Oxylink™: Improved resistance for waterborne coatings

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ABSTRACT

We present an additive technology based on ZnO nanoparticle dispersions that increases the chemical resistance of waterborne coatings. The performance of the additive is evaluated using solvent-rub tests. The additive is highly efficient in a wide range of formulations. Nanomaterials are used for optical reasons to reduce haze in clear coatings as well as to provide a very high surface area for this presumably catalytic effect.

We stress the importance of dispersion quality to produce this high-performance additive. Buhler uses the chemomechanical process to produce nanoscaled dispersions of inorganic oxides from agglomerated nano powders. Oxylink™ is a chemo-mechanically synthesized additive that is highly efficient to improve the chemical resistance of water borne coatings.

Keywords: nanoparticle, dispersion, waterborne, coating, additive.

1 INTRODUCTION

The overall market share of environmentally friendly waterborne coatings is still relatively small compared to solventborne alternatives. Yet, waterborne coatings become increasingly important as a technology to reduce VOC (volatile organic compound) emissions and thus cost. Waterborne coatings are pushed worldwide by regulatory bodies for higher market shares. Today, they are used in a wide selection of market segments, such as wood and furniture, but also on non-wood substrates such as metals (e.g., direct-to-metal, DTM) and plastics for industrial maintenance coatings, coatings for machines and equipment, and metal cans.[1] One obstacle, though, which still limits the use of waterborne coatings in various applications is their sometimes poor solvent and humidity resistance. In order to overcome these drawbacks, different additives are available, mainly based on silicones or paraffin waxes. However, these additives aren't universally applicable and can be used only in specific formulations. In addition, they cause problems later-on when coated parts have to be over coated or refurbished.

In this paper we present an alternative additive technology based on ZnO nanoparticle dispersions called Oxylink™ that increases the chemical resistance of waterborne coatings to enable a wider use of waterborne coatings.

It is well known that the quality of the dispersion critically influences functionality and performance of inorganic nanoparticles as additives. Dispersing nanoparticles needs special attention since colloidal systems are very sensitive to change in the formulation. Dispersing nanoparticles is therefore the enabling technology to provide efficient nanoparticle additives, so we are starting the discussion with a focus on dispersion technology.

2 DISPERSING NANOPOWDERS

For functional nanoparticle additives, the key parameter comprises the degree of dispersion within the final formulation. In this paragraph, we summarize the basics of colloidal dispersion technology as necessary to discuss the Oxylink™ technology. We have discussed the topic of processing nanopowders into functional colloids previously and refer the interested reader for a more detailed discussion [2].

Dispersing nanopowders into functional colloids requires a deagglomeration step. We have found the use of agitator bead mills useful for the deagglomeration of commercially available nanopowders. Because many parameters influence the selection of the agitator bead mill, there is no standard equipment which can be used in all cases. Technical as well as economical considerations have an important impact on the best choice of equipment like, e.g. product viscosity, cooling options for temperature sensitive products, contamination by grinding media and/or the grinding chamber, bead size, targeted particle fineness and the flow rate.

When manufacturing dispersions with particle sizes below 100 nm the energy input into the product tends to be high. In the case of inorganic oxides, even if only loosely agglomerated, the specific energy requirement to overcome the inter-particle interaction is typically in the range of 1 to 10 kWh/kg product, not to speak of aggregated particles or true grinding of materials.

Nanopowders have a high specific surface area of up to several hundred m^2/ml. As the mechanical process turns this surface into internal interfaces in a formulation, the particle-liquid interface needs to be chemically stabilized. In principle, stabilization mechanisms are well known [3]. Colloids can be stabilized by electrostatic, steric, or electrosteric means. Particularly in aqueous media, electrostatic stabilization is fast and efficient. However, for many products the pH value cannot be freely chosen and consequently steric and electrosteric stabilization mechanisms are used in addition or instead if it comes to stabilizing particles in complex formulations.

The chemistry of nanoparticles can be compared to molecular chemistry rather than to the behavior of micron-size particles.[4] The surface of inorganic oxides is mostly covered with OH-functions of various density. The density of functional groups varies with chemical composition, but also with production method of the materials. Usually, high-temperature methods provide a lower density of functional groups compared to wet-chemical precipitation methods. Using molecular bifunctional additives these groups are accessible to a chemical interaction and have to be addressed at the moment when new interfaces are generated.

Chemomechanical processing brings the two critical components of dispersion technology together as it carries out the surface modification reaction under well defined mechanical stress conditions.

3 OXYLINK TECHNOLOGY

Oxylink™ is a chemomechanically synthesized additive based on nanoscaled ZnO dispersed in water. As explained in the previous section, the specific parameters of the process yield a ZnO-based additive formulation. Oxylink™ has a low viscosity of < 10 mPa·s at a solid content of 40 wt.-%. The particle size (DLS) was ca. 50 nm.

We investigated the effect of Oxylink™ on chemical resistance in a variety of different aqueous dispersion coatings. In general, 1% (solid on solid) of the additive was introduced into the suggested coating formulations with gentle agitation. The resulting formulations were stable and no precipitation was observed.

The coatings were drawn onto glass substrates using a coating knife to obtain a wet film thickness of ca. 100 µm (ca. 4 mils). The slides were dried at 70 ºC. The cloudiness was evaluated visually for each coating system to ensure a good degree of dispersion. Only coatings with no or low haze were included in this study.

The chemical resistance of the films was investigated using MEK double-rub tests. We performed the rub test until the film was continuously destroyed. In an additional evaluation, some coatings we subjected to water vapor for 48 h and visually inspected.

We have investigated the solvent resistance as a function of Oxylink™ concentration in steps of 1, 2, and 3% for an acrylic coating (LS 1032, Synthomer, see Figure 1). We have found that a concentration of only 1% is already highly effective to increase the resistance in MEK double rubs by a factor of ca. 3. Higher additive concentrations result in even higher resistance, however, the correlation is not linear.

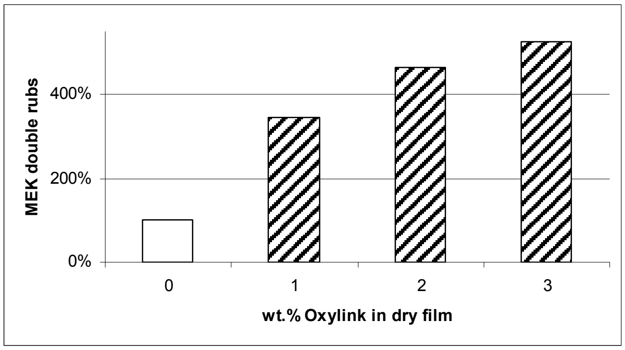

Figure 1: Effect of 0 – 3% Oxylink™ (solids on solids) on solvent stability (formulation based on LS 1032).

Traditionally, additives on the basis of silicones or paraffin/polyolefin waxes have been used to increase the chemical resistance of waterborne coatings. We have therefore formulated waterborne coating systems with wax additives for comparison.

Figure 2 shows the effect of a wax dispersion (Aquacer 535, Byk Chemie) on an acrylic clear sealer for wood based on Worleecryl 7641 (Worlee Chemie). The wax dispersion works well and increases the double rub resistance by factor of ca. 3. In comparison, Oxylink™ works at least equally well. More interestingly, however, the combination of wax and the inorganic nanoparticle dispersion further increases the double rub resistance by more than 30%. The combination of wax and Oxylink™ yields an overall improvement in solvent rub stability by a factor of more than 4 compared to the original formulation. This finding indicates that the mechanisms by which waxes and nanoscaled ZnO affect the chemical resistance of waterborne coatings are fundamentally different.

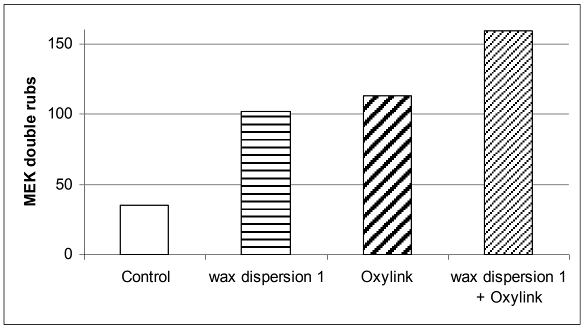

Figure 2: Comparison of wax and Oxylink™ additives on chemical stability
(Test system: Wood sealer based on Worleecryl 7641).

In contrast, Figure 3 shows the effect of different wax dispersions on the solvent-rub resistance of a high-build scumble based on Primal AC 337 (Rohm and Haas). None of the tested wax dispersions increased the double rub resistance by more than 50%. In contrast, the inorganic nanoparticle dispersion (1% solids on solids) improved the solvent stability by a factor of ca. 3.

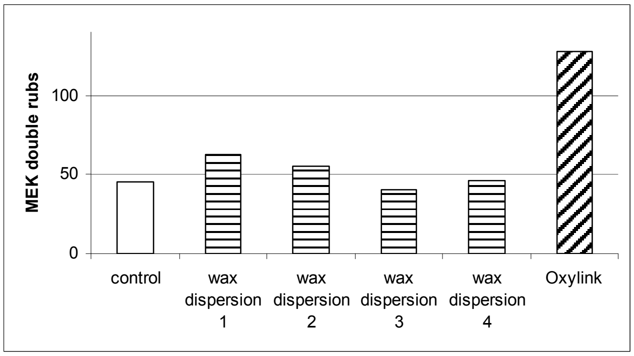

Figure 3: Comparison of wax dispersions and Oxylink™ on chemical stability (Test system: Primal AC 337).

The authors conclude that Oxylink™ is more widely applicable to increase the chemical resistance than traditional organic additives like wax dispersions.

We have compared Oxylink™ with a conventional dispersion of nanoscaled ZnO in two acrylic binder systems (Worleecryl 7940 and Revertex LS 1032). Oxylink™ outperforms nanoscaled ZnO significantly. At the same concentration, Oxylink™ provides consistently a higher performance than nanoscaled ZnO.

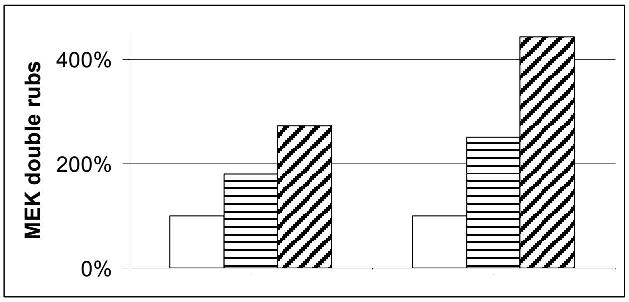

Figure 4: Comparison of nanoscaled ZnO and Oxylink™ on chemical stability of acrylic coatings.
Open bar: no additive (=100%),
horizontal stripes: nanoscaled ZnO,
diagonal stripes: Oxylink™
left set: Worleecryl 7940; right set: Revertex LS 1032.

In another evaluation, we investigated the effect of water vapor on differently formulated films. Coated glass slides were placed on top of water filled petri dishes with the coating facing the water. The samples were kept at 40 °C for 48 h (Figure 5). Afterwards, the coatings were allowed to dry at room temperature and visually inspected (Figure 6).

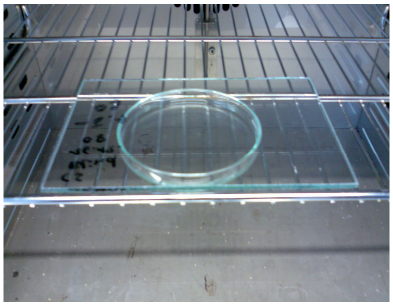

Figure 5: Coatings are placed face-down over water-filled petri dishes at 40 ºC for 48 h.

Neither the wax nor the inorganic nanoparticle dispersion prevented the increase of haze under the saturated humidity conditions at elevated temperature. However, Oxylink™ resulted in a formulation that shows a completely reversible hazing effect, and the coating turned completely clear again after drying. This observation stands in contrast to the coating containing a polyolefin wax additive which was irreversibly affected by the water vapor.

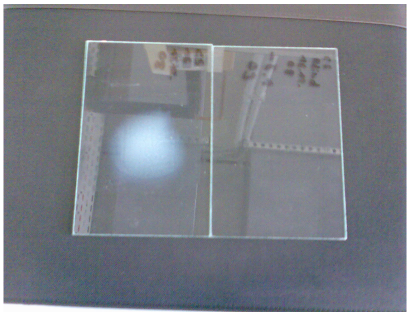

Figure 6: Effect of water vapor on waterborne coatings with (a) wax additive (left sample) and (b) Oxylink™ (right sample) after drying.

The authors hypothesize that the effect of the inorganic additive is due to a nanoparticle-catalyzed cross-linking effect. Whereas the dispersions usually just dry physically, the additive seems to result in an at least partial chemical cross-linking. Studies have shown [5] that a low percentage of nanoscaled ZnO may improve mechanical properties such as dry and wet scrape resistance as well. Presumably, ZnO catalyses the curing process and leads to a denser network of the polymer structure. For this effect, it is necessary to provide a large surface area, which is provided by the use of nanopowders. Proper processing ensures that the active surface is accessible and that the particles are small enough for application in glossy and clear coats. Finally, the surface modification enables a high concentration of actives in the additive as well as low viscosity and easy handling.

4 OUTLOOK

We have found a large influence of specific process parameters on the performance of nanoscaled ZnO as additive in waterborne coatings. Obviously, a better degree of dispersion yields a better transparency (lower haze). More surprisingly, we found also a strong influence of process parameters on efficiency in chemical resistance. This finding stresses the high importance of dispersion technology. We will use the large parameter space accessible by chemomechanical processing to further optimize the performance of nanoscaled ZnO within the Oxylink™ platform.

5 SUMMARY

We have presented an additive technology based on ZnO nanoparticle dispersions called Oxylink™ that increases the chemical resistance of waterborne coatings. We stress the importance of dispersion quality on overall performance and use the chemomechanical process to produce Oxylink™ from agglomerated nanopowders. We investigated the performance of the resulting additive formulation in waterborne acrylic systems. We found it highly efficient and easily as well as broadly applicable in particular when compared with wax additives.

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