

Additives containing Nano Metal Oxides for Enhanced Scratch Resistance in Coating Formulations

U. Nolte^{*}, R. McMullin^{**}, R. Brotzman^{***}, P. Murray^{***}, R. H. Cayton^{***}, T. Sawitowski^{*}, M. Berkei^{*}

^{*}BYK Chemie GmbH, Wesel, Germany, michael.berkei@altanachemie.com

^{**}BYK Chemie USA, Wallingford, Connecticut, USA, r McMullin@bykchemieusa.com

^{***}Nanophase Technologies Corporation, Romeoville, Illinois, USA, rbrotzman@nanophase.com

Abstract

In this paper different mechanisms to improve scratch resistance of coatings by incorporation of nanoparticles are described. Depending on concentration of particles and of their orientation in the coating film, different results were obtained. Not only the nanoparticle core but also surface modification have a great impact on performance.

Keywords: scratch resistance, silica, nanoparticle, coating

Results

In today's coatings the demand for an enhanced scratch and wear resistance is increasing. The idea of an everlasting surface that keeps its properties unchanged has become the driving force for an ongoing research in this field.

Today, not only high class furniture, but also substrates such as ceramic tile, marble, wood and vinyl flooring have applied a clear topcoat to protect their surfaces from abrasion and scratching. There are different ways to enhance scratch resistance in these coatings.

Besides varying the resin system or resin types, it is also possible to use a variety of different additives such as waxes, organic modified polysiloxanes or inorganic particles. Let us look at the how the three additives function within our modern coatings.

The usage of wax particles (nano and micro) to improve scratch resistance is one of the many functions waxes can provide. Waxes will migrate to the coating surface, and in many cases this will alter the properties of the coating. When waxes are added into high gloss and some transparent coatings, there are drawbacks. The main drawback with using waxes is the limit of transparency of the wax thus creating haze. One other drawback is the amount of time the improvement in scratch resistance lasts. The primary reason is because degradation of the surface layer of the coating where the wax has mainly oriented continues to degradate until the wax is no longer in the coating.

A similar approach is to use organo modified polysiloxanes. Polysiloxanes like waxes love the surface to air interface and migrate (Bernard cell migration) to the surface of the coating matrix.

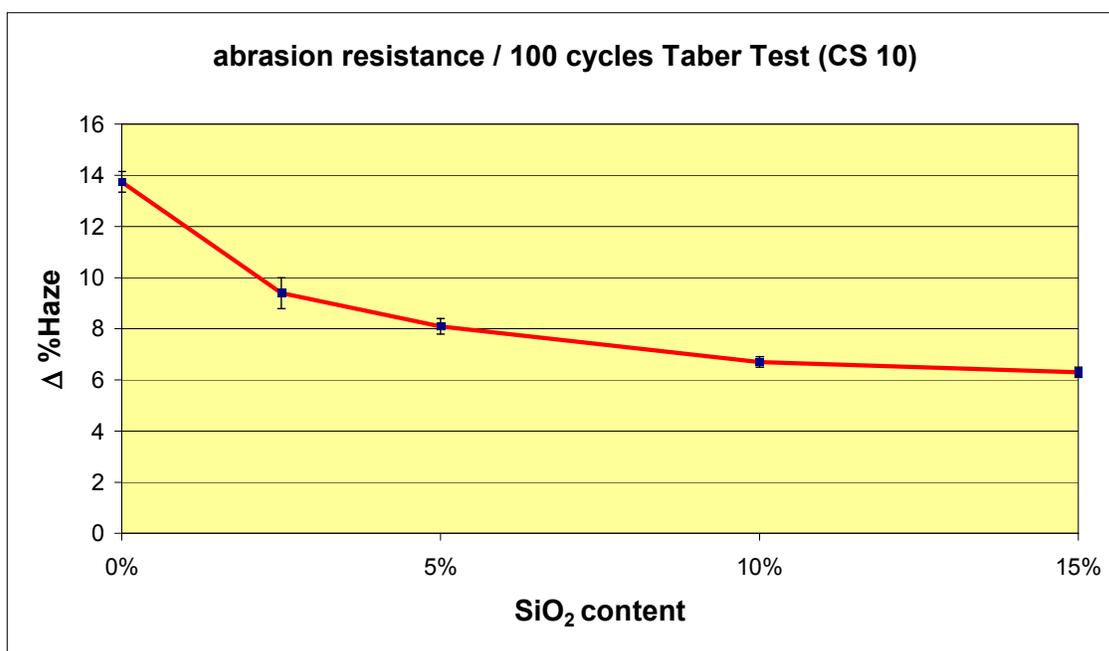


Fig. 1: Influence of silica content abrasion resistance measured as delta haze (haze of unscratched sample minus hazes of scratched sample) after 100 cycles of taber test.

This migration results in increased slip on the surface of the coating. This higher slip leads to an improvement in wear resistance, but this approach can create some problems like limited overprintability or recoatability of the coating. Polysiloxanes can decrease the COF of the cured coating which can be an undesired property for certain types of floor coatings.

The third concept is to use inorganic nano metal oxides to change the properties of these coatings. The amount of nanoparticles added into a coating is quite important for many reasons. One - high gloss and transparent non pigmented systems, nanoparticles can offer many advantages compared to larger particles. Depending on the refractive index and morphology of the nano metal oxides, small particles in the range below 50 nm are most preferred. Small particles, depending on the concentration, will not change the optical properties of coatings. Two - If there is a large amount of nanoparticles in the coating this can lead to undesired changes in properties like haze and opacity.

The next three mechanisms will try to explain how the enhancement of scratch resistance can be achieved by incorporation of nano metal oxides into a coating.

1) Increase of coating hardness

Most inorganic substances exhibit a higher hardness than organic polymers, but to really increase the hardness of a coating high filling levels are required (Fig. 1). A coating loaded with up to 40% of silica will become extremely wear resistant and stay almost transparent due to the good match of refractive index between silica and most polymers. In respect to elasticity there is a drawback. Such coatings become very brittle and are extremely sensitive to thermal expansion because of changes in temperatures. The added cost also can make the coating too expensive to use. Example: An automotive clear coat on a black basecoat can change its temperature on a sunny summer day rapidly from 50° to over 120°. If the coating has no flexibility it will crack and fall off. This is why high filling levels of inorganic particle lead to extremely wear resistant coatings but are not suitable for all applications.

2) Surface concentration of particles

To get a coating that is hard at the toplayer and flexible in the area beneath it is beneficial to orientate the particles at the surface (Fig. 2). This approach requires only small overall dosages of nanoparticles and will result in hard surfaces that are still flexible. Also optical properties may not change too much, as long as particle size is small enough and the refractive index of the particles is close to the polymer one. The most advantageous particles are small silica nanoparticles. The only real disadvantage is the possible disintegration of the top layer. Once this surface area is gone, the remaining coating does only exhibits a very small number of particles and shows no difference in a coating without Nanoparticles.

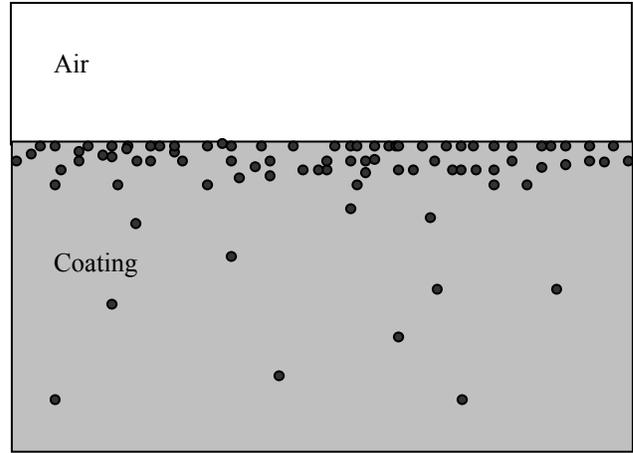


Figure 2: Surface orientation of nanoparticles

3) Alter the boundary phase of the particles

To use only small dosages of nanoparticles but also to get a big impact on scratch resistance there is a way in changing the interaction between nanoparticles and polymeric matrix. Choosing the right surface modification will lead to a more compatible interaction with the polymeric chains and will have an influence on properties (Fig. 3). Changes in crosslinking density, E-modulus and glass transition temperature were observed in some cases. Due to low use levels of only 1 to 2 percent are needed. These low levels will reflect no undesired changes in properties like levelling or surface defects. By choosing 1% of perfectly dispersed 20nm Al₂O₃ or SiO₂ particles it is possible to minimize the distance between two particles to below 50nm.

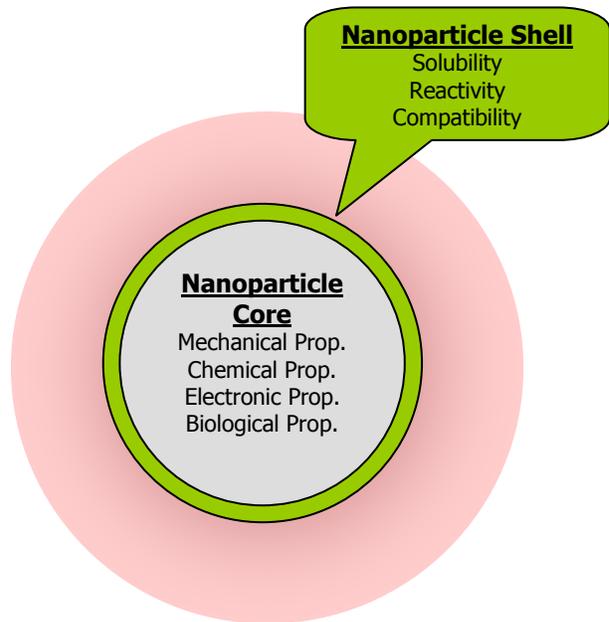


Figure 3: Surface modification of nanoparticles determines the interaction with the surrounding matrix.

Due to low filling levels of only a few percent there are no undesired changes in properties like levelling or surface defects. To achieve best results it is important to homogeneously distribute the particles all over the coating volume (Fig. 4). By choosing 1% of perfectly dispersed 20nm particles it is possible to minimize the distance between two particles to below 50nm. This short distance between nanoparticles will result in a huge volume where the polymer interacts with the particles and only a small volume area where properties are unchanged.

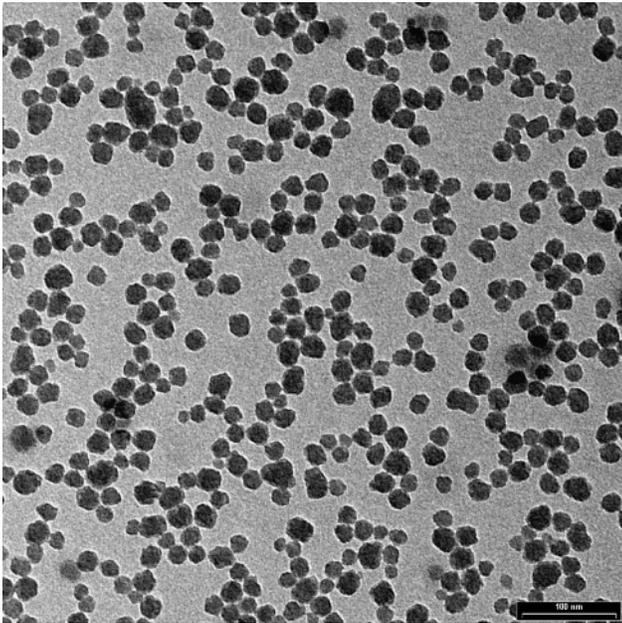


Figure 4: Homogeneously distributed 20nm silica nanoparticles in a 2 pack polyurethane clear coat.

Comparing these three different mechanisms to each other we think that the last one offers most benefits for modern high performance coatings and in this paper we show some of our results on changing the boundary face of particles and how important the role of surface modification is.

We prepared four different dispersions of 20nm SiO₂ nanoparticles in methoxy propyl acetate with different surface modifications. Silica 1 was unmodified and silica two was modified with alkyl groups. In addition to these alkyl groups we combined silica 2 with a polysiloxane resulting in silica three. Using a different polysiloxane we synthesized silica 4. These different nanoparticle dispersions were incorporated into a solvent based 2K polyurethane system and applied to polycarbonate test panels with a film thickness of 50µm. The gloss was measured before and after scratching 10 cycles with a crockmeter tester with 3M polishing paper 9 N. The resulting gloss retention is displayed in figure 5. We observed incompatibility to the coating system of silica 1 resulting in flocculation, thus we skipped this sample. The neat coating system showed a gloss retention of 13%, which could be increased to 22% by incorporation of 2% silica 2 nanoparticles. Using 2% of silica 3 nanoparticles catapulted the gloss retention up to 93%, while silica 4 resulted only in 54%. This example demonstrates how important surface modification is and how tailor made nanoparticles will change the performance of modern coatings.

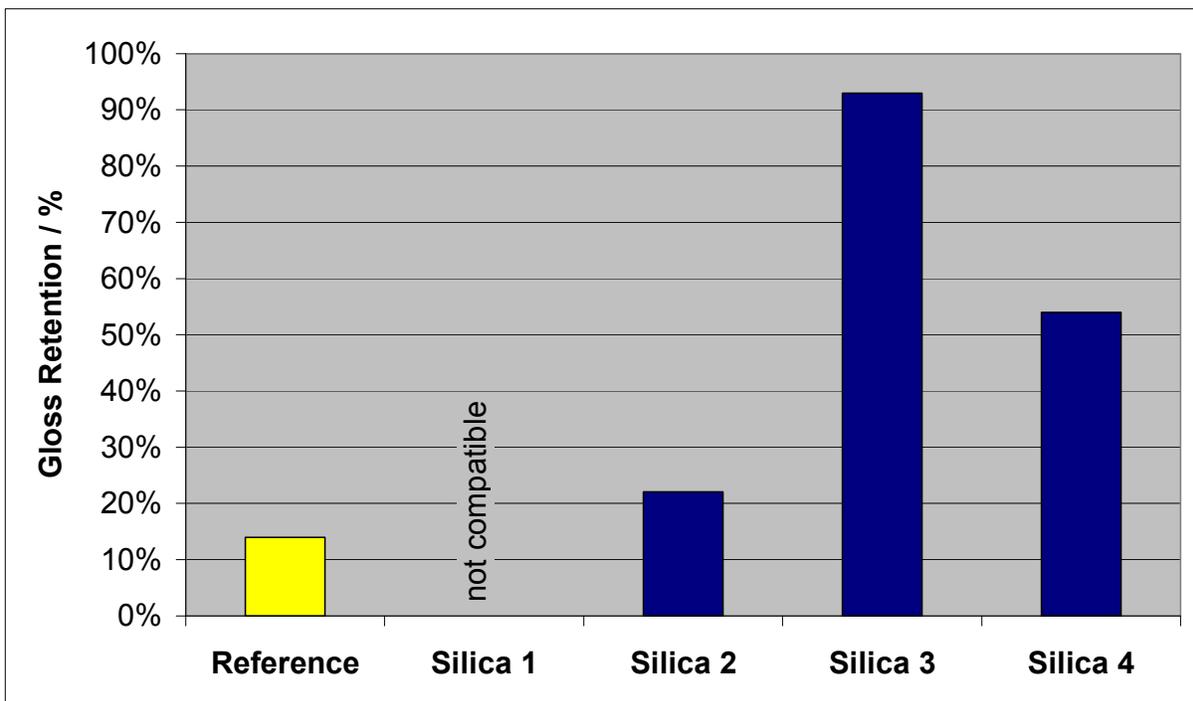


Figure 5: Gloss retention of 2k polyurethane coatings with 2% of silica nanoparticles with different surface modifications after scratching.