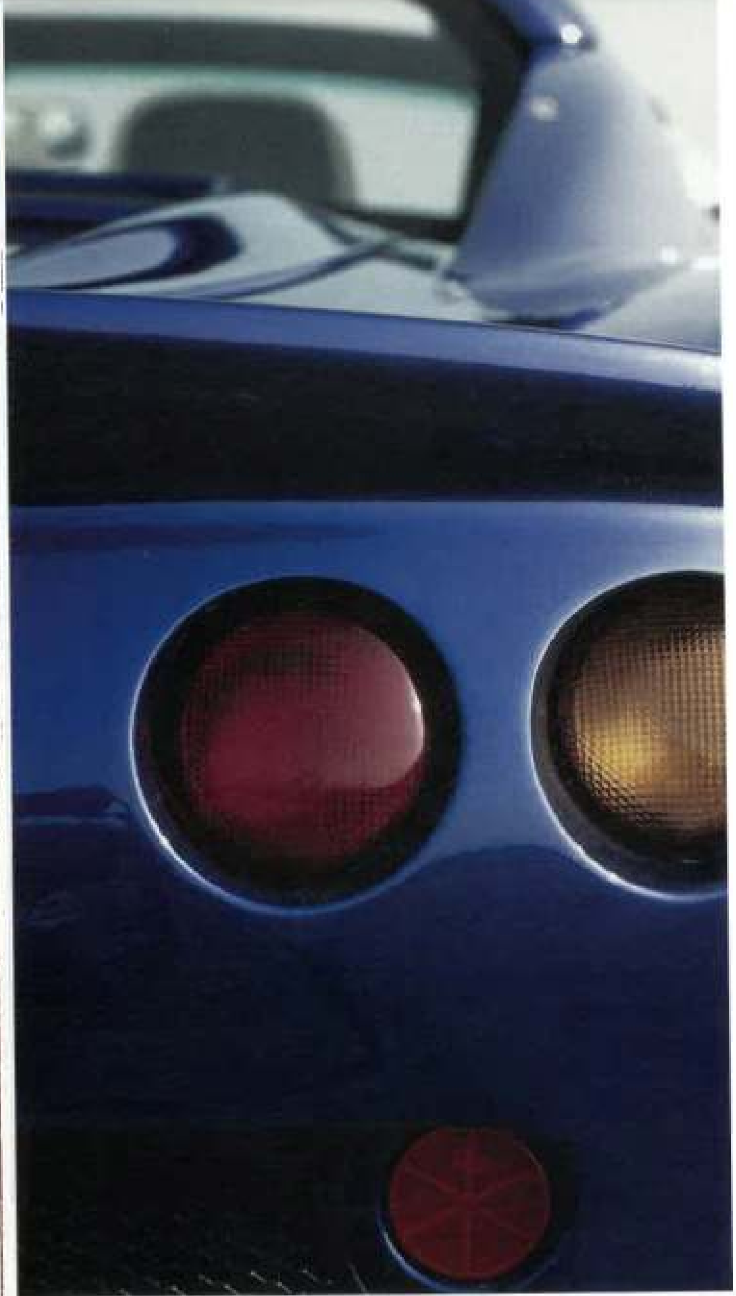

Real World Performance of Painted Plastic Components

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The automotive industry is the largest manufacturing industry in the world. Over 70 separate companies employ more than four million people. At current build rates of 17 million units annually, there are estimated to be over 350 million operable vehicles on the earth today. While steel still accounts for approximately 90% of the weight of a vehicle, plastic usage continues to increase due to styling latitude, cost and weight savings, and low temperature impact performance. Of the nearly two billion pounds of plastics utilized in automotive applications, approximately 30% of plastic components are painted. For the painted applications, performance attributes are governed by the environment to which the component is exposed, e.g., interior versus exterior.

Key attributes that must be attained in painted plastic applications, irrespective of the environment, include adhesion and abrasion resistance. Additional performance requirements attributed to exterior environments include chip and "gouge" resistance. Gouge resistance is defined as the cohesive behavior of a painted plastic when exposed to compressive shear events, e.g., a shopping cart hitting a painted bumper in a parking lot, a low speed impact between two vehicles' bumpers, and the like. All of these performance behaviors are linked to some property or properties of the plastic, the paint, or the paint/plastic interface, but little

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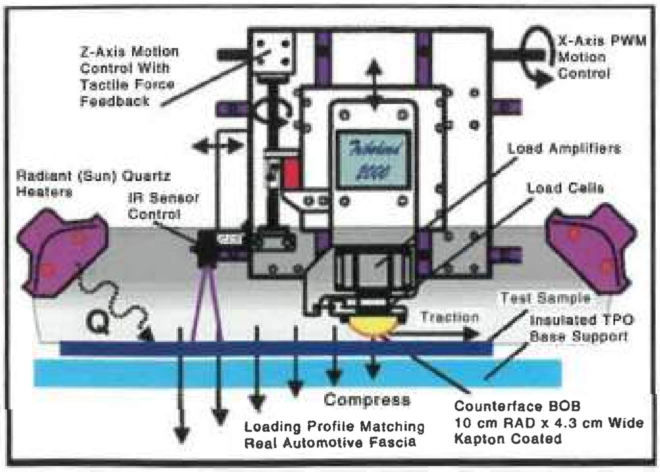
has been done to understand the influence of processing parameters on the performance of the painted plastic composite.

A plastic material known as thermoplastic poly (olefin) (TPO) is gaining acceptance in automotive applications due to its light weight, low cost, and recyclability. TPO is a blend of elastomer and poly(olefin), most often poly(propylene) homopolymer or a poly (propylene)/poly(ethylene) impact copolymer. The TPO's performance has been found to be influenced by the fabrication methods (such as injection molding) commonly utilized in forming automotive parts. Since the injection molding process retains a high cost of capital due to the equipment and tooling utilized, engineers would like to produce as many parts per hour as possible on this equipment to attain payback in shorter periods of time. The high shear rates utilized to accomplish high filling velocities of the molten pellets into the tool impart the shear dependent morphology within the injection molded fabricated TPO parts.[1-3] The shear induced morphology resultant from the injection molding process imparts "boundary layering," the thickness and intercompatibility of which determines the ultimate cohesive tensile strength of the plastic alloy.[4] The cohesive integrity of the TPO component is affected by the degree of dispersion of the elastomer within the poly(olefin) matrix and the degree of crystallinity of the compound within the injection molded substrate. Processing parameters that influence the performance properties of the plastic include melt viscosity ratio of the poly(olefin) to the elastomer, melt and mold temperature, and rate and temperature of cooling.

Thermoplastic poly(olefin) still remains somewhat of a nuisance for painters due to its inherently low surface free energy which often results in poor wettability and low adhesive strength. Adhesion to an untreated (e.g., no flame- or plasma-pretreatment) weak boundary layered TPO plastic is dependent upon the ability of an adhesion-promoting primer formulation (of which a chlorinated poly(olefin) resin is most often the primary component) to wet the surface, diffuse into the top subsurface morphology, and swell and entangle with the amorphous regions (e.g., elastomer or amorphous poly(propylene) of the plastic substrate).[5-8]

The type of chlorinated poly(olefin) (CPO) utilized in enhancing adhesion to the TPO substrate is influenced not only by the crystallinity of the CPO, which is influenced in part by the degree of chlorination, but also by the degree of maleation on the CPO backbone.[9,10] Higher maleation levels provided greater topcoat interlayer adhesion with the CPO containing adhesion promoter, while CPO formulations with higher chlorine levels resulted in poorer gasoline resistance of the topcoated composite (higher chlorine levels resulted in greater solvency of the adhesion promoter in gasoline, thus resolvation). Solvent levels in the adhesion-promoting primer formulation were also found to influence topcoat adhesion.

Figure 1—*SLIDO* compressive shear delamination apparatus.



The effect of topcoat type on the adhesive/cohesive integrity of painted TPO composite was evaluated through the use of a device capable of applying a compressive-shear load to the part.[11] A schematic of the device, herein termed *SLIDO*, is shown in *Figure* 1. In the *SLIDO* CSD testing protocol, the sample (e.g., a painted TPO plaque) is placed on a translating stage (referred to as the "test sample" in the figure). A load is applied to the top surface of the test sample through a 10.2 cm (4 in.) aluminum "bob." The panel, heated if desired by infrared heaters located directly above the panel area, is then translated under the bob at a fixed acceleration and velocity, producing an instrumented load/displacement profile.

When damage is incurred within a painted TPO part, e.g., the fascia, the customer cannot discern whether the damage is adhesive or cohesive (*Figure* 2).

Figure 2—Compressive shear damage inflicted within painted TPO.

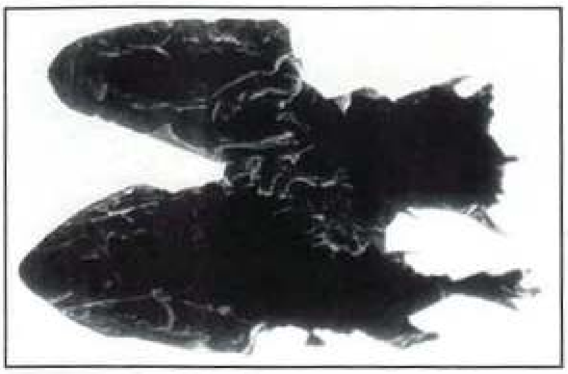


Table 1—Regression Analysis Parameter Estimates of Independent Variables[a]

Basecoat Color (Thickness)	Flash Time (x)	Bake Time (y)	CC Thickness (z)	b_0
White (40 mm)	9.3	17.5	839.6	-589.5
Red (30 mm)	-104.7	-30	-1643	6156.8
Black (35 mm)	9.9	-1.1	552	352.8

(a) where: compression force = b_0 + x(flash time) + y(bake time) + z(CC thickness).

As depicted in *Figure* 2, the damage incurred within the painted TPO substrate is most often cohesive (as evidenced by the dark gray TPO "ripping" cohesively under the white basecoat/clearcoat painted substrate). The corrective action taken by the automotive supplier to alleviate such damage should be one in which the painted substrate is made more robust "cohesively." Early studies indicated, however, that by simply changing the topcoat, the early damage resistance of the painted TPO could be made more resistant to abrasion. Painted TPO damage, however, was not alleviated completely. It was still noted that field returns were cohesive, and that "fixes" imparted to the clearcoat, namely decreasing the coefficient of friction by increasing slip-aid concentration, provided only a temporary improvement due to the loss of slip-aid over time in the field.

Upon exposure to compressive shear events, failure within the painted substrate is most often the result of cohesive ripping within the TPO weak boundary layers. Failure results from removal of topcoat and fibrillation of the elastomer or amorphous poly (propylene) from the top plastic surface.

The ability of a coated plastic to withstand stone/gravel impact has been studied extensively by Ramamurthy[12] and Ryntz.[13] Test methods utilized to simulate coating damage incurred as a result of stone impact or gravel abrasion were developed and include the "precision paint collider" stone impacter[14] and the Erichsen alumina oxide abrasion (erosion) blaster.[15] As opposed to compressive shear loading, chip resistance testing protocol imparts a small, discrete compressive impact to the substrate by means of a projectile, e.g., a rock or steel shot. The damage observed is often in the form of paint loss from the substrate, and is characterized in terms of chip density. An in-depth analysis of such impact damage on painted thermoplastic olefins often displays cohesive "ripping" within the substrate, which can be numerically simulated through delamination under compressive stress of TPO weak boundary layers.

Scratch durability of clear coatings in automotive applications has been ranked as one of the most important performance parameters of a paint system. Yet, no characterization methodology for scratch resistance has been totally accepted by the scientific and industrial communities. Scratch and mar resistance have been the subject of numerous research efforts in the past few years, both by research institutions and manufacturing industries. This research performed has established a series of correlations between certain scratch parameters and field performance surveys results.

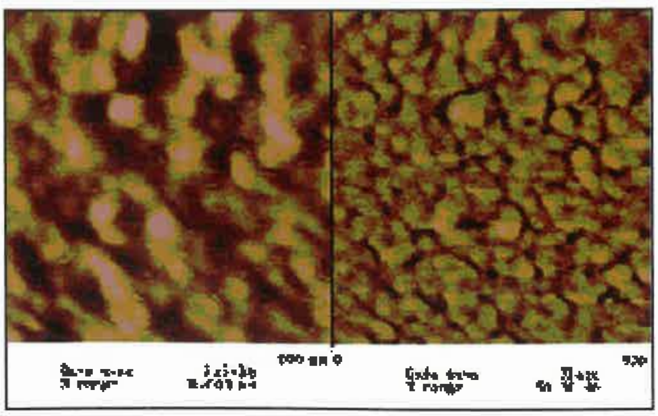
Several researchers related the variation of modulus,[16] toughness,[17] and hardness[18] of the coating to a scratch resistance rating. Conventional test methods utilized to quantify the scratch resistance were measurements such as: reduction in gloss of a coating after being subjected to a traversing tangential load of known particle size abrasive (crockmeter test); measurement of damage depth and recovery after exposure to a single point indenter (nanoindenter[19,20]); or quantitative measurement of elastic response, viscoelastic creep, and fracture response of a coating after exposure to a single point indenter (scanning probe microscope.)[21]

Courter[22] evaluated several acrylic/melamine formulations for automotive sheet metal and proposed that a mar-resistant coating should possess a low-modulus, which translated into a low yield stress and high toughness. She attributed the higher mar resistance of such coatings to their ability to resist cracking when scratched.

However, contradicting results were observed in other studies relating the scratch/abrasion performance to coating material attributes analyzed.

Through the work described above, much has been elucidated regarding damage and test methodologies utilized to depict damage. Little, if anything, however,

Figure 3—AFM of representative basecoat/clearcoat surface.



has been done to understand the role of paint processing conditions on failure. Processing robustness, as one can term the process window effect, may be a major contributor to the large variance seen in field performance of the vehicle produced. Solvent flash time, effect of bake time and temperature, film build effects, and the like, may be key variables that affect end-use profiles. This article attempts to begin to show the effect of process robustness in painted plastic components with the hope that more can be done on the manufacturing side to affect potential performance attributes of components produced.

EXPERIMENTAL

Substrates were obtained from Custom Precision Molding, Romulus, MI as 10.2 cm × 30.6 cm × 0.3 cm (width × length × thickness, respectively) top-gated injection molded pre-colored (dark gray) plaques. All coatings were provided by Red Spot Paint and Varnish, Inc. (two-component isocyanate crosslinked acrylic polyols), PPG Industries, Inc. (one-component melamine crosslinked acrylic polyols), or Rohm and Haas (one component melamine crosslinked acrylic polyols). Coatings were spray applied with conventional air atomized guns onto a substrate and baked for 30 min ambient at 121°C in a gas fired oven (or as delineated). Film thickness measurements were made by cross-sectioning the part and analyzing the cross-section with an optical microscope. All film thicknesses were in the following ranges: adhesion promoter, 7.5 µm; white basecoat, 43 µm (or in the case of alternative color basecoats, red and black, the film builds are listed); clearcoat, 50 µm (or as delineated). All multiple layer (e.g., adhesion promoter/basecoat/clearcoat) coatings were applied wet-on wet with a 3-min ambient temperature flash after adhesion promoter, a 5-min ambient temperature flash after basecoat, and a 5-min ambient temperature flash after clearcoat and before oven, unless otherwise specified. Coatings were allowed to post-cure after final bake for 72 hr prior to testing.

SLIDO testing was performed using the apparatus described in reference 11, and shown in *Figure* 1. As shown in the figure, a painted panel is placed under the "bob" (an aluminum counterface with a 10.2 cm diameter) that is covered with a polyimide film, and the bob is translated across the surface of the panel at a preset loading rate with a known velocity and acceleration. The temperature of the plaque can be maintained above ambient temperature through the use of infrared heaters located in the apparatus. Plots are obtained of load versus displacement, through which the coefficient of friction of the coating can be calculated. Values obtained from the test plot also include the compression force (kg) to failure, defined as the force exerted perpendicular to the coating, and the traction force (kg) at failure, defined as the force exerted parallel to the coating. Actual conditions utilized in the *SLIDO* testing were as follows: 15.3 cm run length (defined as the distance traversed by the bob on the panel); acceleration of 50.8 cm/sec^2, velocity of 5.1 cm/sec, and a temperature of 68.3°C.

Chip resistance evaluations were performed according to SAE J400 protocol at the specified temperatures.

Gloss retention of a marred surface was measured with a 20° gloss meter and reported as a percentage of the initial unmarred surface gloss. Marring was per-

Figure 4—Cross-sectional modulus measurement of white basecoat/clearcoat.

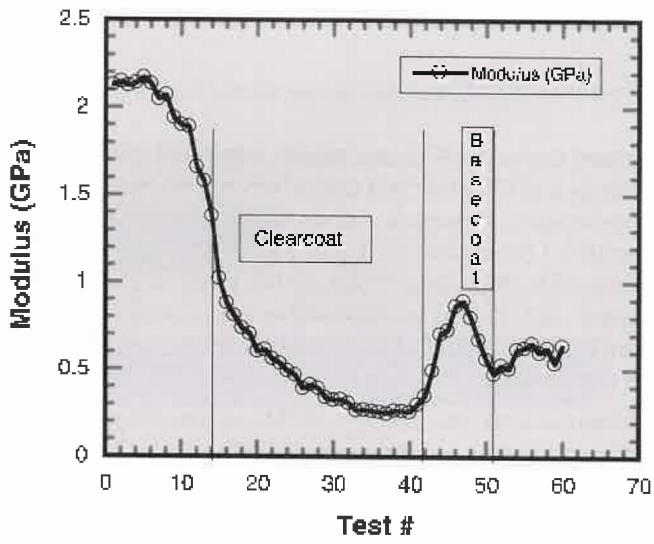


Figure 5—Cross-sectional modulus measurement of red basecoat/clearcoat.

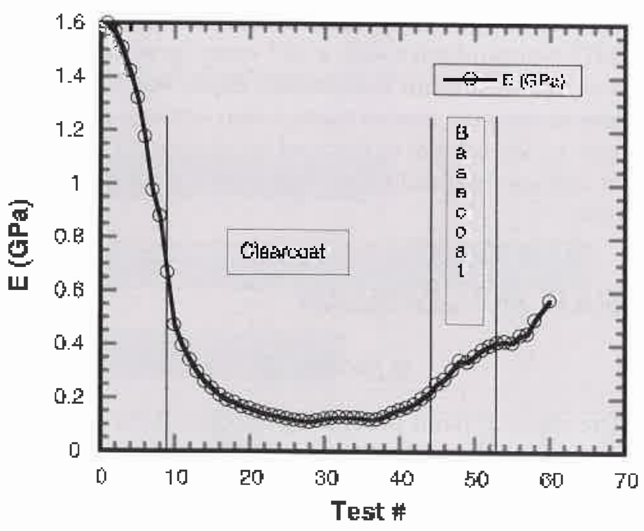
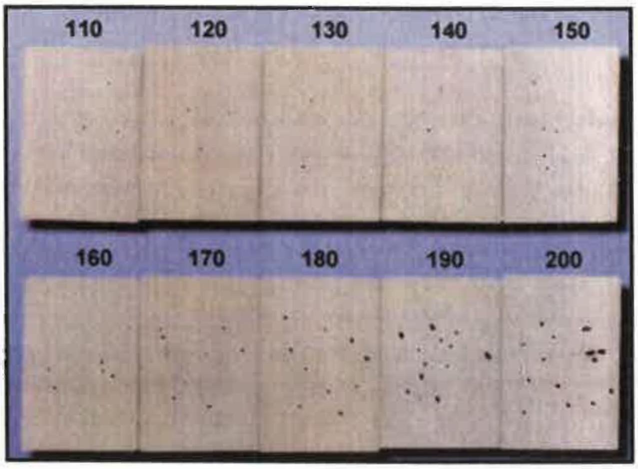


Figure 6—Chip resistance of painted TPO substrates as a function of TPO modulus change (values listed are in kpsi) [all paints are identical one-component basecoat/clearcoat topcoats over chlorinated poly(olefin) adhesion promoter].



formed on an AATCC crockmeter equipped with a cloth pad (DP-cloth, HQ manufactured by Struers, Copenhagen, Denmark and distributed by VWR Scientific) fitted with 0.01 g of 63 μm (220 grit) alumina oxide. A constant load of 940 g was applied, the sliding velocity was maintained at approximately 21 mm/sec, and a total of 2 double rubs were performed on each sample.

Atomic force microscopy (AFM) measurements were performed using a Dimension 3100 Scanning Probe Microscope (Digital Instruments) under ambient conditions (24°C and 45% relative humidity). Both topographic and phase images were taken using a tapping force of between 50% and 70% of the free amplitude. Silicon tips having a drive frequency of approximately 300 kHz and a radius of approximately 5 nm were employed.

Nanoindentation experiments were performed on an MTS Nanoindenter with a 60° cone tip with a 1 μm radius. The maximum indentation depth was 5 μm. Indentations were angled every 7 mm across a cross-section of the sample embedded in an epoxy. The constant stiffness method was run at 45Hz and 5 nm amplitude.

RESULTS AND DISCUSSION

SLIDO Results

The effect of paint processing conditions on *SLIDO* performance of one-component melamine crosslinked acrylic polyol basecoat/clearcoat system is shown in *Table* 1. Numbers listed are the multivariable regression coefficients of the independent variables (flash time, bake time, and clearcoat thickness) in which the gouge compression force was the dependent response variable. Not only was the color of the basecoat varied in the testing, but so too were the bake time, flash time between basecoat and clearcoat, and clearcoat film thickness. All variables in testing were varied from a low to a high value, as listed. The flash time was varied between 3 min and 10 min (flash time is taken as the time elapsed at ambient conditions between when the clearcoat is applied over a wet, noncured basecoat), the bake time was varied between 30 min and 45 min at 121°C, and the clearcoat thickness was varied between 30 and 45 μm.

As seen in *Table* 1, the color of the basecoat has a profound effect on the final compression force reached in the *SLIDO* testing prior to failure. As will be discussed later, cure rates may be affected through migration of additives to the basecoat/clearcoat interface, resulting in changes in frictional characteristics at the clearcoat surface. Gouge resistance is affected by frictional forces, where at lower friction levels the performance increases. While it appears that the white basecoat has the most detrimental effect on surface characteristics, as evidenced by a negative b_0 value, one cannot ignore the influence of the other dependent variable coefficients. Although the b_0 value contributes to a lower compression force prior to any other independent value being accounted for, the coefficients derived for flash time, bake time, and CC thickness can contribute to a larger overall compression force value. As seen in the data, each independent variable for the white basecoat/clearcoat system is positive, contributing to better performance from these parameters. However, the black and red basecoat/clearcoat systems vary, having a definite effect on performance, with red being the most detrimental (as seen in the negative coefficients).

To determine how the basecoat color affected surface attributes, AFM and nanoindentation were performed on the samples. All samples, irrespective of basecoat color, showed evidence of nonhomogeneous surface profiles when viewed with the atomic force microscope in the tapping mode (*Figure* 3). The results indicate that areas of harder (as indicated by the dark areas in the phase image) morphology seem to lie under peaks of softer (as indicated by the light areas in the phase image) morphology at the surface (lighter areas in the height image are higher).

Cross-sections of the white and red basecoat/clearcoat samples were then analyzed via nanoindentation to determine if the surfaces/interfaces varied (*Figures* 4 and 5, respectively). Indeed, as shown in *Figures* 4 and 5, not only does the modulus of the clearcoat surface vary, so too do the interfaces between the basecoat/clearcoat and the basecoat/adhesion promoter as a function of basecoat color. This analysis, although not conclusive for frictional variations, does suggest a variance at the air/clearcoat surface, potentially due to basecoat additive migration and resultant change in clearcoat cure. The white basecoat (as depicted between test #42 to 52, which is representative of the number of indentations through the thickness of the sample) appears to have a nonmonotonic modulus of approximately 0.4 to 0.8 GPa while the clearcoat (between test #14 to 42) affords an average modulus of 0.4 to 1.2 GPa, with the surface (as represented by test #14) the hardest.

The red basecoat/clearcoat cross-section (*Figure* 5), on the other hand, exhibits a relatively monotonic modulus of roughly half that of the white basecoat/clearcoat system. The basecoat (as depicted between test #44 to 54) has a modulus of approximately 0.2 to 0.4 GPa while the clearcoat (between test #10 to 44) affords an average modulus of 0.2 to 0.6 GPa, with the surface (as represented by test #10) the hardest. The surface hardness of the clearcoat, however, is roughly half that of the white basecoat/clearcoat's clearcoat hardness. Does the softer surface cause larger frictional variances at the surface, which accounts for the poorer gouge resistance? More work definitely needs to be done in this area to assess the influence of basecoat on clearcoat cure.

Chip Resistance Results

To assess the impact of substrate modulus on chip resistance of identically painted panels, (white basecoat/clearcoat, one-component melamine crosslinked acrylic polyol paint) chip resistance protocol was performed according to SAE J400 run at 68.3°C. *Figure* 6 depicts the damage incurred. As the modulus of the substrate increased, mainly through increasing the crystallinity of the poly(propylene) homopolymer portion of the impact copolymer blend, the chip resistance of the painted composite decreased. This result was not unexpected. One would expect that as the crystallinity of the substrate increases, the adhesion of the topcoat would decrease due to lower penetration capability of the adhesion promoter, lessening the interfacial strength between the TPO and the coating. One would also expect that as the crystallinity of the substrate increases, the stress-field at the interphase of the TPO/paint boundary would change; hence the worsening of the chip resistance.

The effect of paint processing parameters on resultant chip performance of painted TPO substrate was also studied. The paint utilized was the same one-component melamine crosslinked acrylic polyol described above. The bake temperature time was kept constant at 30 min ambient. SAE J400 was employed with white basecoat/clearcoat samples prepared wet-on-wet with a

Figure 7—Clearcoat (CC) film thickness effect on chip density.

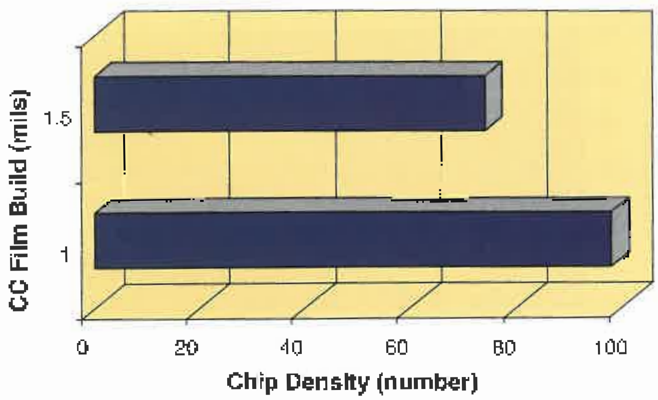


Figure 8—Basecoat/clearcoat bake temperature effect on chip density.

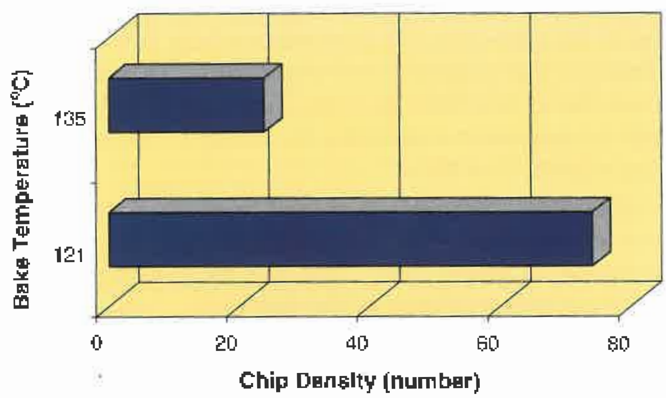


Figure 9—Effect of test temperature on chip resistance.

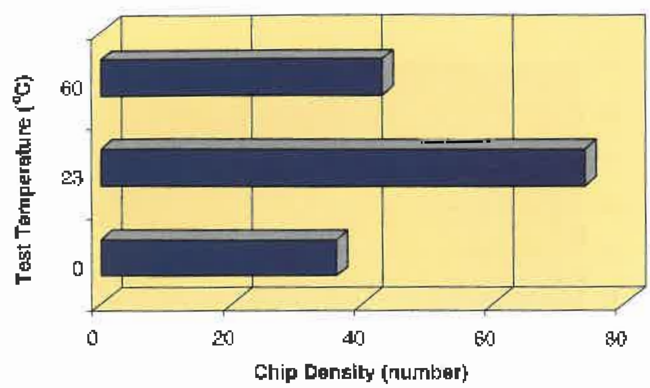
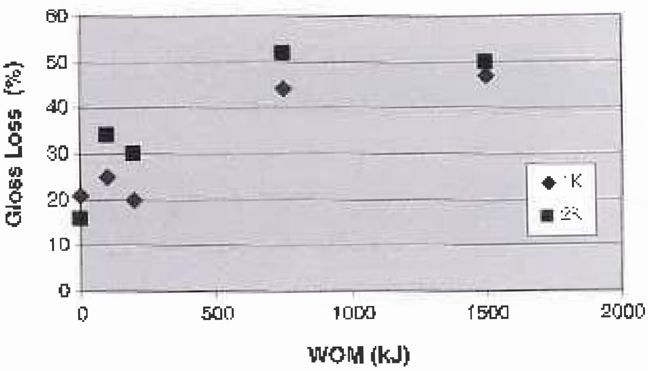


Figure 10—Effect of clearcoat chemistry on abrasion resistance after weathering.

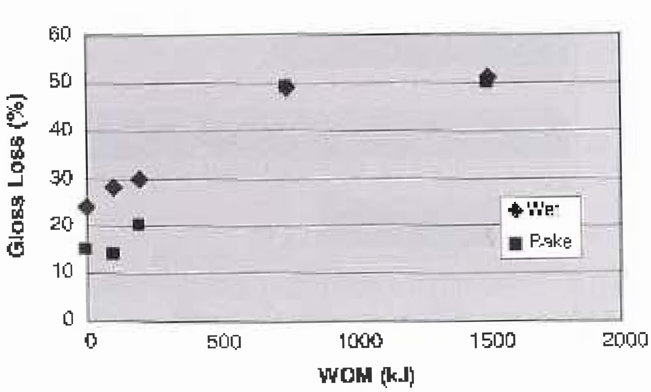


3 min flash time between basecoat and clearcoat. A conventional modulus (150 kpsi flexural modulus) reactor grade TPO substrate was utilized in all the following studies. Chip density was the response measured. Independent variables studied included clearcoat film build, bake time, and testing temperature.

As can be seen in *Figure* 7, the higher clearcoat film build affords better chip performance (e.g., lower chip density). This may be due to the ability of the thicker clearcoat to dissipate the stress impact more within itself as opposed to translating the energy to the coating/substrate interface.

The effect of basecoat/clearcoat bake temperature was also assessed. As shown in *Figure* 8, the higher bake temperature affords better chip resistance. Although hardness and toughness of the resultant basecoat/clearcoat matrix were not checked, the results may be due to the ability of a higher bake to induce a more fully crosslinked matrix. The higher crosslink density may account for a tougher coating that can dissipate the impact stress within itself, as described above, not allowing the stress to translate to the coating/substrate interface.

Figure 11—Effect of topcoat application method on abrasion resistance after weathering.



Finally, the effect of test temperature was assessed on a set of panels, identical to those in *Figure* 6, with a film build of 1.5 mils. As seen in *Figure* 9, the panels tested at room temperature performed the worst, with little variation in chip density seen at the higher or lower testing temperatures. This was somewhat unexpected, in that higher temperatures usually decrease the cohesive integrity of the TPO and lead to cohesive ripping within the substrate.

Abrasion Resistance Results

As opposed to just simply looking at paint processing conditions on the performance of coated TPO substrates, the effect of topcoat, topcoat application method (basecoat/clearcoat wet-on wet versus bake-on-bake), and abrasion resistance after simulated weathering was studied. As described in the Experimental section, the abrasion resistance of black basecoat/clearcoat panels was judged based on 20° gloss loss. The abrasion resistance of the samples was measured prior to their weathering, while identical sets of panels were placed in a Xenon arc weatherometer (borosilicate inner and outer filters, SAE J 1960 specifications) and removed and re-tested after every 500 kJ of exposure.

As shown in *Figure* 10, it is apparent that in their "green" states (e.g., before exposure to artificial weathering) the one-component clearcoat (1K) performs slightly better than its two-component counterpart (2K) (e.g., less gloss loss). After 1500 kJ of exposure in the Xenon arc weatherometer, however, the two coatings perform approximately the same. Usage profiles therefore should be developed that project requirements for coatings in their infancy as well as throughout their lifetime, since performance seems to be predicated on lifetime.

The effect of one-component clearcoat coating application method was studied, and results are shown in *Figure* 11. Application methods were varied by either applying the clearcoat on a wet basecoat that had been flashed 3 min at room temperature prior to application, or by pre-baking the basecoat at 121°C for 15 min prior to application of the clearcoat. From the results shown in *Figure* 11, the performance of the system is determined by amount of artificial exposure the coatings see. Early in their lifetime, it appears that the bake-on-bake system performs better than the wet-on-wet. After 750 kJ of artificial weathering, however, the two systems perform identically.

SUMMARY

Performance profiles of painted plastic substrates can be influenced by not only application parameters, e.g., flash time, heat history, and the like, but also by field exposure over time. This article elucidates early findings on the performance of painted plastic thermoplastic poly(olefins) in adhesion, chip, abrasion, and gouge resistance as a function of composite preparation. From the results it is apparent, as explained by some nanoindentation techniques, that not only processing conditions but also color can play an important role on interfacial coating development and, hence, performance. A more thorough examination of interfacial coating development as a function of application parameters should be undertaken to understand the nuances of additive migration, coating cure retardation or acceleration, as well as other factors. This is one area in which little research has been conducted, even though it is known to be one of the major factors that accounts for performance variation in the field. Perhaps performance maps as a function of environment should be developed and process robustness windows be described for the variety of coating/plastic systems available. Over-engineering the performance of a painted plastic component is not congruent with the "low cost" mandates that automotive engineers must face today. Rather, meeting the requirements of a coating system cost effectively as it is aged in its environment appears to be the "holy grail." To meet this demand, much more work needs to be performed to understand the effect of the processing window on end-use key-life performance attributes.

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References

(1) Ryntz, R.A., *J. Vinyl and Additive Tech.*, 3 (4), 293 (1997).
(2) Morris, H.R., Turner, J.F., Munro, B., Ryntz, R.A., and Treado, P.J., *Langmuir*, 15, 2961 (1999).
(3) Pennington, B.D., Ryntz, R.A., and Urban, M.W., *Polymer*, 40, 4795 (1999).
(4) Fujiyama, M. and Kimura, S., *Obunshi Robunshu, Eng. Ed.*, 4 (10), 777 (1975).
(5) Clemens, R.J., Batts, G.N., Lawniczak, J.E., Middleton, K.P., and Saas, C., *Proc. XIXth Conf. Org. Coat. Sci. Tech.*, Athens, Greece, 105, 1993.
(6) Prater, T.J., Kaberline, S.L., Holubka, J.W., and Ryntz, R.A., Journal of Coatings Technology, 68, No. 857, 83 (1996).
(7) Morris, H.R., Munro, B., Ryntz, R.A., and Treado, P.J., *Langmuir*, 14 (9), 2426 (1998).
(8) Mirabella, F.M., Dioh, N., and Zimba, C.G., *Proc. SPE Automotive TPO Global Conf. '99*, Troy, MI, 183, 1999.
(9) Templeton, L. and Fagan, R., *Proc. Sixth Intl. TPOs in Automotive '99 Conf.*, Novi, MI, 1999.
(10) Fujimoto, F., *Paint and Resin*, February, 36 (1986).
(11) Ryntz, R.A. and Mihora, D.M., *SAE Technical Paper #1999-01-1265*, SAE International, Warrendale, PA (1999).
(12) Ramamurthy, A.C., Ryntz, R.A., and Mihora, D., Journal of Coatings Technology, 67, No. 840, 35 (1995).
(13) Ryntz, R.A. and Buzdon, B., *SAE Paper #950801*, Society of Automotive Engineers, Warrendale, PA (1995).
(14) Ryntz, R.A., Ramamurthy, A.C., and Holubka, J.W., Journal of Coatings Technology, 67, No. 842, 23 (1995).
(15) Ryntz, R.A. and Abell, B.D., *Proc. 25th Intl. Waterborne, High-Solids, and Powder Coatings Symp.*, New Orleans, LA, p. 54, 1998.
(16) Shinto, K., Beseche, S., and Sato, S., *Proc. PRA Fourth Asia-Pacific Conference*: "Advances in Coatings, Inks, and Adhesives," Hong Kong, Paint Research Association International Center for Coatings Technology, paper 4, 1994.
(17) Chen, M.J., Osterholtz, F.D., Pluol, E.R., and Ramdatt, P.E., *Proc. 23rd Intl. Waterborne, High-Solids, and Powder Coatings Symp.*, New Orleans, LA, 23, 222, 1996.
(18) Tonge, J.S., Blizzard, J.D., Schmidt, S.M., and Washer, T.R., *Proc. 22nd Intl. Waterborne, High-Solids, and Powder Coatings Symp.*, New Orleans, LA, 22, 432, 1995.
(19) Lin, L. and Blackman, G., *Proc. Adv. Coatings Technology Conference*, Intl. Body Engineering Conference, SAE/ESD, Detroit, MI, 1998.
(20) Jardret, V., Lucas, B.N., and Oliver, W., Journal of Coatings Technology, 72, No. 907, 79 (2000).
(21) Shen, W., Ji, C., Jones, F.N., Everson, M.P., and Ryntz, R.A., *Polym. Mater. Sci. Eng.*, 74, 346 (1996).
(22) Courter, J.L. and Kamenetzky, E.A., "Micro- and Nano-Indentation and Scratching for Evaluating the Mar Resistance of Automotive Clearcoats," presented at the 5th Nurnburg Congress on Creating Advances in Coating Technology, Nurnburg, Germany, 12 April 1999.