Structure/Property Relationships In Flexible Alkoxyisilane Automotive Coatings

Philip V. Yaneff and Karlis Adamsons—DuPont Performance Coatings* and Rose A. Rynitz and Dottle Britz—Visteon Corporationt

INTRODUCTION

The scratch resistance behavior of automotive coatings has been studied extensively using many different analysis techniques. The ability of a coating to withstand appearance degradation caused by mechanical stress under a specific set of conditions is still not widely correlated with the technique utilized or the coating material attributes. The shape, size, and geometry of the indenter utilized in the scratching event, the temperature at which the scratching occurs, and the rate and load at which the scratch indenter mechanically abrades the coating surface are all variables one must consider. Jardet studied the scratch resistance behavior of several coatings utilizing different indenter geometries to identify three main scratch mechanisms. Elastic-plastic deformation was observed under mild abrasive conditions (e.g., where the indenter geometry angles are small or when the experiments are carried out with a Berkovich indenter). Irregular fracture processes occur when the attack angle is larger (e.g., with a cube corner indenter with its face in the direction of the scratch). When a cube corner indenter is used with its edge in the direction of the scratch, a regular longitudinal fracture propagates in front of the indenter. Indenter geometry therefore played a major role in the elastic-plastic deformation morphology of the coating analyzed.

Scratch resistance of coatings depends upon several factors, such as the chemical composition, the molecular weight of the resin backbone, the crosslinker type and crosslink density, the glass transition temperature, additives, cure temperature, etc. Coatings respond to mechanical stress in several ways, depending on the applied load. In the dynamic process of scratching, several tribological processes can occur, namely viscoelastic creep (time dependent processes of visco-plastic deformation and viscoelastic relaxation), strain hardening, microcracking (fracture), and surface fatigue. If fracture occurs, no self-healing within the coating is evident over time. If the applied stress is of short duration and does not exceed the yield stress of the coating, it will undergo elastic deformations.

Flexible automotive coatings are susceptible to scratch and mar damage, especially during finishing and assembly operations. One-component (1K) flexible clearcoats exhibit very good scratch and mar resistance, but unfortunately suffer from poor durability and environmental etch resistance. Two-component clearcoats offer improvements in both etch and durability, but at the expense of scratch and mar. In this paper, the concept and properties of 1K flexibilized silane clearcoats for use on automotive plastics will be introduced and their structure/property relationships examined as they apply to scratch and mar.

The role of coating crosslink density, toughness, glass transition temperature (Tg), and surface profile on the scratch damage of coated plastic substrates will be described. In addition, a new scratch methodology, termed Scracho, is utilized to determine relative scratch performance and is compared to conventional scratch resistance testing. Results to date indicate that hardness, as affected by the glass transition temperature, and crosslink density, as it contributes to higher essential work values, both affect resultant scratch propensity of the flexible coatings. The relative ranking of different coating systems employing alternate crosslinkers (e.g., isocyanate and melamine) is also presented and compared to the newly developed silane crosslinked coatings.
The increase of one-component rigid alkoxysilane clearcoats on automobile bodies has dramatically increased since their launch in the early 1990s due to their outstanding environmental etch, excellent scratch, and durability exposure. Alkoxysilane crosslinking chemistry is based on the hydrolysis of alkoxysilane to silanol and the condensation of two silanol groups to a silane bond with the evolution of water. The crosslinking, which results in very acid-resistant silicate bonds is in fact acid catalyzed as shown in Figure 1.

Rigid 1K alkoxysilanes offer many advantages over conventional melamine coatings including a durable hydrolytically resistant chemical bond, highly reactive multiple crosslinking sites that can react with themselves, low viscosity (low VOC), low toxicity, and one package technology.

We have explored flexibilizing this alkoxysilane crosslinked technology and have developed two generations of flexible alkoxysilane coatings for automotive plastics. Due to the high cost of the alkoxysilane functional materials, melamine was used as an auxiliary crosslinker to improve out-of-oven properties and reduce product cost in the flexible silane clearcoats. Additional melamine and auxiliary polyurethane-based crosslinker is added to the Generation VI clearcoats. Table 1 describes the clearcoat coatings used in conjunction with black 1K basecoat over solvenborne adhesion promoter on TPO.

Within this paper, we describe the mechanical attributes of one component alkoxysilane crosslinked coatings and compare these to the more traditional melamine crosslinked and isocyanate crosslinked coatings as related to surface damageability, namely scratch and compressive shear loading damage. We evaluate the effects of weathering on retained surface properties as well, simulating six-month exposure in the field. We have utilized conventional scratch techniques, namely the Ford five-finger scratch testing protocol, the ASTM AATC crockmeter test, as well as newly developed scratch techniques (a nanoscratch test and a macroscratch test protocol) to determine the resistance of the clearcoats. We relate these properties to selected mechanical attributes of the clearcoats, e.g., essential work of fracture, glass transition temperature, and microhardness.

**EXPERIMENTAL**

**Coating Preparation**

All coatings utilized in this work were spray applied (atomized air) to black 10 cm x 30 cm thermoplastic olefin (TPO) panels, baked 30 min at 127°C (part temperature), and post-aged 72 hr prior to testing. For samples utilized in any of the testing protocol, with the exception of those utilized in differential scanning calorimetry (DSC) analysis and essential work calculations, the panels were prepared by applying a solvenborne adhesion promotor, a one-component solvenborne basecoat, and the selected solvenborne clearcoat (wet-on-wet-on-wet application), with dry film thicknesses of 8 µm, 20 µm, and 37 µm, respectively. The clearcoats tested were formulated from one of the following solvenborne chemistries, and