Radiation Curable Hardcoats with Generally Improved Weathering Performance

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Transparent weatherable hardcoats are used for protection of plastics and other substrates that are exposed to UV radiation. These hardcoats have been shown to protect plastic from scratches and abrasion, as well as solvents, acids and bases. In addition, they contain UV absorbers to shield the plastic from sunlight, and it has been demonstrated that they help prevent photodegradation and discoloration.

These hardcoats are used in glazing applications with a plastic such as polycarbonate (PC), instead of glass. The PC windows have the advantage of low weight and better impact resistance. Other applications of these coatings have included protective coatings for architectural films, such as window film that reduces indoor heat, for plastics used to protect outdoor signs and graphics, and for solar paneling.

One potential benefit of these coatings is improved lifetime of clear PC used for automotive headlamp lenses (commonly manufactured using PC rather than glass). In addition to the advantages of lighter weight and impact resistance, the PC is easier to form into complex shapes than glass, allowing more styling choices for designers. However, the PC lenses need the protection of a weatherable hardcoat because PC is easily scratched and yellows in less than a year in sunlight.

Most manufacturers of automotive headlamp lenses use transparent hardcoats that are curable using UV light. The combination of good abrasion resistance, rapid processing, and competitive cost for these coatings gives them an advantage. A potential disadvantage of UV cured coatings is that they do not last as long in outdoor weathering as other types of coatings, such as thermally cured siloxane coatings.[1] Current coatings are meet requirements to give enough protection that the coated part lasts a minimum three years in relatively extreme outdoor environments, such as outdoor weathering in Florida or Arizona, as required by AMECA (Automotive Manufacturers Equipment Compliance Agency) for coatings used on automotive headlamp lenses in the US**.** The requirement is that after three years of outdoor weathering the coating/plastic combination has % haze < 7, yellowness index (YI) < 4, no notable cracking, and no delamination.[2] As the average lifetime of cars in the U.S. increases[3], and as modern headlamp design features such as black edges challenge the weatherability of current three-year coatings, it is desirable to have a coating that lasts longer.

Weatherable UV curable hardcoats usually contain acrylate functionalized monomers and oligomers, UV absorbing additives, and one or more photoinitiators. They may also contain other additives, such as hindered phenolic stabilizers, hindered amine light stabilizers, nanoparticles, and flow components such as solvents and surfactants. For clear coatings, the UV absorbers must not absorb much light at wavelengths longer than 400nm, or the coating will appear yellow. The UV absorber also should not absorb all the longer wavelength UV light, or it will be difficult to cure the interior of the coating. Photoinitiators must be non-yellowing and must absorb at some wavelengths longer than the UV absorber. Phosphine oxide photoinitiators are often used because they have low yellowing and have a tail of absorption at wavelengths above 390 nm, so they can give good throughcure in the presence of the UV absorber.

The modes of failure for plastic with weatherable coating include yellowing or decomposition of the plastic due to UV degradation, cracking of the coating or substrate, developing haze that prevents transparency, and delamination of the coating. The initial mode of failure depends both on the types of weather experienced by the coated parts and on the substrate/coating combination.

One way to improve weathering performance would be to improve the UV absorber (UVA) or combination of UVAs. Though UVAs used as stabilizers have relatively low reactivity to UV light, they still slowly change when irradiated, and lose absorption over time.[4] A larger quantity of UVA could be added, but the total amount is limited because too high a quantity will prevent proper UV cure of the coating. Added UVA may also cause the coating to lose abrasion resistance or adhesion.

Coatings containing UVAs with poor stability may initially fail due to yellowing, sometimes in less than three years. When coatings are designed with optimal UVAs to impart good resistance to yellowing, the first mode of failure, particularly after more than three years of weathering, may be cracking. Even when the first observable failure seems to be haze, it can often be seen that microscopic cracks preceded the haze, and may have caused it.   Another mode of failure is delamination at extended weathering times.

In this study coatings were made with the objective of increasing resistance to cracking, and improving coating adhesion after weathering in order to improve overall weatherability. The new coatings must still retain other necessary properties, such as transparency, scratch resistance, abrasion resistance, and solvent resistance. They must also have good processability, including the ability to coat and cure well, and a requirement that runoff material can be recycled.

Experimental:

Coatings were flowcoated on injection molded, 1/8” thick Sabic LS2 PC panels, dried 2 minutes at room temperature, and 4 minutes at 75 ℃.   Unless otherwise noted, coatings were cured using a UV conveyor equipped with two Fusion H lamps at a peak irradiance of 0.5-0.6 W/cm^2 for a total exposure of 6.0 J/cm^2 measured in the UVA using an EIT Power Puck radiometer.

Xenon weathering was done using a 3-Sun Atlas Xenon Weatherometer™. Most samples were tested using a modified ASTM G155 (Gmod) protocol (see Figure 2).   The modified test uses irradiance of 0.75 W/m^2 at 340nm, and a boro/boro water-cooled filter combination.

Adhesion testing was done using a crosshatch adhesion method similar to ASTM D3359-95a, method B.   A crosshatch pattern was cut in the coating using a Gardner scriber. A piece of tape (3M, Scotch 898) was pressed over the crosshatch, left for about a minute, and removed by quickly pulling on the tape. The adhesion is ranked from 5B to0B, with 5B being 0% coating loss, and 0B being >65% coating lost.

Measuring the initial crosshatch adhesion of a sample, then placing the panel in a water bath at 65 ℃ for several days tested watersoak adhesion. At intervals of a few days, the sample was removed from the water bath, dried, and tested for crosshatch adhesion on the same scribe mark. An adhesion of 5B or 4B (≤5% coating loss) is considered to ‘pass’.

Taber abrasion was tested using a method adopted from ASTM D1003 and ASTM D1044. PC panels for abrasion testing were coated and cured as described above. Abrasion was tested with a Taber abrader at $23^{o}C \pm 2^{o}C$ and $50 \pm 5\%$ relative humidity using CS10F wheels, 500g weights, 500 cycles. Haze was measured using a Byk-Gardner Haze Gard Plus meter, model #4725 before and after abrasion to get a delta haze value for the coating.

YI was measured using a Gretag Macbeth Color-Eye 7000A.

Results:

As an initial screening, coatings were tested for scratch resistance, taber abrasion, and for adhesion after soaking in water at 65 ℃. A 4B or 5B rating for crosshatch adhesion is considered passing in the watersoak test. Coatings that fail adhesion prior to 10 days of watersoak at 65 ℃ are likely to be degraded by water in outdoor exposure, and often do not perform well in weathering. Figure 1 shows results for these tests for promising new formulas intended to reduce cracking and improve adhesion after weathering. The new coatings are compared to a standard weatherable coating, called “STDHC” in the charts. The watersoak adhesion was improved compared to the standard coating. Taber abrasion tended to be higher for new formulas, but still was within the desired specification of having a delta haze less than 10 for 500 cycles using CS10F wheels, 500g weights. All formulas shown passed the scratch test, which was 5 double rubs with 0000 steel wool weighted at 2 lb/in^2.

Coating	Scratch Resistance	500 Cycle Taber Delta % Haze	Watersoak Adhesion (days passed)
STDHC	pass	4.12	15
NC1	pass	5.27	33*
NC2	pass	5.45	25
NC3	pass	7.48	35
NC4	pass	6.74	44
NC5	pass	8.70	16
NC6	pass	6.02	30
NC7	pass	8.9	33*
NC8	pass	8.24	33*

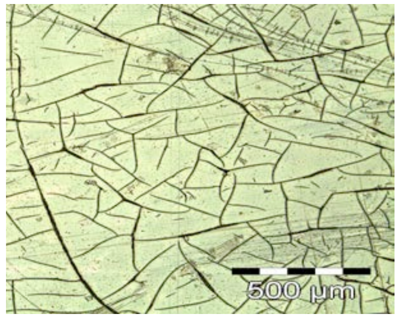
*Did not fail at this time. Not tested further.

Figure 1. Initial test results for hardcoats made to reduce cracking and improve adhesion after weathering.
Note: Test data. Actual results may vary.

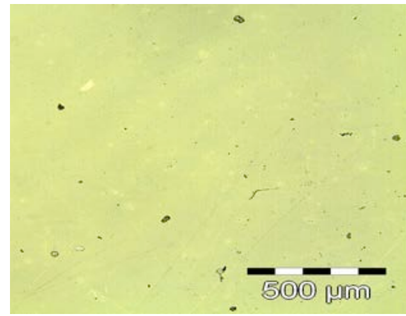
Parameters	ASTM G155 mod (Gmod)
Total number of segments	2
Black sensor (BPT / BST)	BPT
Filter	Borosilicate
Light Cycle Settings	
Irradiance	0.75 W/m^2
Reference Wavelength for Irradiance Measurement	340 nm
Black Panel Temp	65 °C
Chamber Temp	40 °C
Relative Humidity	40%
Segment 1	
Cycle (Light/dark)	Light
Duration / min	102
Spray	Off
Segment 2	
Cycle (Light/dark)	Light
Duration / min	18
Spray	On

Figure 2. Parameters for Gmod Xenon Protocol

Panels were tested using Xenon accelerated weathering for exposures up to about 14,000 kJ/m^2, the amount of UV exposure expected in five years of Florida weathering at a 45-degree angle. In previous studies, it was found that, for the standard hard coating STDHC, a modified ASTM G155 test (Gmod) gives relatively good correlation with real Florida weathering based on radiation (1Yr=2800kJ/m^2), at least for a three-year timeframe.[5] Other factors, including their interactions, can influence real world correlation, such as thermal exposure, impact, humidity, and water. The parameters for this test are shown in Figure 2. The modifications of the test include using two borosilicate filters to better simulate sunlight, and a higher UV intensity of 0.75W/m^2.



STDHC



NC8

Figure 3. Improvement in crack resistance is shown by magnified images from PC panels coated with standard coating STDHC and new coating NC8 after 5 year-equivalents UV exposure (14,000 kJ/m^2) in Xenon accelerated weathering. Note: Test results. Actual results may vary.

Figure 3 shows the improvement in crack resistance for one of the new coatings, NC8, compared to a standard weatherable hardcoat, STDHC. Results are shown after five Florida year-equivalents, 14,000 kJ/m^2, of UV exposure in Xenon weathering.

	Highest Xenon Exposure (kJ/m^2) Before Failure or Before Test Ended			
Coating	By Adhesion	By Haze	By Microcracks	By Yellowness (YI)
STDHC	6,700	11,700	8,400	11,700**
NC1	10,800	12,900	11,700	12,900**
NC2	14,400	15,500	14,400	11,800
NC3	9,000	13,500	10,100	14,200*
NC4	14,200*	13,500	12,500	14,200*
NC5	11,400	16,000	16,000	16,000
NC6	14,400	15,500*	14,400	13100
NC7	14,000*	14,000*	14,000*	14,000*
NC8	14,000*	14,000*	14,000*	14,000*

*Did not fail yet at given exposure. Not tested further.
**Cannot measure YI above these values due to haze.

Figure 4. Highest UV Exposure without failure for new coatings NC1 to NC8 compared to a standard coating STDHC. Coatings are considered passing if adhesion is 4B or 5B, haze<7, YI<4, and they have no visible microcracks. Note: Test data. Actual results may vary.

The standard weatherable hardcoat started cracking after three and a half to four year-equivalents of weathering in this test, and was extensively cracked after five year-equivalents. Coating NC8 did not show cracking after five Florida year-equivalents.

A summary of Xenon weathering results for several new coatings is shown in Figure 4. The highest UV exposures without failing due to a particular failure mode, including adhesion, haze, cracking, or yellowness, are shown. The panels are considered to pass these tests if the crosshatch adhesion is 4B or 5B, haze is <7, YI is <4, and the coatings do not appear to be cracked. The amount of UV exposure before failure by adhesion, cracking, and haze are shown to improve significantly for many of the new coatings.

The YI of many new coatings also remained below 4 for the entire test. It was not possible to compare the YI of the STDHC at the highest UV exposures because, at that point, cracking and haze for the STDHC interfered with the measurement and gave reduced YI values.

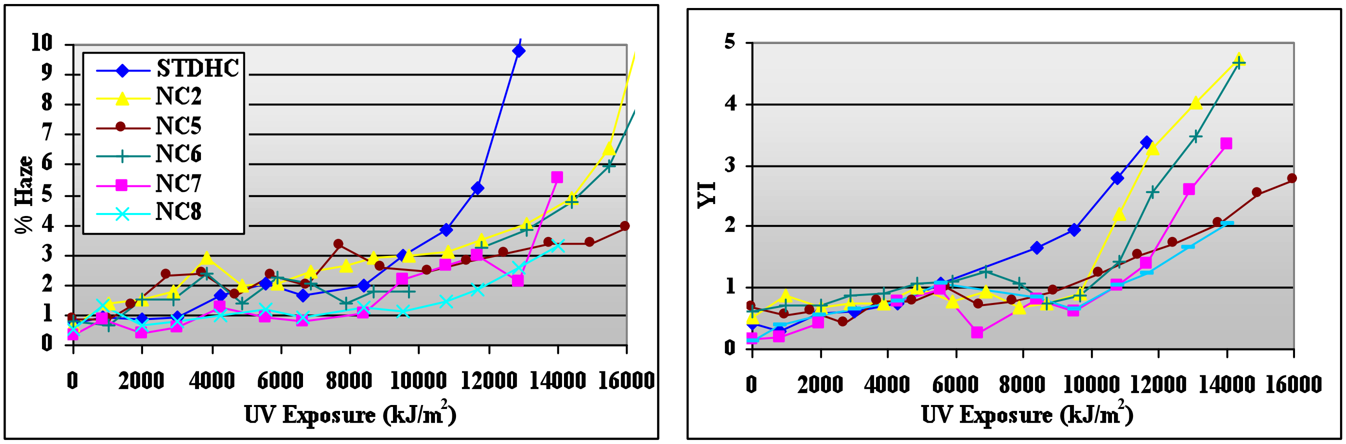


Figure 5. % Haze and Yellowness (YI) after Xenon Gmod weathering for some coatings with improved crack resistance compared to three-year standard formula STDHC. After 14,000 kJ/m^2, all of the new coatings passed the specification of % haze <7. Coatings NC5, NC7, and NC8 pass the specification of having YI<4. Note: Test data. Actual results may vary.

Figure 5 shows the changes in haze and YI during the entire weathering study. In these charts, the haze was improved for all the new coatings shown, and the YI was also lower for several of the coatings. Coating NC5 had the best results for haze, YI, and microcracking, but did not have as good adhesion as NC7 and NC8.

Outdoor Weathering:

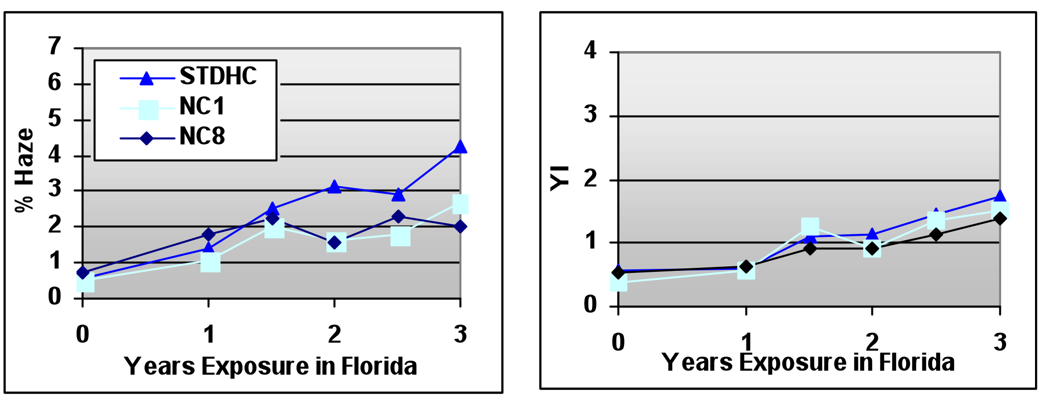


Figure 6. Outdoor weathering results for standard three-year weatherable coating STDHC and for new coatings NC1 and NC8 as of February 2012. All coatings showed good results after three years, as expected. Note: Test data. Actual results may vary.

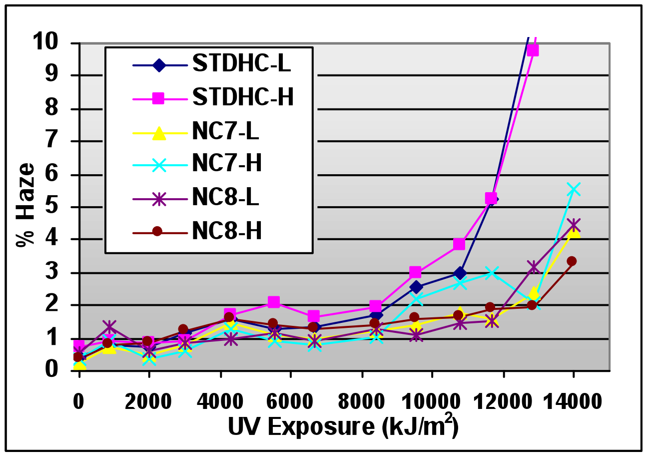
Some of the new coatings have been tested in outdoor Florida and Arizona weathering for three years as of February 2012 with testing ongoing. Figure 6 shows results from PC panels coated with STDHC, N1 or N8 after three years of weathering in Florida at a 45-degree angle. As expected, all of the new coatings, and, of course, the standard coating, still have low haze and YI after three years. The difference between the STDHC is expected to be more evident after four or five years of outdoor weathering. These coatings have also been tested in Arizona outdoor weathering, and similarly gave good results after three years.

Effects of Cure on Xenon Weathering:

Figure 7 shows the effect of varying cure conditions from a high value to 6.0 J/cm^2 UV exposure, 0.5-0.6 W/cm^2 peak irradiance, to a low cure condition of 4.0 J/cm^2, 0.3W/cm^2, for some new coatings compared to the standard coating. For some coatings, haze after weathering is slightly higher for the low cure, but the results are still well below the maximum haze limit of 7. Panels coated with NC7 and NC8 both passed cracking and adhesion tests after 14,000 kJ/m^2 Xenon exposure at both cure conditions. For other formulas, it was found that lower cure energy and intensity had a small tendency to reduce adhesion after weathering and to improve the crack resistance after weathering. Both of these differences could be due to reduced through-cure of the coating at low dosage and intensity.

Effects of Silica Nanoparticles:

Addition of nanoparticles is known to improve abrasion resistance for UV curable hardcoats.[6] Silica nanoparticles can be functionalized with acrylated trimethoxysilane to give reactive nanoparticles used in these coatings (Figure 8).[7] Figure 9 shows the effect on Taber abrasion for coatings with and without silica nanoparticles. For the coatings shown, and most other coatings tested, the nanoparticles improved abrasion resistance.



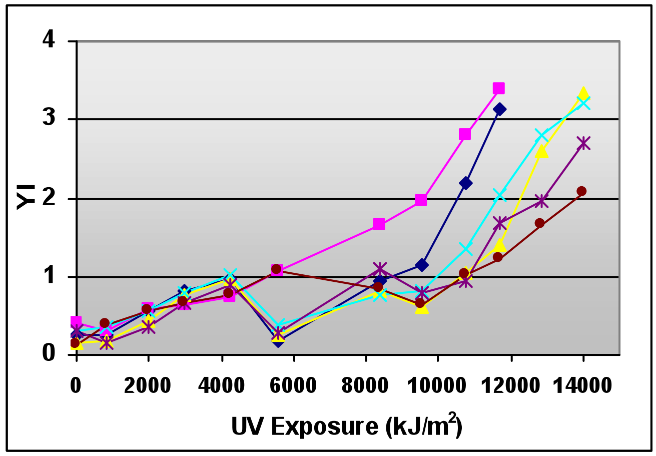


Figure 7. Haze and YI after Xenon weathering for coatings made using a high cure (H) of 6.0 J/cm2, 0.5-0.6 W/ cm2, or a low cure (L), 4.0 J/cm2, 0.3 W/ cm2. Note: Test data. Actual results may vary.

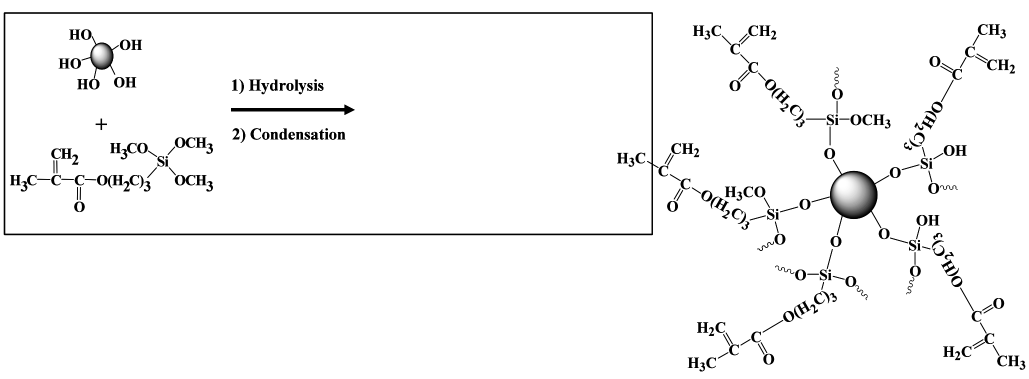


Figure 8. Silica nanoparticles functionalized with acrylated silane can act as reactive filler to improve properties of weatherable hardcoats.

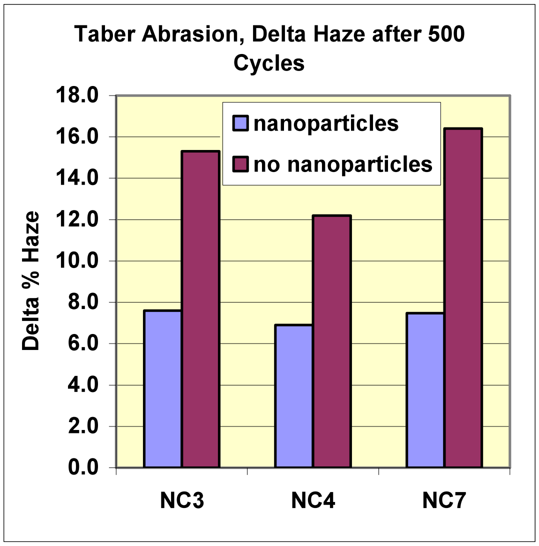


Figure 9. Coatings with Nanoparticles have less abrasion after Taber testing. Note: Test data. Actual results may vary.

It was also found that addition of nanoparticles in some coatings reduced haze after extended times of weathering (Figure 10). It is not known exactly why the nanoparticles help weathering, but it appeared that they might help prevent pitting of the coatings that can raise the haze level.

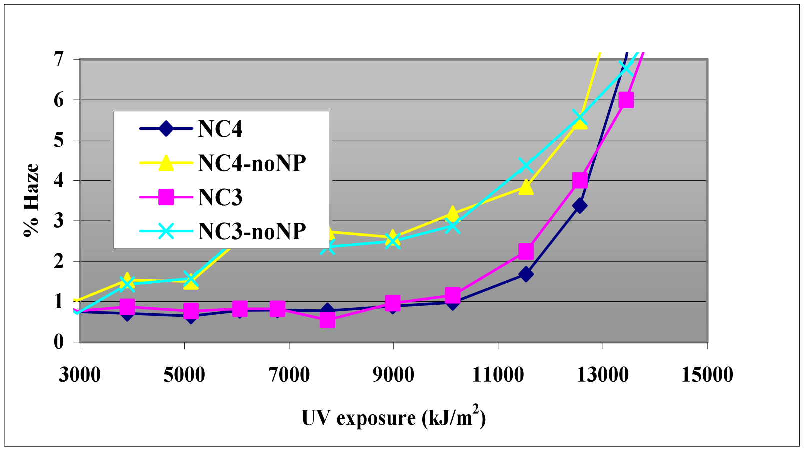


Figure 10. Haze after weathering for formulas NC3 and NC4 with nanoparticles and NC3-noNP, NC4-noNP without nanoparticles. Note: Test data. Actual results may vary.

Conclusions:

Weatherable hardcoats with improved resistance to cracking and improved adhesion after weathering have been shown to last up to five year-equivalents, 14,000 kJ/m^2, of UV exposure in Xenon accelerated weathering. Weathering results for the best coatings were not seriously affected when UV cure was reduced from a dosage and peak intensity of 6.0J/cm^2, 0.5-0.6W/cm^2, to 4.0J/cm^2, 0.3W/cm^2. Using functionalized silica in the formulas improved abrasion resistance and may also have helped reduce haze after weathering. The new coatings have been found to weather well for three years in Florida and Arizona outdoor weathering thus far with testing ongoing.

[1] A. Bonadies, R. Hayes, “A New Hardcoat for Automotive Plastics,” *Finishing Today*, **83**, Issue 12, p24; (2007).

[2] a) List of Acceptable Plastics for Optical Lenses and Reflex Reflectors Used on Motor Vehicles, Automotive Manufacturers Compliance Equipment Agency, Inc. Dec. (2011).
b) SAE J576: “Plastic Material or Materials for Use in Optical Parts Such as Lenses and Reflex Reflectors of Motor Vehicle Lighting Devices.” *SAE International.* January 1st, (2007).

[3] T. Krisher, “Americans keep old cars and trucks in bad economy: average age reaches record 10.8 years” Associated Press, Jan 17, 2012, http://finance.yahoo.com/news/average-age-us-vehicles-hits-141928259.html

[4] J. E. Pickett, J. E. Moore, “Photodegradation of UV Absorbers: Kinetics and Structural Effects,” Die Angewandte Makromolekulare Chemie, **232**, 229 (1995).

[5] S. Slocum, S. Mordhorst, “Correlation of Accelerated Weathering, Material Weathering, and Field Lenses for Protective Coatings Utilized in Forward Lighting,” *Radtech Report*, Nov/Dec, 13 (2008).

[6] M. Myers, “Current State-of-the-Art and Impending Developments of Silica Nanoparticles Use in UV-Curable Systems,” *Paint and Coatings Industry (PCI)*, Jan., (2011).

[7] R. H. Chung, “Process for Coating a Substrate with an Abrasion Resistant Ultraviolet Curable Composition,” US4,478,876, Oct 23 (1984).