Faster finishing

Nanoparticles enhance performance and drying speed of waterborne coatings

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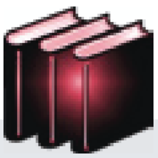
In industrial applications, both performance in end-use and productivity are critical in determining whether waterborne coatings offer an acceptable alternative to established technology. A nanoparticle additive is shown not only to improve performance but to speed up the effective drying time of waterborne coatings.

More eco-friendly industrial processes and products are on the ascendant, not only because of legal pressure but also because of a steadily increasing awareness of environmental issues. Although much has been done in the past, there is still much that can be improved in the creation of environmentally-friendly technology.
One option to reduce environmental impacts is to reduce the VOC content of coating materials or – even better – to switch to waterborne coating systems. Waterborne coatings have attained high quality levels, but there is still room for improvement.
Especially important are end-use properties such as blocking resistance or chemical resistance. On the other hand, there is also an interest in increasing the productivity at the processor's site, which can be achieved, for example, by speeding up the drying process.
This paper will show how nanoparticle dispersions used as additives can improve different coating characteristics of waterborne coatings without adversely affecting others and can thus improve overall performance.



Waterbornes are successful only in certain markets

The overall market share of environmentally-friendly waterborne coatings is still relatively small compared to solventborne alternatives. Yet waterborne coatings have become increasingly important as a technology to reduce VOC (volatile organic compound) emissions. Regulatory bodies worldwide are seeking to increase the market share of waterbornes.
Today, they are used in a wide range of market segments, such as wood and furniture, and 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].
The proportion of waterborne compared to solvent-based coating systems on wood varies greatly according to the application. Whereas on wooden furniture such as kitchen cabinets the majority of coatings are still solvent-based (71 %), 65 % of wooden flat stock finishes are water-based, with an almost negligible 7 % fraction for solvent-based systems.
The situation is similar in architectural applications for wooden substrates, where 55 % of exterior stains are waterborne, as are the majority of exterior deck and floor coatings. Waterborne technology has clearly found its markets and is likely to increase its market share.
One obstacle which still limits the use of waterborne coatings in various applications is that their performance is sometimes poor compared to existing solventborne technologies. In industrial applications, the processing time and productivity are almost equal in importance to

Exterior translucent high build stain based on Primal AC-337 ER (ref: HBST)		Exterior transparent wood glaze based on Worléecryl 7461 (ref: WG)	
Ingredient	**Grams**	**Ingredient**	**Grams**
Primal AC-337 ER *1 (45.5 %)	655.1	Worléecryl 7461*5	763.5
TegoFoamex *2 825	2.0	Water	166.3
Water	100.8	Dow Corning Add. 65 *6	0.2
Texanol *3	23.1	Water/ethylene glycol 1:1	42.0
Aqueous ammonia (28 %)	2.7	Acrysol RM 5000 *1	3.0
Water	201.6	Dow Corning Add. 57 *6	5.0
Oxylink 3103 *4	6.95	Oxylink 3101 *4	11.0
Acrysol RM-12W *1 (19 %)	6.75	Water	9.0
Water	1.0		
Total	**1000**		**1000**

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Table 1: Coating formulations used in tests

the final performance of the coating. Here too, waterborne coating materials have some weakness as their drying time is often too long.
In this paper an alternative additive technology based on oxide nanoparticle dispersions supplied as ready-to-use additives under the brand name "Oxylink" is described. The degree to which this additive can improve the solvent stability and blocking resistance of waterborne coatings will be shown. In addition, their effective drying time can be significantly shortened.

Test procedures summarised

Two coating formulations were prepared in accordance with the data in *Table 1* in order to investigate the influence of the nanoparticle additive on different coating properties. The comparative formulations were also made using the same formulations but without the nanoparticle additive.
The coatings were applied to fir wood panels: three coatings of 100 g/m^2 each with intermediate drying time of 24 h at room temperature. After the third coat, substrates were allowed to dry for 7 days at (23 ± 2) °C. Alternatively, coatings were applied onto glass sheets as single coats with approx. 200 g/m^2 wet weight and drying time was 7 days at (23 ± 2) °C.
Drying time was measured according to DIN 53150 (09/02); gloss (60 ° and 85 °) according to DIN EN ISO 2813 (06/99).
The solvent resistance was determined by the solvent double rub method according to ASTM D 5402. Here, two different detection methods were chosen:
››› Number of double rubs to completely wipe the coating off (= double rub resistance).
››› Number of double rubs before the gloss of the coatings irreversibly decreases (= gloss retention solvent rub). Solvents were isopropanol and MEK.
Abrasion resistance (DIN EN ISO 7784 2 (07/06)) was measured with a "Taber abraser" CS17 wheels, 2 x 500 g weight for 200 cycles.
Crosscut adhesion was determined as described in DIN EN ISO 2409 (08/07); water permeation according to DIN EN 927 5 (03/07) and blocking resistance according to "Guideline 6" by the Institut für Fenstertechnik, Rosenheim, and rated according to "VFF Merkblatt HO.03" [2, 3].

Careful dispersion maximises nanoparticle benefits

The formulations described above containing nanoparticles could be processed into clear, transparent and haze-free coatings. This – as an initial result – shows that the nanoparticles are fully compatible with the coating matrix, which in turn is essential to avoid agglomeration during the drying and film forming process.

The key to these functional nanoparticle coating additives is to supply particles in a highly dispersed, stable, and compatible form. The intended interaction between polymer and particle surface requires that the latter be accessible to the polymer. The state of dispersion of the particle system depends greatly on the process that is used to disperse the nanoparticles and therefore has a strong influence on the performance of the resulting additive.

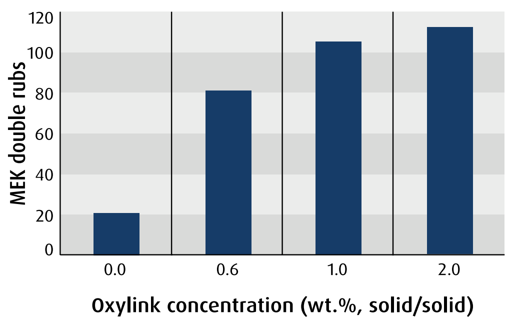

Figure 1: MEK double rub resistance of the HBST coating as function of nanoparticle concentration

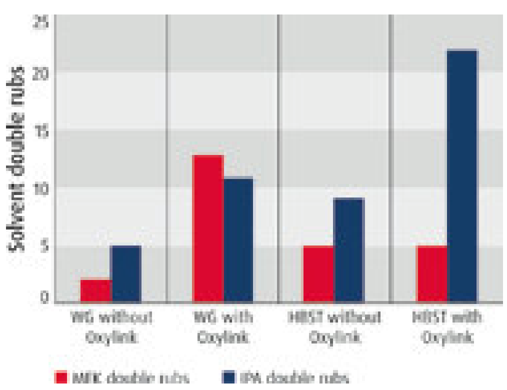

Figure 2: Gloss stability after solvent double rub test

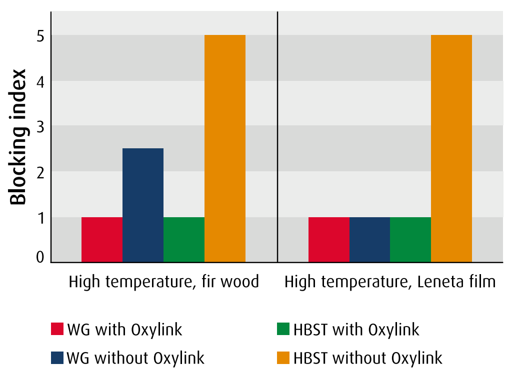

Figure 3: Blocking resistance of coatings on plastic film and fir wood sheets after high temperature loading

Dispersing nano-powders into functional colloids requires a deagglomeration step. The use of agitator bead mills has been found to be effective for this deagglomeration. As the mechanical impact increases the surface area of the particles, the surfaces need to be chemically stabilised.

The mechanical processing of nanoparticles in dispersion brings the two critical components of dispersion technology together: surface modification under well defined mechanical deagglomeration conditions. If these principles are not followed and the particles are either too coarse or they coagulate during the film forming step, the result will be hazy or opaque coatings [3].

Nanoparticle addition improves solvent resistance

In order to find out the extent to which nanoparticles can improve the end-use properties of a coating, it is important to look at more than just one or two selected features. Therefore, a variety of different properties were studied in order to answer the question of whether nanoparticles really can improve waterborne coatings.

As a first benchmark test, the solvent rub resistance according to ASTM 5402 was used to determine the influence of the nanoparticle additive on the solvent resistance of the coating. This test can also be used as a measure of the crosslink density in coating films. In this test, a cloth soaked in solvent (methyl ethyl ketone, MEK) is used to remove a coating from a glass substrate.

The test was originally developed to characterise the curing of 2K coating systems, with a higher double-rub number correlating with a higher degree of network density. The number of double rubs thus characterises the durability of the film. *Figure 1* shows the solvent-rub resistance as a function of nanoparticle concentration for the coating referred to as HBST in *Table 1*.

A concentration of only 1% (nanoparticle solids/coating resin solids) can be seen to be highly effective in increasing the resistance against MEK double rubs by a factor of about five. Higher additive concentrations result in even higher resistance; however, the effect levels off with higher concentrations. It was therefore decided to continue the study at a usage of ca. 1 wt.% (see also *Table 1*).

Damage by solvent rub is much reduced

As can be seen from *Figure 1*, the resistance against solvents can be increased by the addition of nanoparticles. Certainly, this is very important for protective coatings. A much more sensitive aspect is the optical appearance of a coating. In this respect, a coating is considered to be harmed as soon as the gloss is irreversibly decreased, which is likely to happen if aggressive cleaners are used. Some commonly used cleaners contain alcohols such as isopropanol (IPA). In order to find out whether the gloss of these coatings can be retained after solvent rub attack, the same test as shown in *Figure 2* was carried out, but here, the endpoint detected was the beginning of a permanent gloss reduction and, in addition to MEK, IPA was included in the tests as a second solvent.

The untreated coatings all had high gloss values of around 80 (at 60°). As can be seen from *Figure 2*, the addition of the "Oxylink" nanoparticle additive can significantly improve the stability against MEK and IPA. In both cases, the resistance to IPA could be doubled. The effect on the MEK stability seems to be more dependent on the individual resin and is quite remarkable for the WG formulation with a sixfold improvement.

Blocking resistance at high temperature is increased

One other important parameter for coatings is their blocking resistance. If coating materials show a low blocking resistance or a high tendency to blocking, they cannot be used in a wide range of applications. On the other hand, if the blocking resistance of a coating or resin can be increased by additives, the range of application of this particular resin can be considerably broadened.
The blocking resistance of the coatings was evaluated according to Guideline 6 of the German Institut für Fenstertechnik e.V., Rosenheim. According to this guideline, blocking resistance is rated under a 6-level system with 5 being the worst ("complete blocking") and 0 the best ("no blocking") rating.
A coating with a blocking index below 3 (under high temperature load) is considered blocking resistant and can be used for special applications such as window or door coatings. For a substrate-independent evaluation, all coatings were applied onto inert plastic films ("Leneta" brand).
The coatings were allowed to dry for 2 days. Subsequently, the coated films were stored face to face under a pressure of 2.5 kg at 50°C for 24 hours. After exposure, the films were separated and rated. *Figure 3* shows the ratings of the coatings with and without additive on the plastic films and fir wood after high-temperature loading.
As can be seen, a dramatic increase in blocking resistance can be achieved for the HBST formulation. This

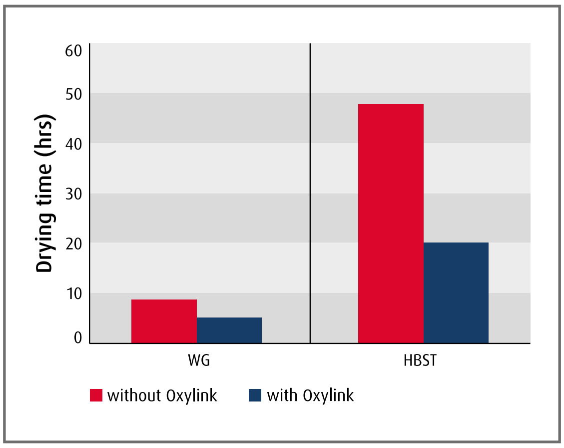

Figure 4: Drying time of coatings with and without nanoparticle additive

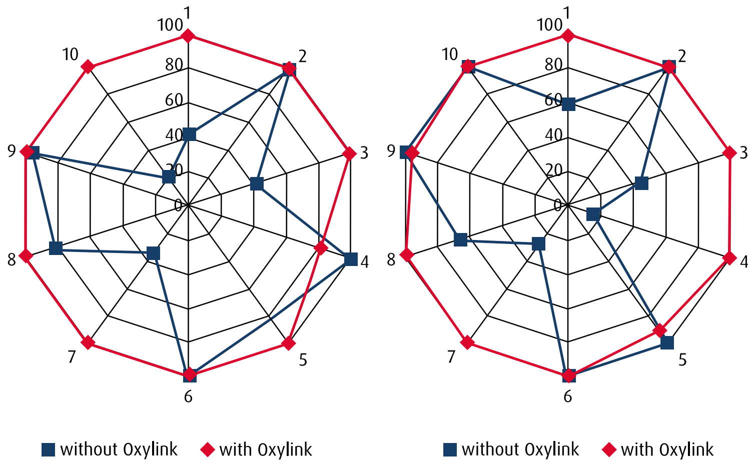

Figure 5: Left: Performance diagram of HBST formulation with and without nanoparticle additive. Right: Performance diagram of WG formulation with and without nanoparticle additive

Key: 1: Drying time (for workability); 2: Gloss (60°); 3: Gloss retention on solvent rub, IPA; 4: Gloss retention on solvent rub, MEK; 5: Abrasion resistance; 6: Adhesion (crosscut, tape); 7: MEK double rub resistance; 8: IPA double rub resistance; 9: Water permeation; 10: Blocking resistance

coating material could be moved from "totally blocking" (index 5) down to a rating of 1, both on plastic and on wood. Some improvement can even be seen for the WG formulation, which is already highly resistant to blocking and was originally developed for window coatings. Here, the blocking resistance on wood could be improved from 2 3 to 1.

Shorter drying time increases productivity

In industrial use especially, processing also plays an important role. Here, productivity is decisive and the quality and usability of a coating material is not determined only by the properties of the final coating.

One possible way to increase productivity is to reduce the drying times in terms of touch dry and overcoatable/workable times. Here too, the nanoparticle additive shows a remarkable improvement (*Figure 4*). Although the drying time can be significantly shortened, the open time remains more or less unaffected.

The drying time of both coatings could be significantly reduced; in both cases the drying time of the samples containing nanoparticles was only about 50 % of the drying time of the comparative formulations without the nanoparticle additive.

In addition to the improvements so far mentioned, the nanoparticle additive has no adverse impact on other coating properties such as adhesion, abrasion resistance, water permeation or optical appearance.

Figure 5 summarises the usage properties of the two coating materials tested and compares the overall performance of the individual formulations with and without the nanoparticle additive. As can be clearly seen, a distinct improvement of the overall performance can be achieved through the addition of nanoparticles to each of the formulations.

Properties and productivity both enhanced

These results show that nanoparticle coating additives can improve the overall usability properties of waterborne coatings significantly. The use of the material tested here increases both the solvent resistance and blocking resistance of waterborne coatings.

As a consequence, the drying time before recoating or reworking is possible is remarkably shortened without adverse impact on other properties.

The effect of this is that the competitiveness of waterborne coatings can be increased and a broader range of applications is possible.

REFERENCES

[1] US Paint and Coatings Market Analysis, National Paint and Coatings Association (2007).

[2] www.window.de/uploads/media/ho01_muster.pdf

[3] Guideline 6 "Verblockung von Anstrichsystemen auf Holzfenstern" (03/99) des Institutes für Fenstertechnik e.V., Rosenheim.

[4] *Burgard D., DiStefano F., Hegedus C., Mercando L., Pepe F.*, European Coating Show, Nuremberg, 2007.

Results at a glance

››› In industrial applications, the performance in end-use and productivity are equally critical in determining whether waterborne coatings can provide an acceptable alternative to established technology.

››› The use of a predispersed nanoparticle additive known as "Oxylink" is shown not only to improve performance but to speed up the effective drying time.

››› The material was tested in two waterborne finishes based on different binders at 1 % addition (solids on solids). Solvent resistance in terms of solvent double rubs using MEK and IPA was greatly improved.

››› Blocking resistance at high temperature (50 °C) was greatly enhanced, leading to an effective reduction in the drying time as measured by the time at which it is possible to stack or work on the coating.

››› Other key properties such as abrasion resistance, crosscut adhesion, appearance and water permeability were very little affected.