Shining performance

Nanoparticle with double surface layer optimise scratch resistance

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The effects of silica nanoparticles on scratch resistance have been studied in two UV-curable clear coat formulations. A double-layer surface treatment of the nanoparticles appeared to give the best results, though some differences were noted between the two test methods used.

Radiation curing systems have been used successfully in various applications and have increased their market share over many years. A distinction can be drawn between electron beam and UV curing materials, though these differ very little in their chemical and physical properties.

In the areas of printing inks as well as wood and plastics coatings in particular, their good resistance properties and optical quality are very much valued. In addition, there are many more arguments for the use of UV technology: short curing times, low substrate warming, emission reductions and low energy costs. It is for these reasons that the market share of UV coatings will continue to grow in future.

Scratch resistance or abrasion resistance?

An important, often crucial, property of coatings is their scratch resistance, which is usually better with UV systems than with many conventional systems due to their naturally high crosslinked network density. The applica-
Results at a glance

- UV-curable coatings provide high performance, but are often used in applications where it is desirable to further increase their scratch resistance.
- Nanoparticles can be used for this purpose, but their effectiveness is dependent on several factors. In particular, different tests will produce different rankings, as is demonstrated in this work.
- By comparing results obtained with nanoparticles having reactive groups which crosslink into the UV cured coating with those also having an additional polysiloxane treatment, it is shown that selecting the type of surface treatment enables the effectiveness of the nanoparticles to be optimised for specific requirements.
- Nanoparticles with both reactive groups and polysiloxane treatment gave the greatest improvement in scratch resistance in a practically-oriented test, while enhancing the haptic properties of the surface at the same time.

Test formulations and procedures summarised

A polyester acrylate and a urethane acrylate system (Table 1) were chosen as typical representatives of UV curing coating formulations and used as test formulations.

Table 1: Test formulations for UV curable coatings

<table>
<thead>
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<th>Component</th>
<th>Amount</th>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Laromer” PE 44F**</td>
<td>37.5</td>
<td>“Desmolux” U 680H***</td>
<td>48.5</td>
</tr>
<tr>
<td>“Laromer” PE 56F**</td>
<td>15.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPGDA**</td>
<td>32.2</td>
<td>TPGDA*</td>
<td>32.0</td>
</tr>
<tr>
<td>IBDA**</td>
<td>11.4</td>
<td>TMPDA**</td>
<td>16.4</td>
</tr>
<tr>
<td>“Irgacure” 500***</td>
<td>3.0</td>
<td>“Darocure” 1173***</td>
<td>3.1</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>Total</td>
<td>100.0</td>
</tr>
</tbody>
</table>

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Surface treatment controls effects of nanoparticles

It is already known that the mechanical properties of a UV curable coating film can be favourably influenced by reactively modified SiO₂ nanoparticles [1]. In particular, this improves the scratch resistance. Ultimately, the crosslink density is greatly increased by the covalent incorporation of the nanoparticles in the coating film, with the result that very hard, but at the same time brittle, coating films are produced. Additionally, the authors’ own attempts to increase scratch resistance in solvent based 2K PU clear coat systems have shown that covalent surface treatment of nanoparticles with polysiloxanes significantly improves their performance [2]. Measurements taken on such coating films attest to a reduction in the E-modulus, even with low additions of nanoparticles. In contrast to the improvement in scratch resistance brought about by an increase in hardness, the covalent treatment of the nanoparticles with polysiloxanes enhances the flexibility of the coating film.

A series of tests was carried out to determine to what extent these effects can be combined and what advantages result if nanoparticles with double surface modification are used. In the context of this work, various surface modified nanoparticle concentrates based on silica were produced in reactive diluent and were tested in two standard UV-cured coating systems.

Figure 1 shows the surface modification of the nanoparticles as studied in the present work. On the left, silica nanoparticles are shown with a surface modification that ensures their covalent incorporation into the coating matrix. This type of surface treatment can be easily achieved by using, for example, alkoxysilanes with unsaturated double bonds for surface modification. On the right, a surface modification is shown that consists not only of reactive groups but also of additional modification with a polysiloxane.

Both products were tested in different concentrations in standard UV clear coat systems. Several control samples were also tested: clear coatings without nanoparticles, clear coatings with a polysiloxane-containing surface active additive and combinations of reactively modified nanoparticles without polysiloxane treatment but with a polysiloxane-containing surface active additive.

Current test methods are the defined scratching of the coating surface by means of, for example, steel wool or a “Scotch-Brite” pad with subsequent gloss or haze measurement, “Crockmeter” testing (especially in the automotive sector), “RCA” abrasion tester and the “Taber Ablaser” test.

One possible way of further improving the scratch resistance of UV coatings is to incorporate nanoscale particles of hard inorganic minerals such as silica, alumina or boehmite.
The concentration of nanoparticles in the coating was in the region of 1.0 – 10.0 wt%. The nanoparticle dispersions were incorporated by a dissolver for 5 minutes at 1800 rpm. A classical polysiloxane-based surface active additive (“BYK-UV 3500”) was also tested at a concentration of 0.1 %.

After the additives were incorporated, the samples were left to rest for 24 hours before they were applied to transparent polycarbonate plates (10 x 20 cm and 10 x 10 cm) by means of a 50 µm wire bar and were immediately cured in a laboratory UV dryer (belt speed: 5 m/min, mercury vapour lamp, 120 W/cm).

The slip resistance was determined with the aid of an “Altek 9505 AER” unit. This apparatus calculates the force required to drag a 500 g weight at constant speed over the surface of the sample.

The abrasion resistance was measured on square polycarbonate plates using a “Taber Abraser” unit (CS-10 wheels, 1000 cycles, 500 g load per wheel). The abrasion loss was determined by means of an analytical balance. To examine the scratch resistance, scratches were first made on the coating surfaces in a defined manner. For this purpose, a “Scotch-Brite” pad was stuck to the underside of a hammer weighing 1.1 kg and drawn over the test plates (10 cycles). Finally, the haziness, expressed as percent haze, was measured on the scratched and un-scratched surface using a BYK-Gardner “Haze-gard plus” instrument.

To illustrate the differences in the scratch resistance, 3-dimensional images were generated and tinted from light microscopic photographs (30-fold magnification) using “Image” software (Version 1.42q, from Wayne Rasband, National Institutes of Health, USA).

**Slip resistance varies with surface treatment**

The results of determining the slip resistance of the coating surfaces with and without nanoparticles or with a surface active additive are shown in Figure 2 for both the polyester acrylate based system and the urethane acrylate based system. Both coating systems behave the same with respect to the change in slip resistance when surface treated nanoparticles or surface active additives are added.

On the y-axis is plotted the force required to drag a weight at a constant speed over the coating surface, where lower values indicate a smoother surface. The addition of reactively modified silica particles increases the slip resistance, and the effect is greater at higher additions. Ultimately, the nanoparticles act as an anti-slip additive.

Similar behaviour, though at a lower level, can be found when these reactively modified nanoparticles are combined with a surface active additive. The surface active additive without added nanoparticles brings about a very strong reduction in the slip resistance compared to the blank sample. The addition of reactively modified nanoparticles then causes the slip resistance to increase.

By contrast, the slip resistance of the coatings containing double surface modified nanoparticles (ie, with both reactive and polysiloxane modification) decreases as the nanoparticle concentration is increased.

**Nanoparticles clearly enhance abrasion resistance**

Figure 3 shows the abrasion resistance results for the two acrylate systems tested. It can be clearly recognised that by adding reactively modified nanoparticles it is possible to reduce the weight loss in Taber abrasion test compared to the blank sample.

The incorporation of the nanoparticles in the binder seems to cause an increase in hardness, the decisive factor for improving abrasion resistance in this test. Only comparatively slight differences were found in the effectiveness of the different nanoparticles in the polyester acrylate system. Figure 3, however, also reveals the more marked effects in a coating system based on a urethane acrylate binder.

With the addition of a surface active additive that increases the surface slip, an improvement in the abrasion test can be observed. If reactively modified nanoparticles are used, the abrasion resistance is further optimised. The use of reactively modified nanoparticles alone likewise enables the abrasion resistance to be increased.

The use of nanoparticles with double surface modification in the urethane acrylate achieves the smallest improvement in the abrasion resistance. Apparently, a com-

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Joncryl® OH 8312 is a highly reactive hydroxy-functional water-based dispersion. The benefits are long pot life (> 6 hours), low solvent demand, good adhesion, toughness, excellent chemical resistance and durability. Joncryl® OH 8312 is easy to mix with water-based urethane hardeners such as Basonat® LR 9056. Joncryl® OH 8312 is ideal for high- and semi-gloss two-component water-based industrial furniture coatings. Experience the new resistance which is shaping the way forward for industrial wood coatings!
If one assumes that the surface slip and the hardness of the coating system are important to achieve resistance to the abrasive pad, one can expect optimum resistance with high coating hardness and high surface slip. Adding classical reactively modified nanoparticles increases the hardness on the one hand while reducing slip on the other. This gives rise to opposing effects, whose overlap can produce results as shown on the left of Figure 4 in the case of the urethane acrylate.

In the next comparison, the scratching of the surface is shown after the abrasive pad test has been carried out (Figure 5). The degree of scratching after conducting the test is well illustrated by means of tinted light microscopic images. The left-hand image of Figure 5 depicts the scratching of the blank sample. Compared to this, a decrease in the scratching can be seen due to the incorporation of reactive nanoparticles in combination with a surface active additive (right). The least scratching of the surface is clearly obtained by using double surface modified nanoparticles (centre).

Nanoparticles are effective when chosen with care

Nanoparticles can be used to increase the scratch resistance of UV-curable coatings. Their effectiveness is dependent on several factors. In particular, varying results are obtained depending on which test is used to determine the scratch resistance. The effectiveness of the nanoparticles will also vary in different coating systems. The type of surface treatment enables the effectiveness of the nanoparticles to be optimised for specific requirements. The present work has shown that by incorporating special surface modified nanoparticles, the property profile of a UV coating can be favourably influenced. Besides improving the scratch resistance in a practically-oriented test, the haptic properties of the surface can be enhanced at the same time.

REFERENCES