J. Coat. Technol. Res., **7** (2) 159–166, 2010
DOI 10.1007/s11998-009-9190-4

The effect of weathering and thermal treatment on the scratch recovery characteristics of clearcoats

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Abstract The scratch and scratch recovery characteristics of two clearcoats, a polyurethane and an acrylic/melamine/silane clearcoat, were measured by a variety of methods. On most size scales tested, the polyurethane possessed superior scratch and mar resistance. The polyurethane also possessed improved scratch recovery after warming for 2 h at 60°C. After 2000 h of accelerated weathering, the scratch recovery characteristics of the polyurethane were largely maintained, while the acrylic/melamine/silane showed a significant drop in scratch recovery performance. Performance of both coatings was related to T_g, hardness, and crosslink density.

Keywords Automotive, Paint, Clearcoat, Urethane, Scratch resistance, Healing, Macro scratch, Nano scratch

Introduction

Automotive basecoat/clearcoat paint systems were introduced to the market in the 1980s to improve the initial and long-term appearance of vehicles. Over the years, a variety of different clearcoat chemistries have been implemented, including acrylic melamine and polyurethane formulations. These chemistries, and the ways in which they are formulated, give rise to performance attributes that can vary greatly between the individual formulations as well as the underlying chemistries. Ultimately, the performance attributes of these systems are balanced to provide the customer with a paint finish that performs to their satisfaction for the life of their vehicle.

Scratch resistance is one attribute that has consistently come to the forefront of customer satisfaction surveys.[1] Customers desire a permanent, scratch-free finish on their vehicle. Scratches occur along a continuum of sizes, from very small, micron-size scratches that do not refract light, to very large, millimeter-size scratches that appear white due to fractures in the clearcoat. Scratches that do not fracture the clearcoat, and hence do not refract light, are often called mars and typically come from car washing.[2,3] Scratches that do fracture the clearcoat are classified as fracture scratches. It is usually difficult for a customer to detect a single mar on a vehicle due to its nature and size. However, as the paint system is subjected to more and more marring events, these mars increase in quantity and eventually reach a point where the customer recognizes their presence, usually as a reduction in the gloss of the clearcoat. On the other end of the continuum, fracture scratches are large and can easily be seen by the naked eye. These scratches are caused by more severe contact damage from keys, tree branches, grocery carts, and anything else that can cause the clearcoat to fracture along the scratch trough. These scratches have the potential to progress through the clearcoat to the underlying layers and even down to the metal substrate.

Both types of scratches are produced under unique conditions, and customer objection to each type of scratch can vary between North American and European customers. Typical rotating brush car washes in Europe induce deeper mars, approaching scratches, on automotive coatings. Hand washing and milder automatic washing in North America minimizes these deeper scratches and produces shallower mars.

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Improving a coating's resistance to one type of damage does not guarantee improved resistance to another type of damage.

Considerable effort has been put into formulating clearcoats with improved scratch and mar resistance. One approach has been to increase the crosslink density of the clearcoat.[4,5] Increases in crosslink density are thought to improve the yield strength of the network, thus raising the resistance to plastic deformation. However, increased crosslink density also typically results in increased brittleness (reduced toughness), which can lead to a lowering of the cracking stress. Another approach has sought to improve the scratch resistance of coatings through the introduction of nanoparticles.[6,7] The nanoparticles can be uniformly distributed throughout the coating or preferentially segregated to the top surface. The nanoparticles are presumed to increase the surface hardness and resistance to indentation. For those coatings that contain nanoparticles primarily at the surface, the long-term resistance to scratching is not known. Morphological changes that occur during weathering may reduce the effectiveness of this approach.[8] Clearly, scratches that penetrate deep into the coatings system will not be aided by the nanoparticles approach.

A possible way to improve the perceived scratch resistance is to develop a coating system that will ''heal'' itself over time, typically after being exposed to elevated temperatures.[2,9,10] The healing is thought to occur due to reflow of the coating into the damaged area. The reflow would potentially reduce the visibility of the scratches by reducing their depth and/or width. Polyurethane-based coatings are attractive candidates for this approach as they possess a large degree of formulation latitude and are currently used as automotive clearcoats.

This article focuses on quantifying the amount of healing that takes place in a model polyurethane clearcoat designed to recover from scratching events compared to that of a commercial acrylic/melamine/silane clearcoat. The resistance to scratching and ability to recover from scratching is assessed both before and after accelerated weathering, as this important variable has been overlooked in previous studies and provides insight into the real-world effectiveness of this approach to improving the long-term durability of automotive coatings.

Experimental

Two different clearcoats were used in this study. Clearcoat A was a conventional acrylic/melamine/silane clearcoat whose exact formulation is proprietary. The clearcoat was sprayed as part of a basecoat/clearcoat system on primed panels using conventional means and was subsequently cured at 135°C for 25 min. Clearcoat B was a 2K polyurethane clearcoat formulated specifically for its ability to recover from mar/car wash scratches. Clearcoat B was formulated with an NCO:OH ratio of 1.0. The polyurethane was created by mixing the polyol with all additives and solvents, followed by the addition of the polyisocyanate. The mixture was then deaerated for 10–15 min. The coating had a solids content of ~60%. The coating was then sprayed by hand as part of a basecoat/clearcoat system, and subsequently cured for 25 min at 140°C followed by 16 h at 60°C. Dry film thickness for both clearcoats was ~40 µm.

Dynamic mechanical analysis

Crosslink densities and glass transition temperatures of clearcoats A and B were determined using a Rheometric Scientific DMTA IV equipped with a tension test fixture. The T_g of a coating was defined as the maximum in the tan δ curve. Crosslink density was calculated using the following equation:

$$\nu_e = E'/3RT \tag{1}$$

where E' is the minimum in the storage modulus (E') curve, R is the gas constant, and T is the temperature at which this minimum in storage modulus was reached.[11] All experiments were conducted at 10 Hz with temperature ranging from 25 to 150°C, ramped at 2°C/min.

Scratch resistance

Scratch resistance was measured with a nano-scratch tester (CSM Instruments, Needham, MA). During nano-scratch testing a force was applied to the coating normal to the coating surface. As the sample was moved laterally, the normal force was increased, from 0 to 35 mN, at a constant rate until the clearcoat fractured and microcracks appeared in the clearcoat surface (viewed under a microscope at 100× magnification). This critical force was recorded as a measure of the ''scratch resistance'' of the clearcoat. The amount of plastic deformation done (residual penetration depth) with 5 mN of normal force was also recorded. This second number is thought to be inversely proportional to the mar resistance of a coating; that is, the ability of the clearcoat to resist light scratches that do not fracture the surface.[12]

The second method used for scratch evaluation of both clearcoat systems was the AMTEC Kistler test (Standard ISO 20566). The test utilized a polyethylene brush (~28 working hours old) drum that was rotated over the surface of the samples. As the panels moved beneath the brush, the brush rotated the bristles against the direction of sample movement. A quartz dispersion (1.5 g silica per liter of water) was sprayed during the test to simulate dirt and other abrasive particles. The samples were exposed to 10 cycles in the test apparatus to simulate car-wash scratching. Gloss and haze (20°) measurements were taken prior to and just after AMTEC Kistler testing using a Micro-haze Plus Hazemeter from BYK-Gardner (Columbia, MD, USA). The samples were allowed to recover at 60°C in an oven for 2 h, after which gloss and haze measurements were again taken on both systems.

Macro scratch

Laboratory simulation of macro scratches was performed using an unique scratch apparatus. Four different diamond scratch tips (The Quad Group, Spokane, WA) with tip radii of 27, 126, 281, and 460 μm respectively were used to create scratches. Each tip had an inclusion angle of 90°.

These tips were attached to load cells from Honeywell Sensotec (AL311) whose full scale load capacity ranged from 2.45 to 45 N. The load cells were connected to a computer through a Transducer Techniques TMO-2 signal conditioner. The load cell/tip assembly was held fixed by attachment to a rigid cross member that could be moved vertically. The paint panels were attached to a 3-axis stage. A purpose-built data acquisition program utilized a PID controller to adjust displacement and load. The scratch-tip speed was set to 1 mm/s for all simulations performed. Each clearcoat system was loaded to a constant set load. The paint panel was then moved along the *y*-axis to provide the motion for scratch damage, during which the load was kept constant (with an error of ~5%). Scratch length was set to 10 mm. Scratches were made with loads starting below those that caused clearcoat fracture and increased up through radial and longitudinal fracturing of the clearcoat trough. The minimum and maximum load applied to each clearcoat system and corresponding tip sizes are shown in Table 1.

Scratch shoulder heights and trough depths were measured using a Wyko NT3300 profiling system. This device used vertical scanning interferometry (VSI) to determine the topography of the scratch damage. The scratch damage was imaged with a 2.5× objective, and scanned through a vertical range of 80 μm. All data were processed using Veeco's Vision32^{TM} software.

Hardness testing

Vickers microhardness measurements were made with a Leco MHT Series 200 microhardness tester utilizing a 25 gmf load and a 10 s hold time. The indentation was measured though the instrument software using the 50× objective. Three measurements were taken for each sample, both pre-weathering and after 2000 h of accelerated weatherometer exposure.

Table 1: Minimum and maximum loads applied to each clearcoat system during macro scratching

Tip size	Minimum load (N)	Maximum load (N)
27 μm	0.5	2.0
126 μm	0.5	11.0
281 μm	1.0	23.0
460 μm	3.0	39.0

Healing process

All panels were subjected to a healing process after macro and Amtec-Kistler scratch simulation. Panels were placed in an oven at 60°C for 2 h. After cooling, panels were subjected to scratch analysis (Wyko for the macro-scratch evaluation, gloss measurement for Amtec-Kistler scratch evaluation) to determine if any scratch recover occurred.

Weathering

Accelerated weathering of the two-clearcoat systems was carried out in an Atlas xenon arc Weatherometer® running test method SAE J2527 with borosilicate inner and outer filters at 0.55 W/m^2 @ 340 nm irradiance. Panels were exposed for 1000 and 2000 h.

Optical microscopy imaging

Optical images of scratches were taken using a Nikon Microphot FX-A upright optical microscope equipped with video capture capabilities.

Results

Material properties

To determine the correlation between material properties and scratch/recovery performance, T_g, crosslink density, tan δ peak width at half height, and Vickers microhardness were determined for each coating. The values for each of these properties are shown in Table 2.

Scratch properties

The nano scratch properties of each clearcoat system were measured to compare fracture scratch and mar resistance for each of the two clearcoats, both before weathering and after 2000 h WOM exposure. The permanent deformation at 5 mN vs the normal force at fracture is plotted for each system in Fig. 1.

Before weathering, clearcoat B had a substantially higher force-to-fracture (26.1 mN) than clearcoat A (8.08 mN). However, clearcoat B also had a slightly worse residual plastic deformation at 5 mN (0.39 mm) than clearcoat A (0.33 mm). After 2000 h of accelerated

Table 2: Tabulated values of T_g and Vickers hardness (pre- and post-weathering) for each clearcoat system

	T_g (°C)	Crosslink density (mol/cm^3)	tan δ peak width at half height (°C)	Vickers hardness, pre-weathering (HV)[a]	Vickers hardness, 2000 h WOM (HV)[a]
Clearcoat A	72.1	0.5×10^{-3}	47	14	11
Clearcoat B	79.6	3×10^{-3}	28	16	10

[a] Average of three measurements

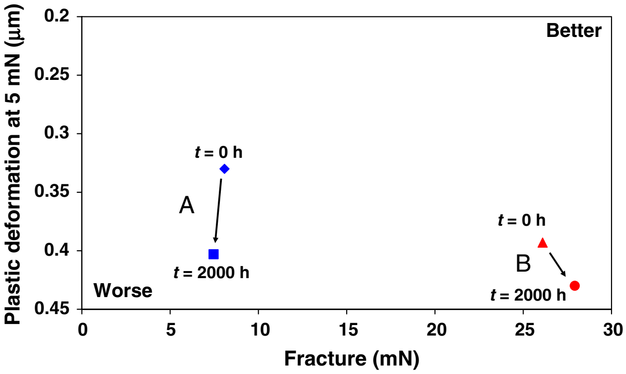


Fig. 1: Nano-scratch test results from clearcoats A and B, both prior to weathering (*t* = 0 h) and after 2000 h weathering (*t* = 2000 h)

weathering, both clearcoat systems saw an increase in residual plastic deformation at 5 mN of force (0.40 mm for clearcoat A and 0.43 mm for clearcoat B), indicating poorer mar resistance. Clearcoat B actually saw a very slight improvement in force-to-fracture (27.92 mN) while clearcoat A saw a slight reduction in force-to-fracture (7.46 mN). Thus, weathering had little effect on the fracture scratch performance of either clearcoat and minimally degraded the mar performance of both clearcoats.

Macro-scratching of both clearcoat systems allowed for the examination of fracture scratches using optical microscopy. By examining scratches both pre- and post-healing, qualitative observations could be made regarding the healing of cracks in the scratch trough. Figures 2 and 3 are images of scratches made in both clearcoat systems, both pre- and post-healing (2 h, 60°C). In both cases, fracture in the clearcoat was not ‘‘healed’’, and still was clearly visible after the healing process. However, some healing of the plastically deformed material occurred on each side of the fractured region.

Macro-scratching also allowed for the analysis of scratch deformation profile of both clearcoat systems. Utilizing the Wyko imaging system, shoulder and trough heights/depths (see Fig. 4) were measured for each scratch load both pre- and post-healing. The method used was similar to that used by Shen et al.,[13] but instead measured only the height/depth and not the area of the shoulders and trough.

Depth and height measurements were taken pre- and post-healing on both clearcoat systems before weathering and after both 1000 and 2000 h of accelerated WOM exposure. An example of the scratch 2-D cross sections is shown in Fig. 5.

Scratch recovery percentages for the shoulder and trough regions of each sample were calculated for non-fracture scratches. The mean and standard deviation for both shoulder and trough recovery are shown in Fig. 6.

In all cases, clearcoat B appears to exhibit improved scratch recovery compared to clearcoat A. It also appears that most of the scratch recovery that clearcoat A exhibits before weathering is reduced after it has been weathered. Clearcoat B shows a slight reduction in shoulder recovery after weathering; however, it does

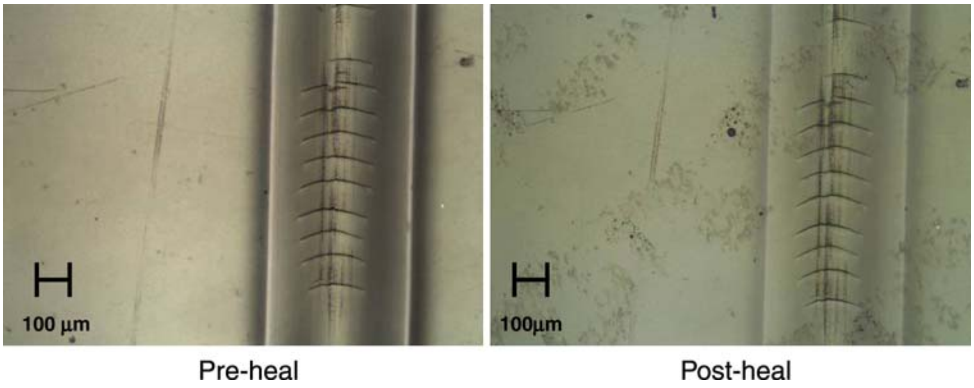
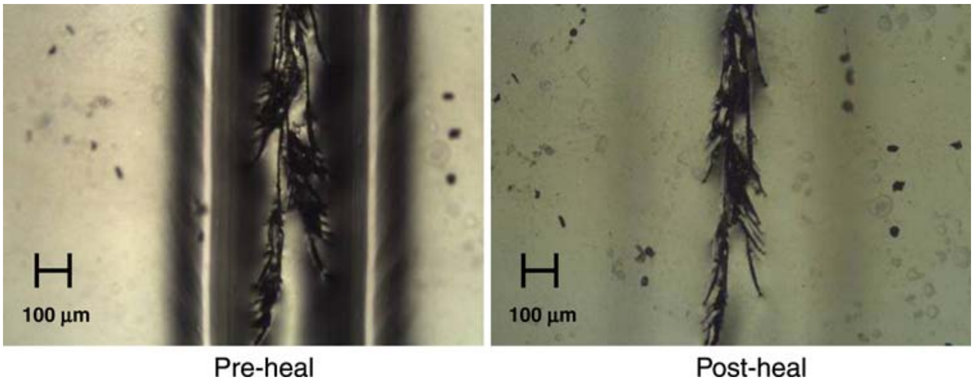


Fig. 2: The 2000 h WOM sample of clearcoat A, both pre- and post-healing, 100× magnification



Pre-heal Post-heal

Fig. 3: The 2000 h WOM sample of clearcoat B, both pre- and post-healing, 100× magnification

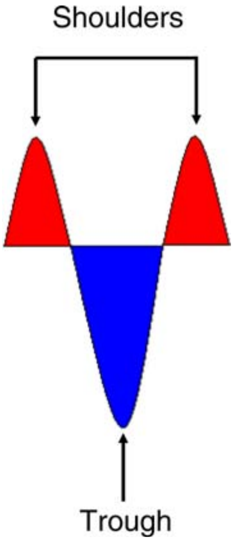


Fig. 4: 2-D drawing with shoulder regions of the scratch deformation shown in red while the trough region of the scratch deformation is shown in blue

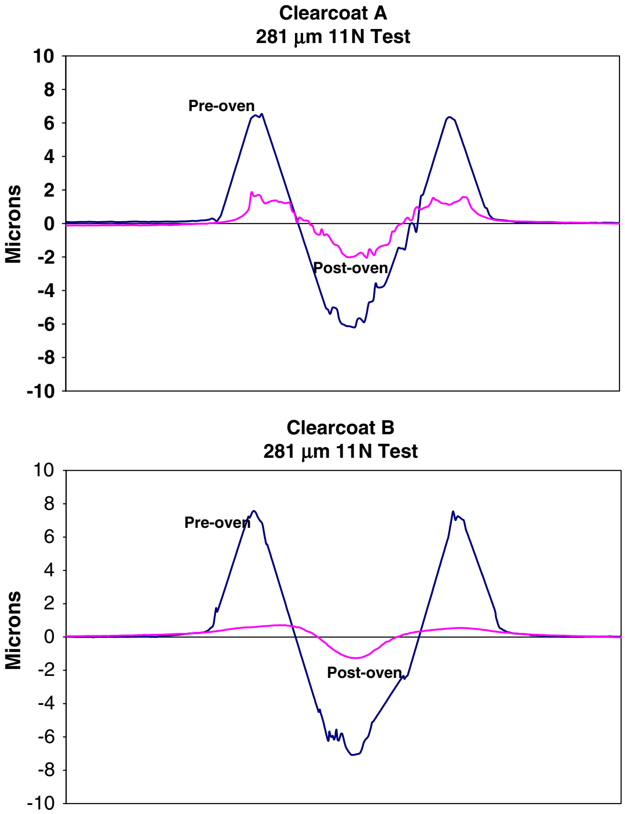


Fig. 5: Representative examples of 2-D scratch data measured for both clearcoats A and B (281 µm tip diameter, 11 N normal force) both pre- and post-healing, before weathering

not appear to be as severe as the reduction in clearcoat A. A statistical analysis was conducted to determine if the differences between samples and conditions were significant. This analysis was conducted to determine if the differences in means seen in Figs. 6 and 7 are statistically significant. In all cases, the difference between clearcoats A and B and between pre-weathering, 1000 h, and 2000 h of weathering were significant ($p < 0.05$) except for the difference in recovery for clearcoat A between 1000 and 2000 h of accelerated weathering.

AMTEC Kistler testing was performed on both clearcoat systems. Gloss and haze measurements were taken both pre- and post-testing, as well as after the healing process. These results are shown in Table 3. Clearcoat B exhibited superior gloss retention after initial AMTEC Kistler testing, retaining an average of 89.0% of the original gloss compared to clearcoat A, which only retained an average of 78.6%. Haze results followed a similar trend, with clearcoat B undergoing a 22 point increase in haze while clearcoat A had an average haze increase of 38.5. The ability to recover from these car-wash scratches was also superior for clearcoat B, which recovered an average of 57.8% of the gloss loss and 45.5% of the haze damage. Clearcoat A only recovered an average of 14.0% of the gloss loss and 9.8% of the haze damage.

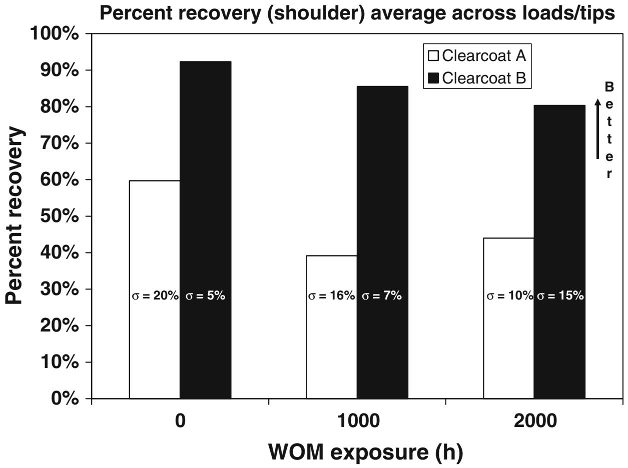


Fig. 6: Percent recovery of the scratch shoulder for clearcoats A and B after accelerated weathering of zero, 1000, and 2000 h. σ represents the standard deviation of the data for each set

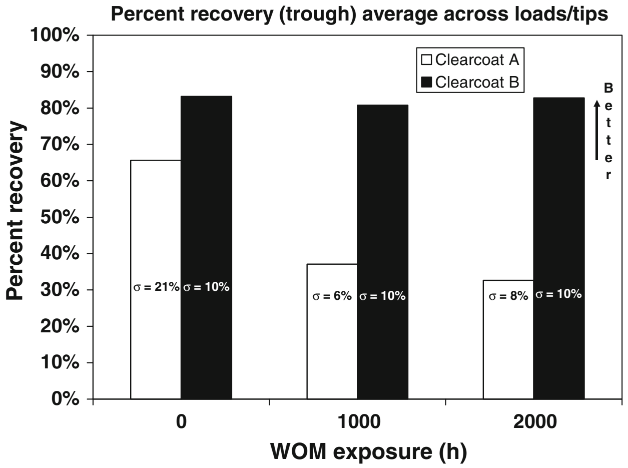


Fig. 7: Percent recovery of the scratch trough for clearcoats A and B after accelerated weathering of zero, 1000, and 2000 h. σ represents the standard deviation of each dataset

Discussion

Because different scratch testing methods probe different size scales and deformation regimes, significant confusion can occur when comparing the performance of a coating evaluated in different scratch tests. Previous work has shown comparisons between a number of scratch evaluation systems that are used across the industry, and have arrived at mixed conclusions.[14–16] Clearly, a number of different fundamental properties govern the scratch performance of a clearcoat. For shallow scratches (mars) the yield strength of the coating dominates, as the deformation that occurs is controlled by the plasticity of the clearcoat. At higher deformations where fracture occurs, the fracture toughness of the coating dominates. In all cases, these material properties are influenced by the viscoelastic nature of the coating, and subsequently depend strongly on characteristics such as distance from T_g and crosslink density.

When considering the recovery of scratches, the ability of the coating to reflow during heating excursions is crucial. For the two model systems studied in this work, the polyurethane clearcoat clearly displays superior scratch healing performance. To a first approximation, the viscoelastic creep that must occur during reflow should be in proportion to the proximity to T_g. However, for the clearcoats studied here, the polyurethane (clearcoat B) has the higher T_g and would thus be expected to reflow less at 60°C than the acrylic/melamine/silane. Thus, the reflow is governed by more than just proximity to T_g. The reflow that occurs is observed across all scratch scales—from the smaller sizes produced in the Amtec-Kistler to the larger sizes created by the macro scratch tester—and results in improved gloss retention and reduced scratch visibility. The presence of both hard and soft segments in the polyurethane backbone may contribute to its recovery characteristics. Other polyurethane coatings have shown the ability to heal slowly, even at room temperatures.[9] Thus, the accelerated healing at higher temperatures is not surprising.

For the work presented here, the initial amount of damage is less important than the ability of the material to undergo recovery both before and after weathering. The polyurethane clearcoat B clearly possesses improved scratch recovery characteristics prior to weathering. Additionally, the recovery characteristics are largely maintained after accelerated weathering. We were not able to measure the glass transition temperatures of the coatings after weathering, but previous work has shown that clearcoats similar to clearcoat A show a large increase in T_g as weathering progresses, perhaps as much as 20°C in the time frame studied here.[17] This may explain the drop in recovery characteristics of clearcoat A (Figs. 6 and 7). The ability of clearcoat B to retain scratch recovery performance after weathering could be related to a smaller increase in T_g as weathering progresses.

The effect of T_g proximity is complicated by the viscoelastic nature of the coatings. On the time scale of the recovery process (2 h), the effective T_g of both coatings is likely to be significantly lower than that measured during the DMA experiments at 10 Hz. Thus, the recovery temperature may approach or even exceed the effective T_g of the coating during the healing process. It should be noted that the surface temperature of automobiles painted with dark colors and exposed in warm, sunny climates will exceed the 60°C recovery temperature used in these experiments. In addition to the location of T_g, the breadth of the T_g relaxation is significant. The polyurethane's tan δ peak is significantly wider than that of the acrylic/melamine/

Table 3: Testing results (gloss and haze) from AMTEC Kistler panels, both pre- and post-healing

Labeling	Initial gloss 20°	Initial haze 20°	Loss of gloss ΔGl. 20°	Relative gloss retention (%)	Increase of haze	After healing 2 h 60°C				
						Loss of gloss ΔGl. 20°	Relative gloss retention (%)	Increase of haze	Healing (gloss) (%)	Healing (haze) (%)
Clearcoat A (sample #1)	89.5	14	18.0	79.9	36	17.1	80.9	36	5.0	0.0
Clearcoat A (sample #2)	89.8	14	20.5	77.2	41	15.8	82.4	33	22.9	19.5
Clearcoat B (sample #1)	86.9	8	9.5	89.1	22	4.8	94.5	13	49.5	40.9
Clearcoat B (sample #2)	86.5	9	9.7	88.8	22	3.3	96.2	11	66.0	50.0

silane (Table 2). Previous studies have suggested that the breadth of this peak is related to network heterogeneity.[18] Thus, the acrylic/melamine/silane network may have areas of high and low crosslink density which may impair reflow until significantly higher temperatures are reached.

From a formulation perspective, polyurethanes offer an opportunity to design in scratch recovery. The goal for a self-healing clearcoat may be to increase the crosslink density while keeping the T_g optimal. The T_g of the self-healing clearcoat should be low enough so that the polymers in the network are mobile under reflow conditions, but higher than ambient conditions.[19,20] The ability of polyurethanes to undergo hydrogen bonding also may improve scratch healing. The hydrogen bonds act as dynamic crosslinks, which improve network properties, but allow reflow to occur.

Conclusion

The scratch and scratch recovery characteristics of two model clearcoats—clearcoat A, an acrylic/melamine/silane clearcoat, and clearcoat B, a polyurethane clearcoat—were studied by various means. The initial scratch performance of the two clearcoats was significantly different, with the polyurethane possessing better nano scratch, car wash, and macro scratch performance. However, the polyurethane clearcoat showed markedly better scratch recovery performance after heating to mild temperatures. Importantly, the scratch healing performance was maintained after accelerated weathering, unlike the acrylic/melamine/silane clearcoat. This work demonstrates that functional scratch healing performance can be maintained under real-world use conditions, and may open the path to improved scratch performance and gloss retention for automotive finishes.

References

1. Courter, JL, "Mar Resistance of Automotive Clearcoats: I. Relationship to Coating Mechanical Properties." *J. Coat. Technol.*, **69** (866) 57–63 (1997)
2. Bertrand-Lambotte, P, Loubet, JL, Verpy, C, Pavan, S, "Understanding of Automotive Clearcoats Scratch Resistance." *Thin Solid Films*, **420–421** 281–286 (2002). doi: 10.1016/S0040-6090(02)00943-4
3. Courter, JL, Kamenetzky, EA, "Micro- and Nano-Indentation and Scratching for Evaluating the Mar Resistance of Automotive Clearcoats." *Eur. Coat. J.*, **7–8** 24–26, 28–30, 32–34, 37–38 (1999)
4. Lange, J, Luisier, A, Hult, A, "Influence of Crosslink Density, Glass Transition Temperature and Addition of Pigment and Wax on the Scratch Resistance of an Epoxy Coating." *J. Coat. Technol.*, **69** (872) 77–82 (1997). doi: 10.1007/BF02696246
5. Evans, DC, Lancaster, JK, "The Wear of Polymers." In: Scott, D (ed.) *Treatise on Materials Science and Technology*, pp. 85–139. Vol. 13, Academic Press, New York (1979)
6. Barna, E, et al., "Innovative, Scratch Proof Nanocomposites for Clear Coatings." *Compos. A*, **36** 473–480 (2005). doi: 10.1016/j.compositesa.2004.10.014
7. PPG Patent, US Patent #US6387519B1
8. Shi, X, Croll, SG, *J. Coat. Technol. Res.* (2009) (in press)
9. Ryntz, R, Abell, BD, Pollano, GM, Nguyen, LH, Shen, WC, "Scratch Resistance Behavior of Model Coating Systems." *J. Coat. Technol.*, **72** (904) 47–53 (2000). doi:10.1007/BF02698019
10. Van der Zwaag, S (ed.) *Self Healing Materials: An Alternative Approach to 20 Centuries of Materials Science*, pp. 139–159. In: Springer Series in Materials Science #100 (2007)
11. Hill, LW, Korzeniowski, HM, Ojunga-Andrew, M, Wilson, RC, "Accelerated Clearcoat Weathering Studied by Dynamic Mechanical Analysis." *Prog. Org. Coat.*, **24** 147 (1994). doi:10.1016/0033-0655(94)85012-7
12. Lin, L, Blackman, GS, Matheson, RR, "A New Approach to Characterize Scratch and Mar Resistance of Automotive Coatings." *Prog. Org. Coat.*, **40** (1–4) 85–91 (2000). doi:10.1016/S0300-9440(00)00113-2
13. Shen, WC, Jiang, B, Jones, FN, "Measurement of Mar Resistance and Study of Marring Mechanism of Polymeric

Coatings with Scanning Probe Microscope.'' *J. Coat. Technol.*, **72** (907) 89–95 (2000). doi:10.1007/BF02698027

14. Seubert, CM, Nichols, ME, ''Scaling Behavior in the Scratching of Automotive Clearcoats.'' *J. Coat. Technol. Res.*, **4** (1) 21–30 (2007). doi:10.1007/s11998-007-9006-3
15. Wagner, G, Osterhold, M, ''Comparison of Different Test Methods for Determining the Mar Resistance of Clearcoats.'' *Materwiss. Werksttech.*, **30** (10) 617–622 (1999). doi:10.1002/(SICI)1521-4052(199910)30:10<617::AID-MAWE617>3.0.CO;2-J
16. Nothhelfer-Richter, R, Klinke, E, Eisenbach, CD, ''Evaluation of the Scratch Resistance with Nano- and Multiple Scratching Methods.'' *Macromol. Symp.*, **187** 853–860 (2002). doi:10.1002/1521-3900(200209)187:1<853::AID-MASY853>3.0.CO;2-Y
17. Peters, CA, Ellwood, KR, Srivastava, Y, Nichols, ME, Greenfield, ML, ''Ultraviolet Light Absorber Mobility in Crosslinked Coatings: Experiments and Modeling.'' *Prog. Org. Coat.*, **58** 272 (2007). doi:10.1016/j.porgcoat.2006.12.004
18. Hill, LW, ''Mechanical Properties of Coatings, Plenary Lecture.'' *Proceedings of the Twenty-Seventh International Waterborne, High-Solids & Powder Coatings Symposium*, p. 1. New Orleans, LA, March 1–3, 2000
19. Meier-Westhues, H-U, Klimmasch, T, Tillack, J, ''On the Road to Improved Scratch Resistance.'' *Eur. Coat. Conf.*, Zürich, 2001
20. Mechtel, M, Glanzende Aussichten für 2K-Polyurethan-Klarlacke, JOT 09/2005, p. 540