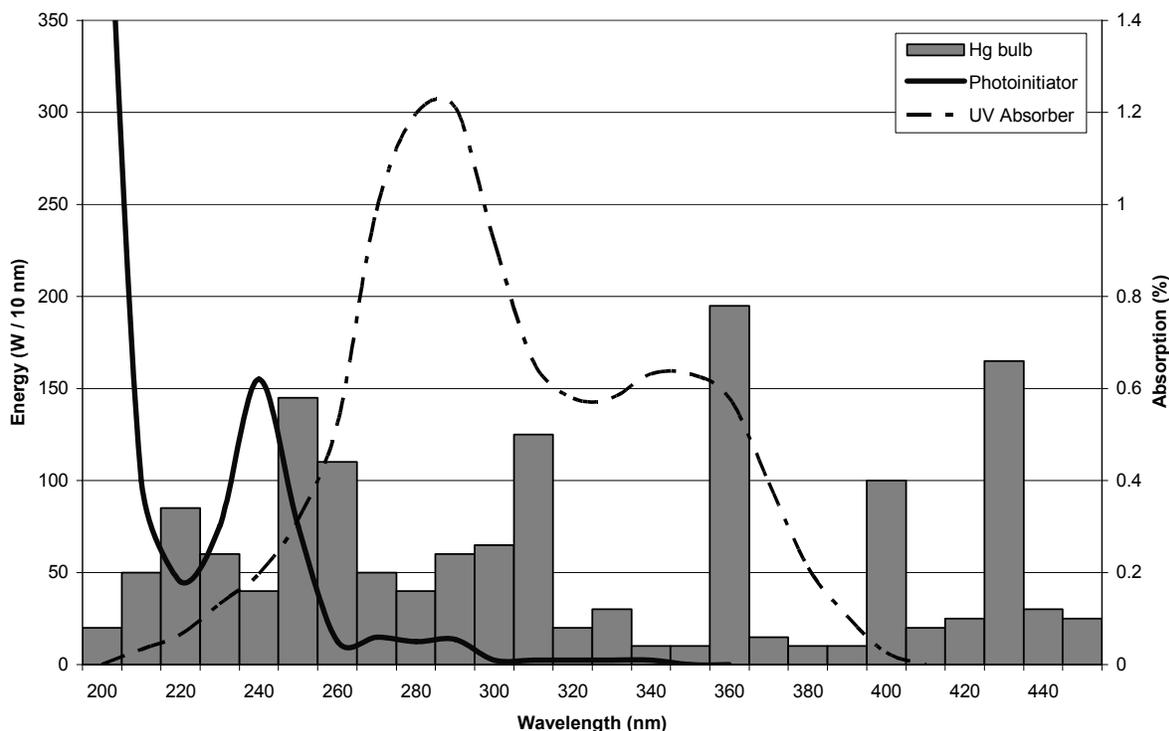


Figure 5: Illustration of absorbance of  $\alpha$ -hydroxy ketone photoinitiator and hydroxyphenyl triazine UVA vs. energy output of standard mercury vapor UV bulb.

From an evaluation standpoint, failure mode varies depending on substrate. On coated plastic systems, there are two primary modes of failure. First, the coating can have an intrinsic weakness, and the film will microcrack, craze, or haze upon prolonged exposure. Secondly, there can be an inherent weakness of the plastic, and it will discolor or promote loss of coating adhesion (Figure 6). In this study, evaluations were conducted on polycarbonate due to its high susceptibility to UV degradation. Since previous studies indicate that the next generation resin system is quite robust, adhesion loss is more likely to be the mode of failure in this experiment. Adhesion loss occurs because prolonged exposure to the UV rays from the sun degrades the top layer of polycarbonate causing it to become a much weaker interface which in turn results first in loss of adhesion by a crosshatch test and then finally total delamination of the film layer. UV absorbers and hindered amine light stabilizers assist in the prevention of this phenomenon. The concentration of UVA necessary to protect the system is dependent on the film build, but because UV absorbers also can undergo photodegradation in outdoor exposure conditions, there is also a maximum load level.

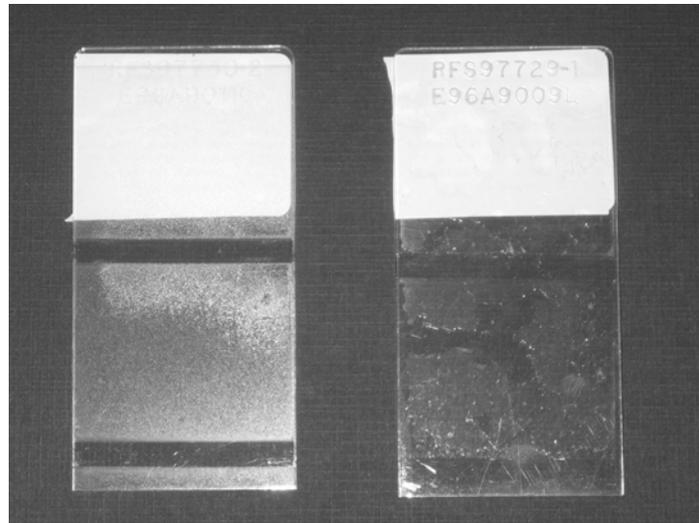


Figure 6: Panel on Left exhibits microcracking (coating failure) while Panel on Right exhibits loss of adhesion (substrate failure)

To test this in the new hardcoat system, various accelerated weathering evaluations that exploit different wavelength weaknesses were carried out. Several different families of UV absorbers – which vary in structure, wavelength absorbance, and coefficient of extinction – were incorporated into the system at various levels and then the delta yellowness, delta haze, and adhesion of these systems, as well as the surface hardness were monitored over exposure time. Additionally, FTIR and pyrolysis analysis were done to examine changes in the bulk film. In summary, at low UVA levels most of the stabilized systems exhibited good yellowness and haze readings but premature adhesion loss was observed, indicating that the UVA load was less than required for the target film build range. As the UVA levels increased, adhesion was improved, but often at the sacrifice of some surface hardness. As the UVA levels were increased further, signs of degradation such as surface hazing and cracking or extreme loss of surface hardness occurred (Table 2). From the accumulated data, careful consideration had to be taken in order to match the photoinitiator package and UVA as not to severely sacrifice surface hardness, yet maintain proper protection of the polycarbonate. Ultimately, a combination of good surface cure photoinitiators such as those in the  $\alpha$ -hydroxy ketone family and UV absorber materials from the triazole or triazine family were determined most adequate in providing protection while maintaining good hardness.

System	Photoinitiator Load	UVA Load	Appearance (O = Pass, X = Haze)	Hardness (0-5 Rating)	Adhesion (% Retention)
A	LOW	LOW	O	1	0
B	HIGH	LOW	O	0	20
C	LOW	MEDIUM	O	2	75
D	HIGH	MEDIUM	O	1	100
E	LOW	HIGH	X	3	100
F	HIGH	HIGH	X	2	100

Table 2: Effect of UVA and PI load level on Next Generation Hardcoat System after Long Term Xenon Boro/Boro Exposure

## ***Additional Experiments***

Optimized resin, photoinitiator and stabilizer packages provide the majority of improvements to this next generation UV hardcoat. However, performance can be enhanced further through additive changes. Some of these alterations can greatly affect some very specific elements – such as surface tension, clarity, and cost – so it is imperative to consider target application and market requirements to ensure that the coating system falls within the expectations of the end user.

A couple of areas of interest among these experiments are flow additives and nanotechnology. Flow additives containing fluorine or silicone can positively influence surface properties such as mar, scratch and abrasion especially if they react into the system providing a permanent effect. However, they can also negatively affect the system primarily if secondary applications are required for aesthetic purposes. Additionally, some flow additives can promote incompatibility issues and an increase in foam formation.

Nanotechnology is a ground-breaking field that can also enhance a coating's performance – most notably by significantly improving scratch and abrasion resistance. Other improvements can be seen in thermal stability, stain & dirt resistance, and to some degree exterior durability. However, nanotechnology can also have a negative impact on the coating performance – such as reduced clarity with certain grades or particle treatments – and it can greatly increase raw material cost, which is passed on to the customer.

## **Conclusion**

The introduction of plastic as a replacement for glass and its evolution over the past two decades has had positive global ramifications for a multitude of applications. Plastics offer numerous advantages over glass, but they also have inherent weaknesses. Thus, the plastic industry would not be as successful without the concurrent development of hardcoat technology. Hardcoat technology and in particular UV hardcoat technology offers unique benefits to coating plastics, but in order to continue the positive forward trend and meet customer demand, it has been imperative to develop a next generation of UV hardcoat, such as the one discussed here, that provides a quantum leap in exterior durability.

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UV Bulb Output Spectrum based on information distributed by Fusion UV Systems, Inc.

Photoinitiator and UVA absorbance spectra based on information distributed by Ciba Specialty Chemicals, Inc.