All layers count

Silica nanoparticles in the optimisation of scratch and abrasion resistance of high performance UV multi-layer coatings.

Can Vu, Olivier Laferté.

The sensitivity of organic coatings to scratching, abrasion and chemical attack can be significantly reduced by using UV curable monomers containing inorganic nanoparticles. The properties of multi-layer coating systems consisting of nanocomposite topcoats over hard or soft basecoats show that high performance scratch and abrasion resistant coatings can be achieved by the optimum use of silica nanoparticles.

The sensitivity of coatings to scratching and micro-abrasion is important to manufacturers. Acrylic silica organosols have been used to protect the surface of many substrates against abrasion, scratching and the attack of aggressive chemicals [1].

We now know that silica nanoparticles can enhance these properties. They work in two ways: Resistance to scratching and abrasion is given by the hard silica nanoparticles covering the surface, while hardiness comes from nanoparticles intimately dispersed in the bulk of the polymer. A mixture of small and large particles [2-5] gives optimal performance.

There are many methods of measuring the scratch-resistance characteristics of coatings. Among these, static or dynamic micro, nano-indentation techniques are state-of-the-art tools to determine the surface hardness and viscoelastic properties. Mechanisms of fracture and delamination can also be followed in detail with dynamic indentation [6-12]. Crosslinking density, glass transition temperature and viscoelastic properties are often considered to be the most important parameters influencing the scratch resistance of coatings. Resistance to scratching and to micro-abrasion of UV-cured clearcoats are found to depend not only on the coating itself but also on the basecoat and substrate [13]. Furthermore, the test method and the abrasive material used influence results [14].

Most industrial coatings such as automotive paints and wood coatings are multi-layer. The structure of these coatings is illustrated in Figure 1. Each layer plays a specific role contributing to the total properties of the coatings.

We have studied the surface and mechanical properties of a number of multi-layer coatings. The topcoat was a hard nanocomposite UV-coating containing silica nanoparticles.

The mechanical properties of the topcoat and basecoats were recorded at a 60° angle and varied between 85 and 90.

Good particle distribution

AFM observation of the nanocomposite topcoat containing 25% silica nanoparticles showed well distributed particles across the surface. The particle size of 50 nm created a locally micro-heterogeneous surface (Figure 2a).

Improved resistance to scratching and abrasion

The micro-indentation test records the force vs. penetration depth of the indenter tip (Figure 4). It gives basic information on the surface hardness HU (N/mm²); Young’s modulus Ey and elastic recovery %ER, once the load is removed [14]. A dynamic indentation procedure using a ramp-load procedure is also used to obtain detailed information on scratch traces and interfacial properties [13].

When the SAN substrate was used in the tests, it showed low values of both surface hardness and Young’s modulus (HU= 18 N/mm²; Ey= 0.55 GPa). Its scratch resistance is poor.

The mechanical properties of the topcoat and basecoats (measured at 25°C) differ: The surface of the topcoat (Tg= 80°C) was hard (HU=134 N/mm²; Ey= 6.5 GPa). Both the hard basecoat (Tg=50°C) and the soft basecoat (Tg=10°C) at 25°C showed much lower HU values (24 and 14 N/mm², respectively) and Ey values (0.44 and 0.48 GPa, respectively).

Basecoat affects hardness and scratch resistance

As the silica content in the topcoat increased, the values of hardness (HU) and Young’s Modulus (Ey) increased for all composites (Figure 5). Above 30% the increase becomes
The hardness and modulus of the bi-layer composite are greatly influenced by the nature of the basecoat. Over the whole range of SiO₂ content, the system (TC/BCsoft) shows lower hardness and modulus than the system (TC/BChard), or than the hard topcoat alone. In contrast, when the basecoat is soft, the surface hardness of the TC/BCsoft composite decreases significantly. When the basecoat is hard, however, the HU and Eₜ values of the TC/BChard composite are similar to those of the topcoat TC alone.

The Erichsen scratch resistance is commonly measured using the ISO 4586-2 method: A hard tip makes a circle on the surface to be tested and the minimum load which shows a visible scratch is then recorded. The higher the force value, the higher the scratch resistance.

The tests showed that the scratch resistance is enhanced when the topcoat contains colloidal silica and is also influenced by the properties of the basecoat. Thus, with a 25% SiO₂ load, the system TC/BChard (Fₑ₉₀° = 9 N) provides much better results than the system TC/BCsoft (Fₑ₉₀° = 4.5 N). However, hardness HU, elastic modulus Eₜ and scratch resistance Fₑ are linked, as can be seen in Figure 6. The incorporation of SiO₂ nanoparticles in the topcoat enhances all three properties. But the basecoat definitely influences the mechanical properties of the composite. This is best seen in the photographs. The scratch resistance of system TC/BChard, 25% SiO₂ is better than TC/BChard, 0% SiO₂ composite. The pure TC/BCsoft, 0% SiO₂ is particularly sensitive to scratching. Levels of 10-15 % SiO₂ are the best for excellent scratch resistance.

The Taber abrasion resistance test uses a loaded abrasive wheel circling on the tested surface. Weight loss is recorded for excellent scratch resistance.

Abrasion is surface sensitive, hardness is bulk sensitive

Scratching is a complex phenomenon. Many tests have been proposed, but results differ from one test to another on the same material. Manufacturers rely more on on-site practical tests to validate their formulations. Results differ depending on the chemical composition and coating properties, on the test method and on the substrate used. In our case, the Taber abrasion test, where the applied force is mostly tangential to the coating surface, is rather a measure of micro-abrasion. It is therefore not dependent on the basecoat. In the Erichsen scratch test, a normal force is applied to the coating surface causing an effect on the whole bi-layer composite.

REFERENCES
[1] "Highlink@NaNO G" silica organosols commercial brochure - Clariant (France) 2003

Acknowledgements
The authors express their thanks to Dr. Noireaux (Centre Transfert de Technologie du Mans) for the indentation measurements and to Dr. Oudet, Mazeron and Mr. Nadaud from Compiègne University of Technology for AFM/SEM and nano-indentation measurements.

Results at a glance
- The scratch and abrasion resistance of the surfaces of coatings are improved with the use of silica nanoparticles.
- AFM and SEM analysis showed that the silica nanoparticles evenly cover the coating surface. The degree of coverage produces the good scratch and abrasion protection.
- In a multilayer coating, the level of hardness of basecoats has an influence on the overall properties of a composite in which the hard top-layer is loaded with silica nanoparticles.
- These multilayer coatings give better scratch resistance when the basecoat is hard.
- Scratch resistance is correlated to hardness and to elastic modulus.
- Abrasion is surface sensitive while hardness is bulk sensitive.

The authors:
-> Professor Can Vu received his BSc and Msc in chemical engineering from Cornell University, USA, and his PhD in Polymer Science from the University of Paris 6. He is Assistant Professor of Chemical Engineering and Colloid Science at the University of Technology in Compiegne. At Clariant, he is Product Manager of ceramic polymers and nanocomposite materials.
-> Olivier Laferté studied engineering at the Ecole National Supérieure de Chimie de Mulhouse before he joined Clariant France. He is an application specialist for UV nanocomposite materials at Clariant’s Research and Development Center in Mulhouse. He is the author of a number of papers on UV nanocomposite materials.

This paper was presented at the RadTech Europe Conference, Barcelona/Spain, 18 - 20 October 2005
Figure 2: Surface and cross section of bi-layer coatings
Figure 3: Viscoelastic properties

Figure 4: Micro indentation data (load-displacement)
Figure 5: Hardness, modulus of nanocomposite coatings
Figure 6: Correlation between scratch, modulus and hardness

Figure 7: Taber abrasion of bi-layer nanocomposites