Improving waterborne coatings using a formulated nanoparticle additive Oxylink

S. Pilotek* K. Steingroever** and M. Herold**

* Buhler Inc.
Business Unit Nanotechnology, Austin, TX 78701

**Buhler PARTEC GmbH
Saarbrücken, Germany 66123

Waterborne coatings have several important benefits over solvent borne alternatives. Stricter regulations worldwide to lower VOC emissions are the main reason for a use of waterborne solutions. However, in addition, waterborne coatings have the benefit of being less hazardous in the application, as they do not emit hazardous fumes and odors, not flammable, and safe clean up of equipment.

We present a study on the nanoparticle additive Oxylink™ that increases the crosslink density of waterborne coatings. Previous studies have focused on the use of nanoparticles to increase mechanical properties such as scratch resistance as well as UV protection by mineral UV absorbers.

Generally, the key to functional nanoparticle coating additives comprises particles in a stable dispersion that is compatible in the application. The intended interaction between polymer and particle surface requires that the surface has sufficient accessibility for the polymer. The degree of dispersion of the particle system has therefore a strong influence on the efficacy of the resulting additive. We have previously discussed the topic of processing nanopowders into functional colloids in more detail[2]. Dispersing nanopowders into functional colloids requires a deagglomeration step. We have found the use of agitator bead mills useful for this part when the particle surface is chemically stabilized at the same time. This concurrent action of mechanical and chemical forces on agglomerated particles is called chemomechanical processing. We have used this process to disperse a ZnO nanopowder in water and to formulate it as a coating

---

[1] Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

[2] See e.g., S. Pilotek, S. Schär, K. Steingröver, K. Gossmann, F. Tabellion, NSTI-Nanotech 2007, Vol. 2, 64 (2007). S. Pilotek, D. Burgard, M. Herold, K. Steingröver, The Waterborne Symposium 2009, New Orleans, LA (2009).

additive. The dispersion has a low viscosity of < 10 mPa·s at a solid content of ca. 40 wt.-%. The dispersion has a pH value of 8. The material under investigation in this study is commercially available in three versions under the trade name Oxylink™. The three types allow to cover a broader range of formulations. For this study, the most suitable type of Oxylink™ was identified experimentally.

Table 1 a, b shows the formulations W1 and M1 used in this study for wood and metal, respectively.

Table 1: Formulations discussed in this study

a) Exterior translucent high build stain (HBST) for wood based on Primal AC 337 "W1"

Ingredient	Amount /g
PRIMAL™ AC337 ER (45.5%)	64.9
TEGO® Foamex 825	0.2
Water	8.6
Texanol®	2.4
Aqueous ammonia (28%)	0.3
Water	20.9
Nanoparticles Oxylink™ 3103	*0.0 / 0.8*
Acrysol™ RM12W (19%)	0.7
Water	1.2
	100.0

b) Direct-to-metal coating based on Neocryl XK-86 "M1"

Ingredient	Amount /g
Pigment grind	
Butylglycol	2
Water	2.9
2-Amino-2-methyl-1-propanol	0.2
Dehydran 1293	0.4
Surfynol 104 (50 %. in Etylene glycol)	0.2
Disperbyk 191	0.3
Neocryl BT-24	2.5
Ti Pure R706	19.5
Mix ingredients in the given order and grind	
Premix 2 (mix separately)	
Neocryl XK-86	58.1
Adjust pH to 8.5 with aq. ammonia (15 %)	
Premix 3 (mix separately)	
Butylglycol	3.6
Texanol	0.7
Lusolvan FBH	0.9
Byk 346	0.8
Dehydran 1293	1.4
Erbslöh flash rust inhibitor CHE Coat LNF A4	0.5
Water	0.8
Mix well, adjust pH to 8.5 with aq. ammonia (conc.) and add while stirring to Premix 2. Homogenize for 5 min.	
Add the resulting mixture to the Pigment Grind D 1855-4 while stirring, homogenize with rotor stator device, then add while stirring:	
Nanoparticles Oxylink™ 3101	*0.0 / 0.8*
Water	3.1
Nacorr 1652	0.6
Butylglycol	0.5
Homogenize well for additional 5 min.	

We have used the solvent-rub resistance test according to ASTM 5402 as a benchmark to characterize the effect of Oxylink on latex coatings. In this test, a solvent-soaked cloth (methyl ethyl ketone, MEK) is used to remove a coating from a glass substrate. A higher number of double rubs characterizes a higher cross link density in the film. We have used the same test also using *iso*-propanol (IPA). We find that the nanoparticle additive consistently increases the number of MEK-double rubs by a factor of 4-6. Likewise, the number of IPA-double rubs is increased by 30 – 50%, see figure 1. We attribute the different response to the different swelling behavior of the latices with MEK and IPA, respectively, where the latter is more polar and protic in contrast to the ketone. We propose that the difference in is an indication for the non-covalent nature of the cross linking by the inorganic particles.
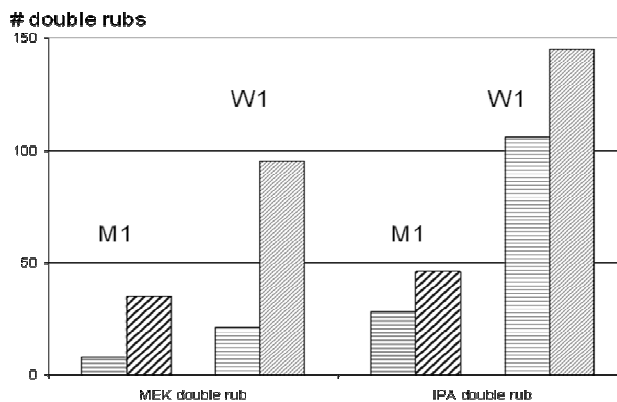

**Figure 1: Solvent-rub test for formulations M1 and W1 with MEK and IPA
without (left bars, horizontal stripes) and with (right bars, diagonal stripes) Oxylink.**

As a consequence of the increased cross link density further coating properties are significantly improved. E.g., metal coating M1 as well as other metal formulations gains improved humidity and weathering resistance with Oxylink as compared to the same formulations without the additive (figure 2). The degree of blistering is markedly reduced.
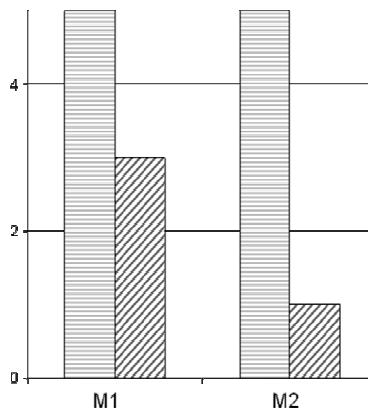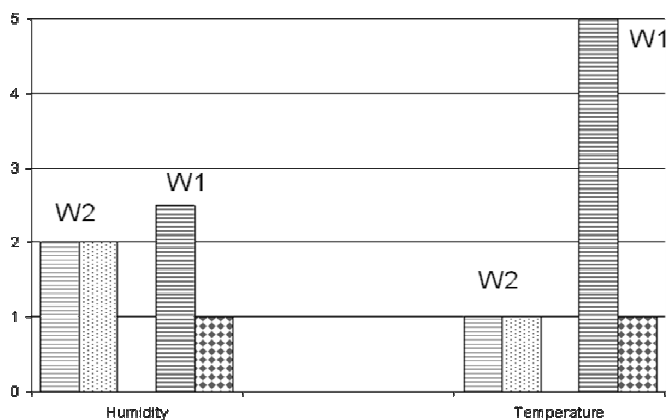

**Figure 2: Humidity resistance of formulation M1 and another metal formulation M2 without (left bars,
horizontal stripes) and with (right bars, diagonal stripes) Oxylink.
0: No blisters, 5: Complete failure due to blistering.**

For the wood coating formulation W1 we evaluated the drying time and blocking resistance as properties of special interest. Both parameters are positively and significantly affected. The rate of blocking resistance is improved from 5 (complete blocking) to 1 under increased temperature conditions on both Leneta™ foil and standardized fir plates (figure 3). Interestingly, also the time to through-dry was reduced by half. We attribute this effect to a fast kinetics of the Oxylink-resin interaction so that a certain grade of drying is reached after a shorter period of time. Consequently, Oxylink results in improved values for resistances in early water and chemical impact.

Figure 3L Blocking Resistance of W1 and another wood formulation W2 on Leneta foil without (left bars, horizontally striped) and with (right bars, dotted) Oxylink.
Left set: Increased humidity conditions. Right set: Increased temperature conditions.
0: no blocking, 5: complete failure due to blocking.

In summary, we present a formulated performance additive based on ZnO nanoparticle dispersions. The additive improves the general property profile of waterborne coatings by increasing the cross- link density of the systems. The coatings benefit from higher resistance properties against, e.g., humidity, solvent rubs, and blocking as well as from a decreased time to through-dry.