Understanding the Effect of Processing Conditions on the Scratch and Mechanical Behavior of Automotive Plastic Coatings on TPO

by

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Scratching of plastic components has been a growing concern among automakers. Scratching may result from pre-delivery or post-delivery events. The coatings chemist may formulate differently for "green" properties, such as those related to pre-delivery, than for those properties resulting from aged, weathered coatings. Unfortunately, manufacturers' warranties cannot separate out which event is the more prevalent contributor to damage of coatings on plastics. While automotive coating producers measure such properties as tensile strength, modulus, and hardness in attempts to relate these mechanical properties back to the "green" scratch resistance, little has been done to show how mechanical properties change as a function of weathering.

This article attempts to correlate the scratch resistance behavior of different one-component (1K) crosslinked systems to the mechanical properties developed as a function of processing conditions and weathering. Of the parameters studied, cure temperature was found to be more critical than time at temperature, thus negating the concept of bake equivalents for coatings on plastics. In addition, it was found that for some 1K cured coatings, scratch resistance did not change significantly with the processing conditions used, while mechanical properties did, especially after accelerated weathering.

INTRODUCTION

Scratch damage of painted automotive plastic components continues to be of concern, particularly when the parts are freshly painted. Damage can occur during handling, shipping, or assembly. Unfortunately, there is no accepted "test" capable of duplicating the above damage. Researchers attempt to quickly reproduce damage in the laboratory that duplicates what occurs in the field over a prolonged period of time. In the laboratory, simply rubbing a painted part with a cloth that may or may not contain an abrasive can

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produce scratch and mar damage. This is the basis for the conventional crockmeter test.[1] However, with some pieces of equipment, the weight of the head can be increased, i.e., the Taber test device.[2] The resultant scratch damage is typically observed visually or measured by gloss loss or changes in haziness or grayness of the coating. Single or multiple tips have also been used to produce surface and/or deep scratches as the stylus tip size and/or load are changed. Tools such as a nanoindenter, a Ford five finger apparatus, and a Scratcho device are all currently in use.[3-9]

Scratch and mar are terms that are usually used interchangeably. Marring is typically characterized by gloss loss and is therefore associated with a high density of small, shallow scratches over a large area. Scratching is usually associated with deeper deformation lines that may occur alone or in multiples. Finding a technique that can be used to produce scratch and mar damage identical to that seen in the field can be quite a challenge.

Many of today's automotive coatings are not fully cured directly out of the oven, but require some degree of post-cure to develop full properties. This is particularly characteristic of isocyanate and silane crosslinked flexible coatings. Silane crosslinked flexible coatings, in particular, exhibit superior scratch resistance due to the their ability to re-flow and heal minor damage on plastics, especially when exposed to sunlight and/or heat. On the other hand, melamine 1K cured coatings do not require much post-cure (if any), and exhibit less damage when subjected to the same scratch damage protocol as two-component (2K) coatings. They do not substantially re-flow when exposed to elevated temperatures. Since freshly painted parts can be subjected to situations or environments that may cause damage out-of-the-oven or during the post-cure period, studying the conditions used to prepare and cure the coating can be very informative. This is important because most fascia parts (i.e., bumpers) are relatively large and have fairly complex shapes. It is not uncommon for localized areas of a bumper to see a cure variance of 5 to 100°C with significant differences in oven air flow.

Many of the available studies have concentrated on fully cured parts prepared under optimum condi-

Figure 1—Processing robustness measurements of hardness and elastic modulus for AP/BC/CC samples "P" and "D."

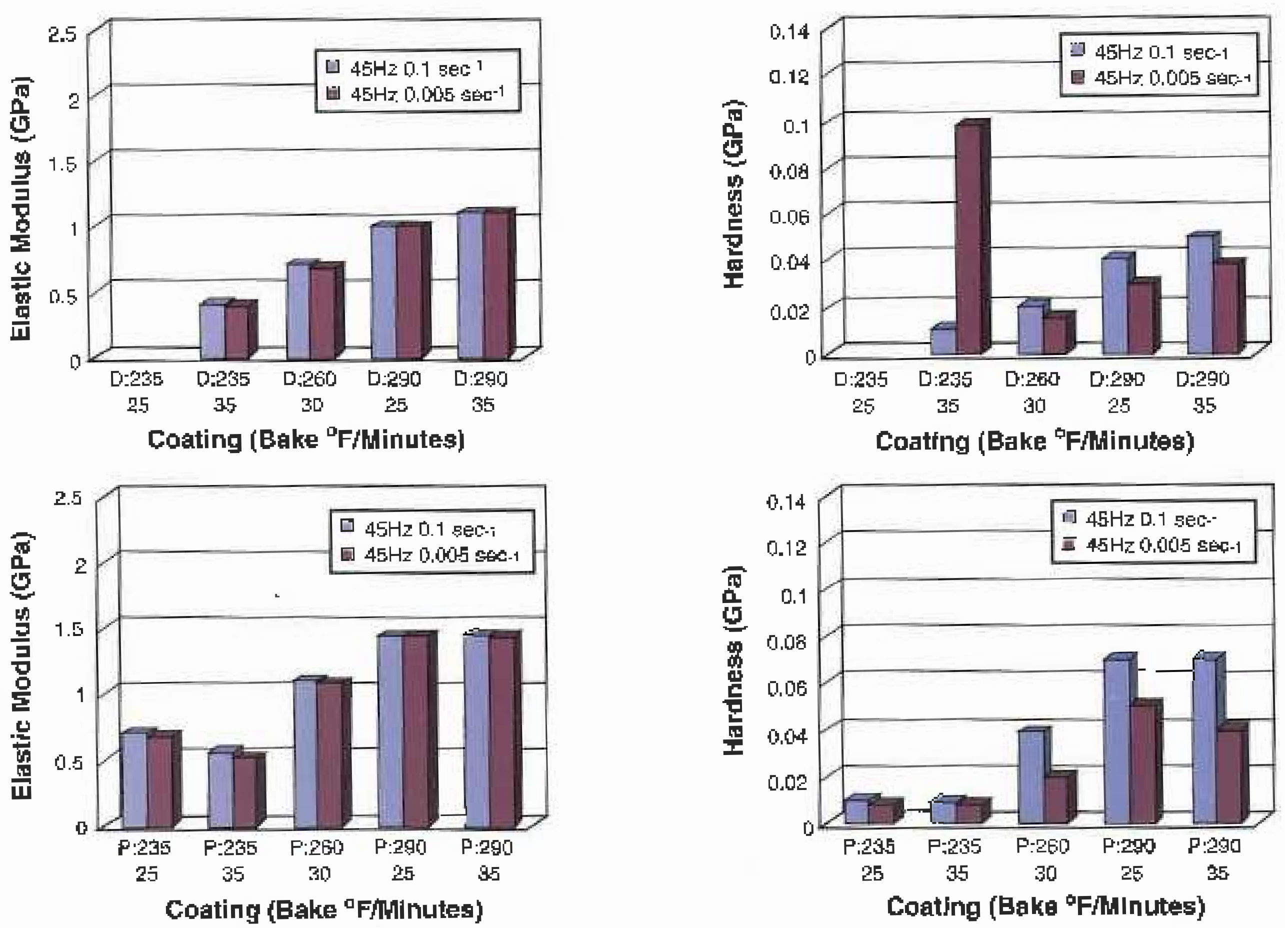
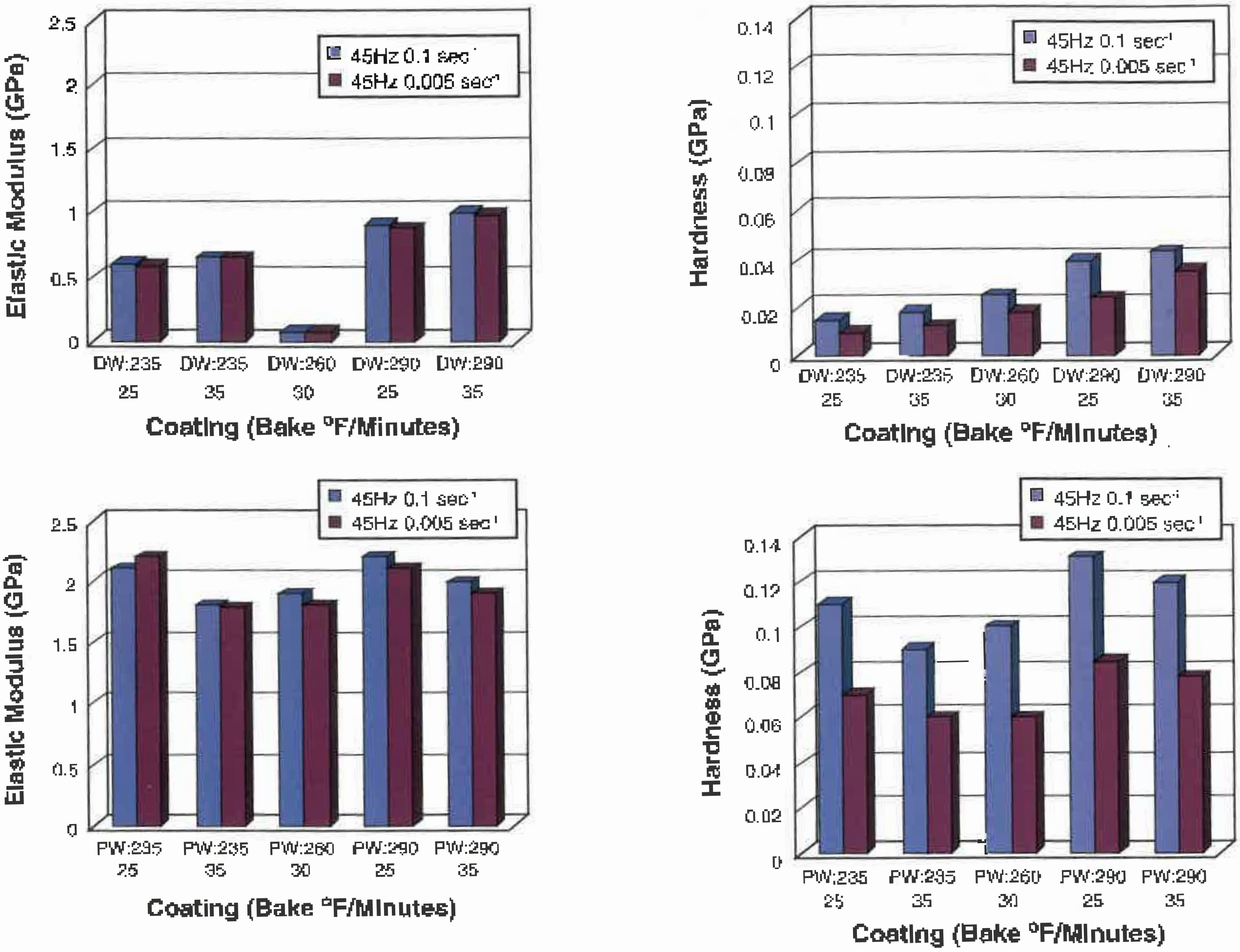


Figure 2—Elastic modulus and hardness properties of weathered AP/BC/CC coating systems for technologies "P" and "D."



tions.[10-12] Automotive components often are painted in different facilities, utilizing different paint systems which may be cured under a variety of different conditions, and are then attached to the vehicle during final assembly. Compositionally, these coatings may vary in resin backbone, which may affect hardness, mechanical properties, surface tension (that will affect the coefficient of friction), and toughness.

In this article, we examine the effect of processing conditions (bake temperature and time at temperature) for a series of 1K crosslinked coatings on TPO from different paint suppliers as measured by their scratch and mechanical behavior (elastic modulus and hardness). Also, to understand how scratch and mechanical properties may change with time, we compare these properties before and after accelerated weathering. A coating system that exhibits good scratch and mechanical properties when new, but which substantially deteriorates upon weathering, may not be attractive to the automotive consumer.

EXPERIMENTAL

All solventborne flexibilized coatings were spray applied to thermoplastic polyolefin (TPO) panels (Basell DRS715X) wet-on-wet and baked at the prescribed temperature and time in an indirect-fired natural gas convection oven. The coatings consisted of a chlorinated polyolefin in conjunction with an auxiliary resin adhesion promoter (AP), a one-component acrylic-melamine black basecoat (BC), and a one-component acrylic-melamine or acrylic-polyester melamine clearcoat (CC). Two different coating systems (labeled "P" and "D") utilized in the automotive components business were obtained from commercial paint suppliers (PPG Coatings and DuPont Performance Coatings). Dry film thicknesses of each layer ranged from 5–7 microns for the adhesion promoter, 6–8 microns for the basecoat, and 35–38 microns for the clearcoat. Curing conditions ranged from 235°F to 290°F for 25 to 35 minute ambient.

Instrumented indentation was performed at room temperature using a NanoIndenter XP equipped with a diamond conical indenter of 90° included angle and a 2 micron radius available from MTS Systems. Forces applied ranged in general from 0.2 mN to 100 mN. Constant strain rate loading cycles with the continuous stiffness mode option were used, at frequencies of 0.1 sec^{-1} and 0.005 sec^{-1} at 45 Hz. Evolution of the hardness and elastic modulus measured throughout the loading phase was used to record the properties of the coatings.

Single probe scratch testing was performed at room temperature on MTS Instruments' XP Nano-Scratch apparatus equipped with the same probe described above. Testing parameters used included a scratch length of 1 mm and a scratch velocity of 2 microns per second. A progressive force scratch method was utilized in which the applied force was increased linearly from 2 mN to 40 mN along the scratch area.

The static coefficient of friction was performed on the SLIDO machine described in reference 10. The Kapton-covered bob was translated across the sample at a load of 4.5 kg and a velocity of 5.08 cm/sec. The static coefficient of friction was derived from the plot of frictional load versus distance, where at the onset of movement the peak frictional load obtained was divided by the compressive load utilized.

Figure 3- Coefficient of friction measurements for AP/BC/CC technologies "D" and "P" before and after Xenon weathering.

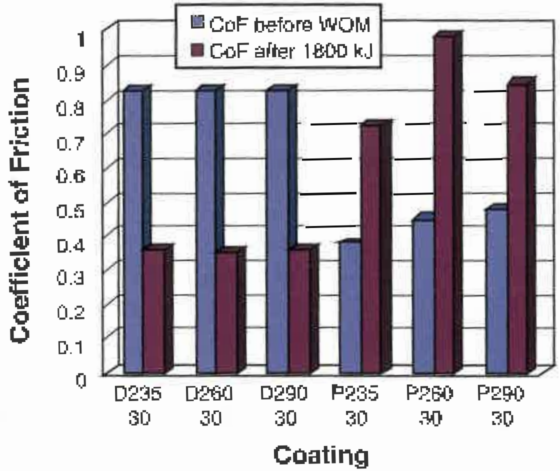
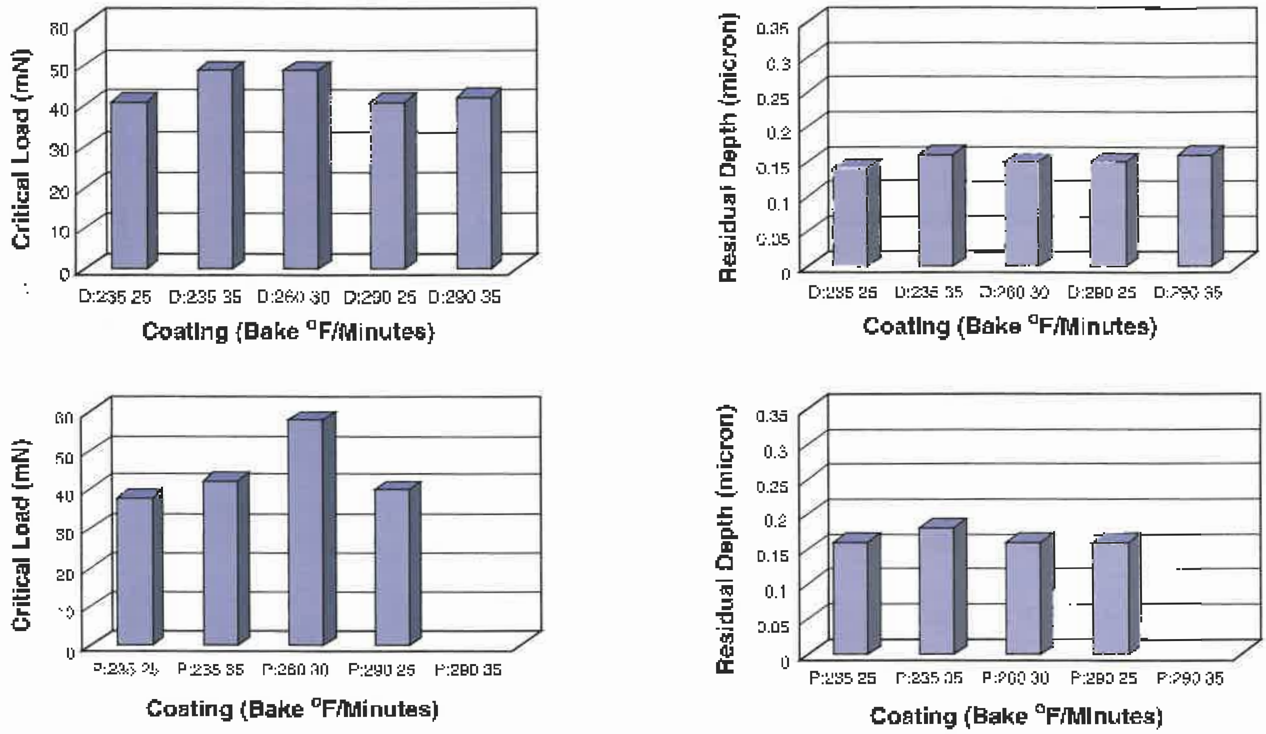


Figure 4—Scratch performance as measured by critical load and residual depth for AP/BC/CC technologies "D" and "P" as a function of process condition.



RESULTS AND ANALYSIS

Effect of the Process Conditions on Mechanical Properties of the Coating System

To assess whether the hardness and elastic modulus values obtained for the "P" and "D" AP/BC/CC coating systems changed as a result of the way the materials were processed, e.g., time and temperature of "cure," the coatings were prepared at various bake times and temperatures as listed in *Figure* 1. Values of elastic modulus from the experiments performed at two different strain rates should be equal. The small variations apparent in this data may be a result of thermal drift between the slow and fast strain rates. What is important in this data, however, is the significant difference in hardness between a strain rate of 0.1 sec^{-1} and 0.005 sec^{-1}. This indicates the time dependency of the properties of the surface. A significant evolution of both plastic and yielding properties with bake conditions can be observed. The temperature has a much more significant effect than the time of bake. The higher temperature bakes result in higher elastic modulus and hardness for both technologies.

Effect of Weathering and Process Conditions on the Mechanical Properties of the Coating System

Accelerated weathering (1800 kJ in a Xenon Arc Weather-Ometer performed according to SAEJ1960 with borosilicate/borosilicate inner and outer filters on the lamp) was carried out on samples of both the "P" and "D" AP/BC/CC technologies baked at various conditions. Weathering has an important effect for low baking conditions in the "D" technology and is present in all baking conditions for the "P" technology, as shown in *Figure* 2. In all cases, for the weathered samples of the "P" technology, the hardness increases by over six times for the low temperature cured systems and approximately two times for the high bake conditions versus the unweathered samples (*Figure* 1). The elastic modulus increases by four times for the low bake condition and approximately one and one half times for the high bake condition versus the unweathered samples. Weathering seems to "erase" the effect of cure condition for the elastic property. It is interesting to note that the weathered "D" technology has relatively little change in either mechanical property when compared to the unweathered counterpart in *Figure* 1.

Effect of Weathering and Process Conditions on Static Coefficient of Friction

With mechanical properties determined for each technology as a function of weathering, one variable known to affect scratch, but yet undetermined, was the coefficient of friction. Therefore, the AP/BC/CC systems for the "P" and "D" technologies were evaluated for static coefficient of friction values as described in the Experimental portion of this article. As shown in *Figure* 3, the "D" technology coefficient of friction drops by over 60% when weathered, whereas the "P" technology increases by over 50% when weathered. The process conditions do not seem to affect the coefficient of friction value in either the weathered or unweathered samples of "D" technology, but they are affected in the "P" technology. This seems to suggest additive migration, possibly a surface active agent that in "D" is more permanent, and potentially the loss of additive technology upon weathering in "P." The lower coefficient of friction is more desirable since it usually correlates with less surface damage in compressive/shear damage, e.g., Slido.

Effect of Weathering and Process Conditions on Scratch Performance

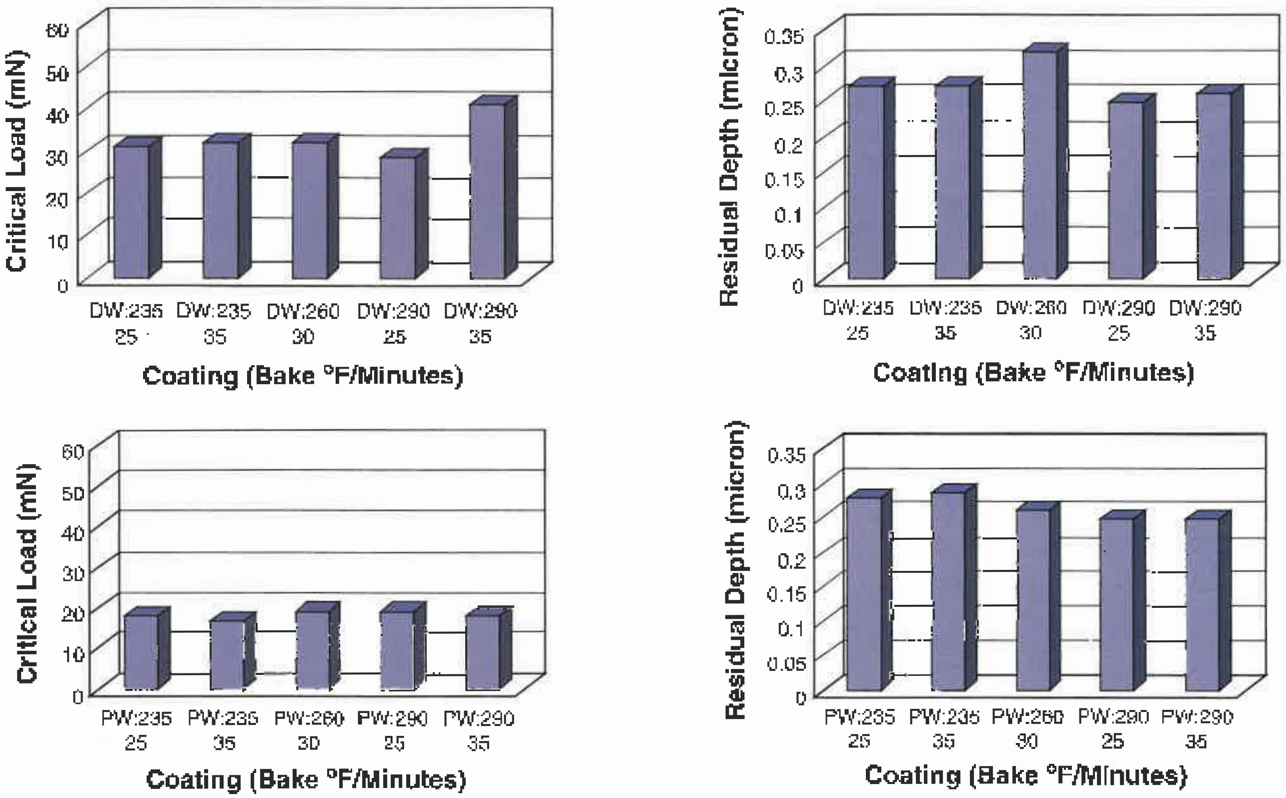
Figure 4 displays the scratch performance as measured by critical load to fracture and residual depth measurements for AP/BC/CC systems for technologies "P" and "D" as a function of processing conditions. Process conditions do not seem to significantly affect the scratch performance of the "D" technology, although, as seen above, the mechanical properties are changing. The effect of frictional changes in the surface may profoundly convolute these results. The "P" technology however seems to be optimized for a 260°F bake, with the highest critical load achieved at this cure. Both coating systems have roughly the same residual depth after the scratch is made, indicating similar elastic recovery.

Weathered samples were subjected to scratch testing as shown in *Figure* 5. The "D" samples maintain the great majority of the scratch performance they exhibited in the unweathered condition, particularly at the higher temperature bake, even at increased residual depths of scratch after weathering. The "P" technology, however, is dramatically affected by weathering, losing approximately 50 to 70% of its scratch performance as measured by the decrease in critical load to fracture. This would have been suggested when taking into account the large increase in frictional coefficient upon weathering of this technology, along with the dramatic change in mechanical properties, particularly the increased elastic modulus of the "P" AP/BC/CC system.

SUMMARY

The mechanical properties of coatings can change dramatically as a result of the way in which they are processed. In this study, two 1K acrylic melamine technologies, obtained from different suppliers, were evaluated under varying cure temperatures and times. The mechanical properties were found to vary as a result of the cure condition. It was determined that variations in

Figure 5—Scratch performance as measured by critical load and residual depth, for weathered (1800 kJ) AP/BC/CC technologies "D" and "P" as a function of process condition.



temperature had a stronger effect on mechanical behavior than time at a that temperature.

Scratch performance of technology "D" was much more robust than the "P" technology, as it was not significantly affected by cure condition. Weathering the technology did not significantly lower the scratch resistance either, which may have been partly due to the dramatic decrease in frictional characteristics of the surface upon weathering. This suggests that the incorporation of additives that migrate to the surface and maintain their permanence may play a vital role in affecting continued scratch resistance. In addition, resin selection may also play a vital role. The evolution of scratch performance upon aging is generally not evaluated in automotive specifications, although perhaps it should be. A new car's appearance, e.g., initial "green" scratch characteristics, is important, but so too are performance characteristics upon aging. Flexible coatings that retain sufficient mechanical properties for a long period of time are expected to damage less than coatings that become more brittle.

Finally, this study shows the importance of bake temperature on 1K melamine cured coatings as related to scratch performance and mechanical properties. Coatings that are optimized for a particular cure condition may exhibit inferior performance when exposed to temperature swings that routinely occur in the painting and curing of automotive plastic parts. Coatings that retain their mechanical properties will offer performance superior to coatings that deteriorate. Since scratch damage is a major issue with today's automotive vehicles, it would be beneficial to know how scratch and mechanical properties change with weathering, in addition to the visual and adhesive measurements commonly taken today. CT

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