Accelerated understanding

Joseph Hoefler, Ibrahim Eryazici, Bradley Hageman, Edwin Nungesser and **Richard Rosen** from Dow Leather Solutions explain the effect of binder selection on topcoat property retention after accelerated weathering.

Within the new car-purchasing process, the selection of leather seating is viewed as a premium upgrade over less-expensive alternative options. In keeping with this premium status, leather seating carries with it high expectations for comfort, appearance and durability.

To meet these expectations, Dow Leather Solutions has developed an acrylic topcoat binder with an exceptional balance of performance properties when combined with conventional polyurethane dispersion (PUD) binders.

When considering state-of-the-art topcoat systems, however, a continuing unmet need involves retention of properties after seating materials are subjected to a range of accelerated weathering conditions. Here, we compare the performance of fully finished automotive upholstery leathers after they are subjected to a range of accelerated weathering conditions including heat, hydrolysis and several xenon-arc chamber conditions. A broad range of PUD chemistries and blends of chemistry types were tested, along with an examination of the effect of blending each of these with an acrylic topcoat binder in a standardised upholstery screening formulation. In order to assess performance, colour, gloss and flexibility were measured before and after exposure to each accelerated weathering condition.

An examination of the data showed that xenon arc methods using quartz filters resulted in the lowest performance, with performance dropping proportionally to the length of the test. An analogous xenon-arc method involving use of an auxiliary lantern and filters was found to result in comparable sample damage, but only after much longer exposure duration. Exposure to hydrolysis and dry heat conditions produced the fewest changes in the samples. The data made evident that certain classes of PUD binders were preferred depending on the weathering specification being considered. Regardless of the various strengths and weaknesses of a particular class of PUD, a strong moderating effect was noted in many PUD-acrylic blend systems. This indicates that the two chemistries produce a measurable synergistic effect when used together in leather upholstery topcoats subjected to accelerated weathering conditions.

Predicting long-term durability

High-performance automotive upholstery leather must meet many stringent original equipment manufacturer (OEM) specifications. These include aesthetic properties such as colour, gloss and touch, as well as flexibility, abrasion resistance, and chemical resistance. These quality control tests are conducted shortly after production, yet the true measure of quality is how well the upholstery performs after many years in service. To ensure that newly manufactured seating can stand the test of time, OEMs also specify a number of tests designed to predict long-term durability.

The variety of these methods, including exposure to UV light, heat, humidity, and combinations thereof, is partly due to the difficulty in developing a truly predictive accelerated weathering specification. When considering topcoat binder selection, formulators and tanneries typically choose PUDs due to their excellent property balance. The hydrogen bonding across polymer chains and alternating hard-soft morphological domains of PUDs allow them to simultaneously provide high levels of toughness, flexibility down to low temperatures and minimal tack. The isocyanates chosen to synthesise automotive upholstery PUDs are universally aliphatic, typically isophorone diisocyanate, which supports long-term durability.

Conversely, a variety of polyols are used and each has unique strengths and weaknesses with implications for weathering. Polyester polyols often have an excellent cost/performance balance and are not particularly susceptible to UV radiation, but the ester linkages contribute to degradation through hydrolytic cleavage under hot, humid conditions. Polyethers are more resistant to hydrolysis, but are susceptible to UV photo-oxidation of the ether groups, leading to chain scission. Polycarbonate-based PUDs are more durable than the former types, but usage tends to be limited due to higher cost. An additional complication is that most systems used for upholstery finishing contain more than one class of PUD. Traditionally, formulators and tanneries have viewed acrylic binders as inferior to PUDs when used for topcoat formulations. This perception is changing, however, as acrylic performance steadily improves.

In a recent publication, Dow Leather Solutions introduced a new acrylic particle designed for gloss control and described its enhanced durability over existing PUD-based particles. The primary factors studied were aesthetics such as touch, colour and gloss after accelerated weathering.

More recently, Dow Leather Solutions reported development of new acrylic binder technology with performance capable of fulfilling typical automotive topcoat requirements. The present study considers the performance after accelerated weathering of not only pure PUD systems of the types mentioned, but also coatings using PUDs blended with this new class of acrylic binder.

Topcoat testing

Commercial full-grain automotive crust was cut into 1ft^2 test pieces. A basecoat was applied in two hand-sprayed applications at a total wet add-on of 13–16g. The freshly basecoated leather was dried for four minutes at 90°C after each coating. The pieces were stored overnight to facilitate complete curing and were smoothed afterwards at 135°C using a Finiflex ironing machine. A topcoat was then sprayapplied in two applications to a total dry add-on of 2.0-2.5g. The topcoats were dried for two minutes at 90°C between applications and again for four minutes after final coating. The finished leather was allowed to cure for at least five days at ambient conditions, and then cut into smaller pieces and subjected to accelerated weathering processes.

The study also explored a number of binder variables in the context of coating performance after accelerated weathering. A variety of polyurethane dispersion binders were used including polyester, polyether and polycarbonate polyol chemistries, as well as blends of polyester and polycarbonate polyols. Multiple examples of each polyol type were tested in order to provide averages of performance, but the conclusions drawn cannot necessarily be extended beyond the specific binders tested.

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In addition to variations in the PUD binder, an acrylic binder designed for use in leather topcoats was substituted for 50% of the binder solids in a number of experiments. This was done in order to test the effect on performance of a combined PUD/acrylic topcoat system after accelerated weathering.

After application of the leather finishes, leather swatches of each topcoat were subjected to a variety of accelerated weathering methods:

- **SAE J-2412:** a method that involves high heat and exposure to UV and visible light generated by a xenon arc within a controlled irradiance chamber. The method also includes a dark cycle at high humidity conditions. This method was run at an irradiance level of 225kj/m².
- **FLTM BO 116-01:** a related method that utilises auxiliary glass panels designed to filter light below a wavelength of 335nm. Exposures using this method were conducted at levels of 225 and 976kj/m².
- **Dry heat:** exposure to heat was accomplished by placing the samples in an oven at a temperature of 90°C for 500 hours.
- **Hydrolysis-producing conditions:** hydrolysis was promoted by placing the samples in a controlled humidity chamber at a temperature of 50°C and 95% relative humidity for 500 hours.
- A control sample stored at ambient conditions.

After exposure, the leather samples were evaluated for change in gloss, colour stability and flexibility.

Dissecting the data

In general, the data shows that the methods involving UV exposure resulted in the largest gloss changes, while oven and hydrolysis chamber exposure produced small changes. At equal irradiance levels, the modified wavelength distribution of the Ford method resulted in minimal gloss changes when compared with the SAE J-2412. However, when the irradiance under the Ford method was tripled, much larger gloss changes were observed, indicating that in this case the milder spectral light distribution delayed, but did not prevent, coating degradation.

A comparison was also made between the performance of topcoats containing solely PUD binders versus a 50:50 blend of PUD and acrylic binders. After exposure to the J-2412 test, a system of combined PUD/acrylic polymer types manifested improved performance over pure PUD, with an average normalised gloss level much closer to 1.0. In all cases, the addition of the acrylic binder resulted in at least comparable performance. An additional beneficial effect of adding acrylic content was that the standard deviation of many of the gloss measurement averages decreased, indicating more consistent, predictable performance after weathering.

The polyester-based PUD type showed comparatively poor performance, especially in the oven and hydrolysis chamber tests. The best performance was observed in the case of the polycarbonate PUDs, which manifested only slight gloss changes after each of the weathering methods employed. An additional observation was that the PUD binders containing a combination of polyether and polycarbonate polyols tended to show the weaker performance of the pure-polyether systems, rather than a compromise between the two pure systems.

The beneficial effect of adding acrylic content to the topcoat systems was observed in the case of the polyester, polyether and mixed polyether/polycarbonate PUDs. In almost every case, the normalised gloss of the blended systems was closer to '1', showed lower experimental scatter, or both.

Colour changes

Colorimetry data was also collected for both the unexposed and exposed samples, and reported as a delta E value. Once again, the samples underwent the most change after exposure to xenon discharge weathering methods, with delta E values in excess of 2.0 being recorded. The performance was again very similar when comparing the SAE method at 225kj of exposure and the Ford method at 976kj, although significantly less colour change was recorded when the Ford method was run at a 225kj exposure.

When the samples were exposed to the heat and hydrolysis conditions, only minimal changes were noted. As with the gloss measurements, increased stability was observed in the coatings using PUD/acrylic blended polymer chemistries, with several delta E levels being reduced by approximately 50% and in no case were the delta E measurements higher in an acrylic-containing sample. Similar or lower standard deviations were also seen in the acrylic-containing topcoats.

When considering gloss change, the polycarbonate was clearly the best-performing class in terms of colour stability. As shown previously, preparing a mixed polyether/polycarbonate PUD largely resulted in reproducing the weaker performance of the pure polyether binder rather than performance in-between that of the two pure types.

Addition of acrylic content to the topcoat systems had the largest effect when the weakest PUD types were used. In many of those cases, the introduction of the acrylic polymer improved performance noticeably. This effect was most readily seen after UV weathering by the SAE and Ford methods when the polyether/polycarbonate blend was used, and in the case of the polyester type, after oven and hydrolysis chamber exposure.

The impact of weathering

In addition to appearance measures, the flexibility and softness of leather articles is often negatively impacted by weathering processes. In order to assess this property, the Bally flexibility test was run on the samples produced for this study. While the standard specification calls for 100,000 flex cycles, many of the weathering conditions led to catastrophic failures after this large number of flexes. In order to better assess the relative performance of all of the experimental systems, the much less demanding level of 5,000 cycles was also selected.

The samples exposed to 225kj of energy using the SAE J-2412 method underwent the most dramatic changes, manifesting a large increase in embrittlement. By contrast, the Ford BO-116 method at the same irradiance level showed almost no change, indicating the light-filtering effect of the bandpass filters in the lantern. When the irradiance level of the Ford test was increased to 976kj, a more noticeable decrease in performance was observed; however, performance was still higher than after testing using J-2412.

When considering ageing in dry heat conditions, the trends observed when testing gloss and colour were maintained. The average performance was high at the test level of 5,000 cycles. Similarly, only a small loss of performance was observed after exposure in the hydrolysis chamber.

The results averaged across PUD types did not show a measurable improvement in flexibility based on the presence of the acrylic binder. However, performance was also not harmed by the acrylic addition.

When considering the performance of individual PUD types, it can be shown that performance was similar across PUD types after 5,000 flexes. A notable exception was in the case of the polyester PUD, which suffered a significant loss of flexibility after hydrolysis. Another observed trend was that the polycarbonate PUDs retained the most flexibility after being exposed to solar testing methods.

Results also show the effect of acrylic polymer addition to the experimental systems. This data indicates that the acrylic effect was most beneficial when added to the polyester and polyether/polycarbonate blended PUD. In those cases, it tended to improve hydrolysis and UV weathering resistance.

A second set of Bally tests evaluated performance of the samples after 100,000 room temperature cycles. Due to extensive cracking, none of the samples exposed to 225kj using J-2412 or 976kj using the Ford method were evaluated after 100,000 cycles. However, at the same 225kj exposure level using the Ford test, a measure of performance was retained. Exposure of the samples to both heat and hydrolysis conditions produced modest decreases in performance.

The addition of acrylic polymers to the experimental systems modestly improved performance when exposed using the Ford method and had no negative consequences in the other cases. Concerning the performance of specific PUD chemistries in the figure (page 69), this data indicated that the polyester-containing PUDs tested showed lower overall performance than the polyester and polycarbonate-containing polymers, with polycarbonate PUDs manifesting the best performance. The polyester composition primarily showed weakness after oven and hydrolysis chamber ageing. As discussed above, the polyether/polycarbonate binder had UV resistance worse than either of the pure compositions.

Addition of acrylic polymers to these systems was beneficial in improving flex performance after exposure using the Ford method, especially when using polyether PUDs. The heat and humidity resistance properties of the polyester backbone were also improved by the addition of acrylic polymer.

Performance indicators

A study was undertaken to examine the performance of topcoat formulations as the PUD and acrylic binder composition was systematically varied. The finished leather samples were exposed to accelerated weathering methods involving UV, heat and humidity exposure, and then tested for gloss and colour stability, as well as flexibility. An analysis of the data allowed a number of conclusions to be drawn.

With regard to the exposure conditions, the most rigorous were the xenon methods, which included UV light in addition to heat and humidity. This is not surprising in that UV light is known to produce chain scission and radical generation in a number of coating systems, in addition to chain degradation brought about by hydrolysis. Furthermore, heat exposure may induce stiffening of films due to loss of plasticising solvents and hydrolysis due to the generation of water through thermal oxidation. The Ford BO 116-01 method was found to be less destructive than the SAE J-2412 method at equal irradiance, and when the irradiance under the Ford method was increased to three times the irradiance of the SAE method, the performance was found to be similar across both methods. This effect is thought to be due to the long-wavelength bandpass filters used with the former method, which filters out wavelengths shorter than 335nm.

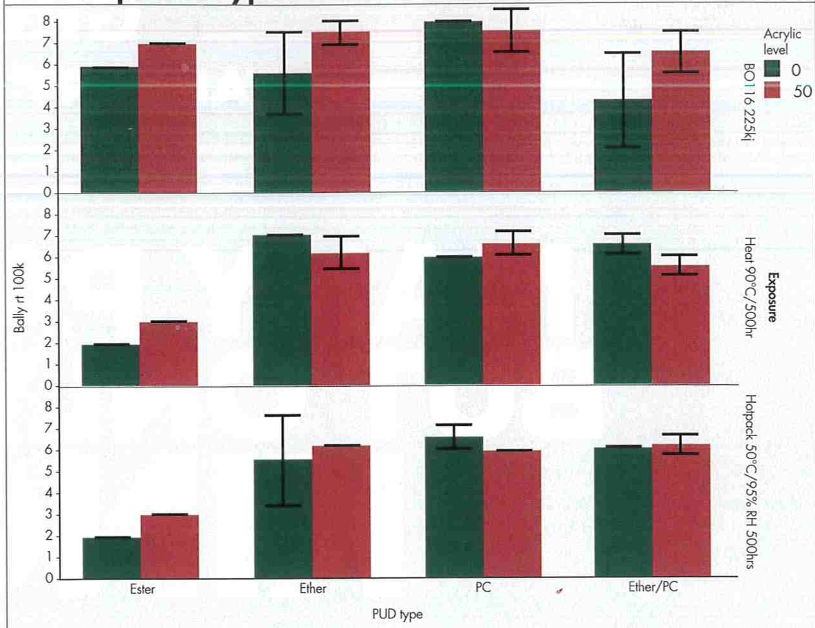
When compared with natural sunlight, the J-2412 method supplies an unnaturally high irradiance of these short UV wavelengths, which leads to destructive photochemistry in many polymers. The filters employed under the Ford method sharply reduce the intensity of these wavelengths. Exposure of the polyester polymers under conditions of heat and humidity consistently led to significant loss of performance. This is attributed to the tendency of the ester linkages to undergo hydrolysis under humid conditions. Oven ageing can also lead to hydrolysis as hydrogen peroxide formed through thermal oxidation decomposes, producing water molecules.

In further considering polymer chemistry, the polycarbonate class of PUDs was shown to consistently demonstrate the best balance of properties in gloss and colour stability, as well as retention of flexibility.

The relatively high expense of this class of PUDs has often led formulators to choose a different chemistry or minimise the polycarbonate content. Minimisation of polycarbonate may be accomplished through use of auxiliary binders of a different composition or a single product utilising a polycarbonate blended with a different class of polyol. The use of these mixed polyol systems may not be an effective solution if weathering resistance is a desired property.

This study showed that in many cases, PUD systems containing both polyether and polycarbonate polyols did not have performance in-between the two pure systems, but instead tended to perform like the weaker component. One subject of particular interest was the effect of combining PUD and acrylic binders. Traditionally, formulators and tanneries have been reluctant to incorporate acrylic polymers in high-performance automotive topcoats since a very high PUD content was regarded as necessary in order to achieve the stringent performance requirements. This study showed a significant acrylic binder fraction may be used without a performance penalty when considering the properties studied. In fact, in many systems, the addition of 50% acrylic binder solids had the effect of improving performance, including flexing performance. Acrylic polymers were especially effective at improving overall UV weathering performance and also the hydrolysis resistance of polyester PUDs. ●

Bally Flex (5,000Cy) results by PUB and exposure type



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