

Surface-modified Nanoparticle Additives for Wear Resistant Water-based Coatings for Galvanized Steel Plates

Carsten Becker-Willinger[†], Gisela Heppel, Michael Opsoelder,
H.C. Michael Veith, Jaedong Cho¹, and Jae-Ryung Lee¹

INM - Leibniz-Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany

¹*POSCO Technical Research Laboratories; Gwangyang, Jeonnam; 545-090, Korea*

(Received August 31, 2009; Revised August 18 2010; Accepted August 18, 2010)

Conventional paints for conversion coating applications in steel production derived mainly from water-based polymer dispersions containing several additives actually show good general performance, but suffer from poor scratch and abrasion resistance during use. The reason for this is because the relatively soft organic binder matrix dominates the mechanical surface properties. In order to maintain the high quality and decorative function of coated steel sheets, the mechanical performance of the surface needs to be improved significantly. In fact the wear resistance should be enhanced without affecting the optical appearance of the coatings by using appropriate nanoparticulate additives. In this direction, nanocomposite coating compositions (Nanomer[®]) have been derived from water-based polymer dispersions with an increasing amount of surface-modified nanoparticles in aqueous dispersion in order to monitor the effect of degree of filling with rigid nanoparticles. The surface of nanoparticles has been modified for optimum compatibility with the polymer matrix in order to achieve homogeneous nanoparticle dispersion over the matrix. This approach has been extended in such a way that a more expanded hybrid network has been condensed on the nanoparticle surface by a hydrolytic condensation reaction in addition to the quasi-monolayer type small molecular surface modification. It was expected that this additional modification will lead to more intensive cross-linking in coating systems resulting in further improved scratch-resistance compared to simple addition of nanoparticles with quasi-monolayer surface modification. The resulting compositions have been coated on zinc-galvanized steel and cured. The wear resistance and the corrosion protection of the modified coating systems have been tested in dependence on the compositional change, the type of surface modification as well as the mixing conditions with different shear forces. It has been found out that for loading levels up to 50 wt.-% nanoparticles, the mechanical wear resistance remains almost unaffected compared to the unmodified resin. In addition, the corrosion resistance remained unaffected even after 180° bending test showing that the flexibility of coating was not decreased by nanoparticle addition. Electron microscopy showed that the inorganic nanoparticles do not penetrate into the organic resin droplets during the mixing process but rather formed agglomerates outside the polymer droplet phase resulting in quite moderate cross linking while curing, because of viscosity. The proposed mechanisms of composite formation and cross linking could explain the poor effect regarding improvement of mechanical wear resistance and help to set up new synthesis strategies for improved nanocomposite morphologies, which should provide increased wear resistance.

Keywords : nanoparticle, coating, wear resistance, corrosion resistance

1. Introduction

Steel surfaces with nice optical appearance are more favored for preparing decorative surfaces to create a new design in many areas such as consumer electronic applications and the like. These surfaces with special design should be protected against damages, scratches and finger-

prints which can occur during fabrication and transportation. From the state of the art appropriate protective paint systems are applied which should be almost invisible in order not to influence the metallic appearance of coated surfaces. Such paint systems usually are applied on steel by a wet chemical coating process. Besides a good protective performance against contamination and general appearance, such coating systems mainly suffer from low scratch and abrasion resistance. It is because this process

[†] Corresponding author: nanomere@inm-gmbh.de

requires using environmentally friendly water based systems which are curable under moderate conditions. Relatively soft organic coating layer with moderate cross linking density is formed during application and curing procedure, where the layer is sensitive against mechanical damages. In order to maintain the high quality and protective function, such organic coating systems need an improvement of the mechanical performance in particular the wear resistance. The approach of nanocomposite formation could lead to increased cross linking density with reactive nanoparticles as cross linking points. The use of nanoparticulate additives was motivated by the possibility to introduce solid state physical properties of inorganic materials such as e.g. hardness into organic resins without affecting optical appearance because nanoparticles that are smaller than 50 nm in particle size do not scatter light in the visible wavelength range even when there is a refractive index difference between particle and matrix.

2. State of the art

Many approaches exist worldwide to derive protective coating systems for metal surfaces when anti-fouling behavior, chemical protection against e.g. oil as well as a certain mechanical protection is addressed. Mainly waxes, silica based delustering agents or coupling agents are used as additives.¹⁾ From the view point of resin, e.g. radiation curable acrylic systems as well as polymer dispersions or emulsions are described in the literature.^{2),3)} Some of the compositions described also comprise hydrophobic substances or superamphiphobic nanoparticulate material based on carbon nanotubes as additives for anti-fouling behavior.⁴⁾ The addition of nanoparticles to improve scratch resistance of paint is a quite old concept for solvent borne coatings.^{5),6)} On the other hand water based emulsions exist where nanoparticles have been dispersed in monomer droplets prior to emulsion polymerization leading to acrylate type emulsion particles with intrinsic nanocomposite morphology when emulsion polymerization reaction has been completed.⁷⁾ The latter approach is very interesting, because it enables to achieve a quite homogeneous particle distribution over the matrix already in the formed polymer particles, but on the other hand is more expensive because it is a sophisticated synthesis technology and has less flexibility to change the nanoparticulate filler content. Some researchers described the formation of polyurethane nanocomposites for coating applications.⁸⁾⁻¹¹⁾ These are solvent borne or sometimes 100 %-systems not containing any solvent. On the other hand polyurethane dispersions in water containing additional nanoparticles have not been described. In summary it seems that cost

effective ways of dispersing functionalized nanoparticles into water based polymer dispersion usable for wet chemical coating process has not been investigated so far. Furthermore water based homogeneous hybrid type nanocomposite coatings have been developed using a sol-gel type approach in the past that show excellent scratch and abrasion resistance.¹²⁾⁻¹⁴⁾ For the reasons mentioned before it was of high interest to investigate the mechanical behavior of water-based polymer dispersions with hybrid nanoparticles in dependence on the degree of filling, the interaction between nanoparticles and polymer and the mixing conditions using different shear fields, which would help to find a cost effective way for new coil coating systems with improved wear resistance.

3. Experimental

For nanocomposite formation, a commercially available water based polymer dispersion paint with mean particle size around 100 nm has been equipped with water based silica dispersions having a mean particle size of about 30 nm. The silica particles have been surface modified with selected organo silane prior to dispersion in the resin. Unmodified silica particles with the same particle size have been used as reference. The nanocomposite mixtures with silica content up to 50 wt.-% based on solid content have been prepared by magnetic stirring and with ball milling. The mixtures have been spin-coated on steel plates and cured. The morphology of the cured layers has been investigated by scanning electron microscopy (SEM) on fractured surfaces and transmission electron microscopy (TEM) on ultramicrotomed thin slices. One important issue was the determination of wear resistance. It was tested by cyclic rubbing of a small steel cylinder (4 mm Ø) with a loading of 12.5 kgf/cm² repeating 10 times over the coated surface (rubbing distance: 25 mm, frequency: 1 Hz). The rubbing leaves a dark metallic gray abrasion track on the matte light grey surface. A fraction of damaged surface area was monitored.

Micro hardness measurements test have been performed using an automated indentation (indenter: Vickers diamond, indentation depth: 1 µm).

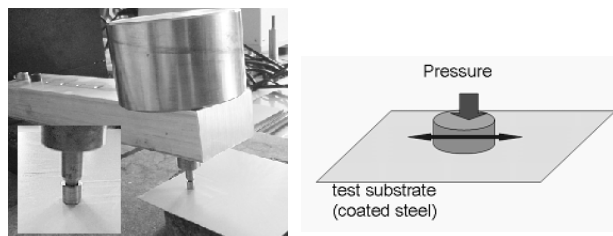


Fig. 1. Wear resistance testing apparatus and testing principle.

4. Results and discussion

Silica nanoparticles with 30 nm mean particle size in water dispersion have been surface modified prior to use in order to achieve compatibility with the polymer matrix and to enable the particles to form covalent bondings with the organic polymer network. An organo silane that can react with the silanole groups on the particle surface via hydrolysis and condensation reaction and on the other hand is bearing an organic functional group that can undergo cross linking reactions with e.g. nucleophilic groups of the polymer resin has been chosen as surface modifier. Fig. 2 shows the principal structural scheme of the surface

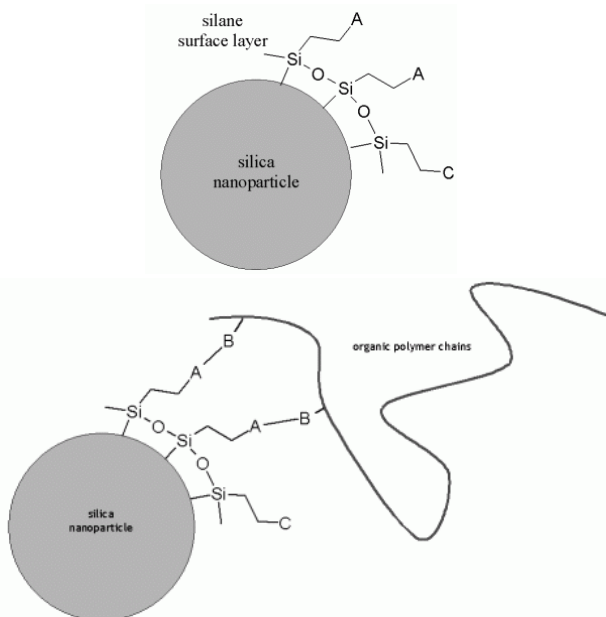


Fig. 2. Silica nanoparticle with surface modification (left) and bonded to polymer chain (right).

modified silica nanoparticles and possible cross linking reactions with the polymer matrix.

The selected organic functional group keeps the particle surface hydrophilic to obtain stable nanoparticle dispersions in water based reaction mixture.

Different morphological concepts have been followed in the nanocomposite materials in order to improve scratch and wear resistance compared to the pristine unfilled resin. One edge point of the variation was the incorporation of nanoparticles with cross-linkable surface functionalities which can react with the cross-linkers of the matrix and should increase the overall cross-linking density in the mixtures. The second edge point of variation was the formation of nanoparticles covered with a larger extended organic-inorganic network in order to achieve a more intensive network formation in the resulting nanocomposite resin compared to the pure dispersing of nanoparticles into the matrix material. The intended morphology to improve wear resistance is shown in fig. 3.

It was assumed that the extended silane layer on the particle surface leads to a more intensive network formation especially by formation of an increased number of entanglements between polymer resin and silane network at the particle matrix interface similar to an interpenetrating system. The increased interfacial interaction could improve wear resistance by transferring stress from the polymer matrix to the nanoparticulate inclusions more effectively. The structural model of the intended nanocomposite structure is shown in fig. 4. As the polymer matrix is present as a dispersion of more or less compact polymer particles in water it was of interest to investigate if high shear forces during mixing of the polymer dispersion with the nanoparticulate silica dispersion would have an effect on the resulting distribution of the inorganic nanoparticles over the polymer matrix.

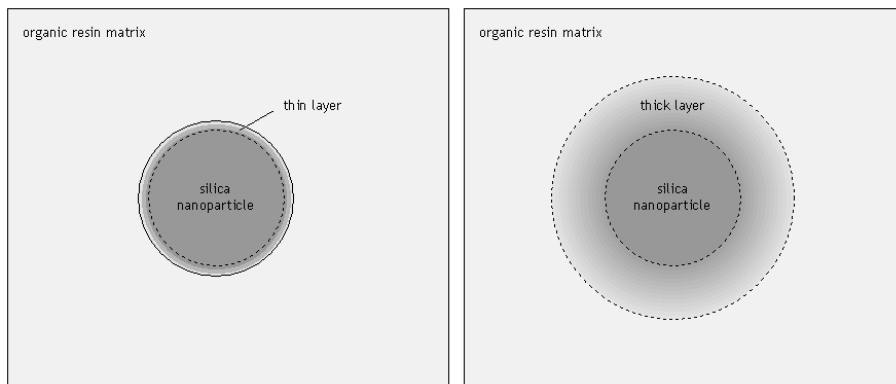


Fig. 3. Surface modified particle with thin silane layer (left) and core shell type particle with thicker layer of condensed silane allowing a higher number of entanglements to be formed leading to increased interfacial interaction (right).

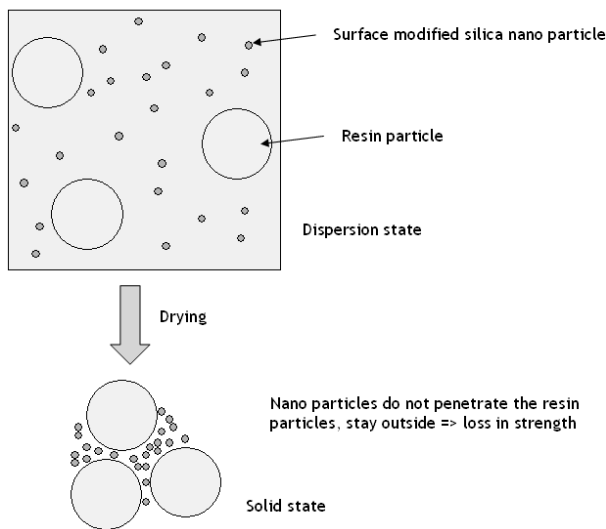


Fig. 4. Model for drying process of resin / nanoparticle dispersion and structural scheme of the resulting nanocomposite in the dried solid state.

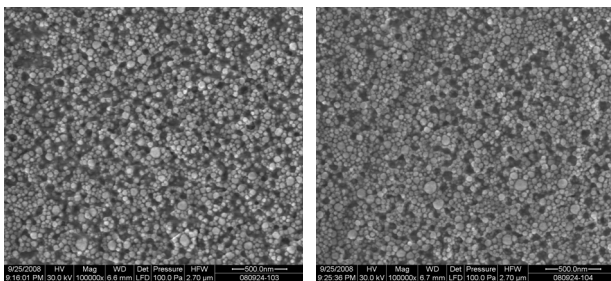


Fig. 5. SEM micrographs of fracture surfaces of the dried resin dispersion with 50 wt.-% silica nanoparticles (30 nm) spin-coated on glass (left: simple mechanical stirring; right: high speed ball mill).

For this purpose mixtures of polymer dispersion with different amount of silica have been prepared by simple mechanical stirring and a high speed ball mill for comparison. Fig. 5 shows the result on the morphology in the scanning electron microscopy (SEM) analysis on fractured surfaces from nanocomposite coatings containing 50 wt.-% silica based on solid content in dependence on the intensity of mixing.

It can be derived from fig. 5 that a particulate structure remains present in the nanocomposite mixtures formed. By comparison of the two different mixing procedures no principal difference can be detected in the SEM analysis. Two types of categories of particle sizes seem to exist where the smaller one of them may be attributed to the silica nanoparticles and the larger one may be the polymer particles. The remaining holes visible in the surface structure may come from organic resin particles which have been removed by evaporation caused by the scanning elec-

tron beam. Around these holes the remaining inorganic SiO₂ nanoparticles seem to form agglomerates. From that point of view it could be concluded that the shear field applied seems to have almost no influence on the nanoparticle dispersion over the matrix. Nevertheless a clear identification of silica and polymer particles is not possible because SEM only shows the surface topography in the sense of a relief contrast. For this reason also transmission electron microscopy (TEM) has been performed on ultramicrotomed thin films prepared from the dried nanocomposite coating systems because TEM visualizes the elemental contrast between carbon rich matrix and silicon rich silica phases. The results from the TEM analysis are shown in fig. 6. A concentration of only 1 wt.-% silica has been chosen for the TEM investigation, because the particle size of the silica is much smaller than the layer thickness of the ultramicrotomed slices which would result in an overlap of silica particles while projecting the three dimensional morphology on a two dimensional image. High particle concentrations would then make an interpretation of the particle distribution over the matrix almost impossible.

From fig. 6 it can be derived that the silica should be distributed quite homogeneously over the polymer matrix. This observation seems to be in contradiction to the results from the SEM (fig. 5) where some agglomeration of the silica has been assumed to occur. Nevertheless the particle free areas visible in fig. 6 have approximately the dimensions of the polymer dispersion particles with a particle size around 100 nm. For this reason it could again be concluded that the final morphology is built by enrichment of the silica nanoparticles at the interface between adjacent polymer particles as already indicated in fig. 4.

To test adhesion, elasticity and corrosion protection the samples were bent on an 8 mm mandrel by 180° and put in the neutral salt spray test for 48 h. This investigation

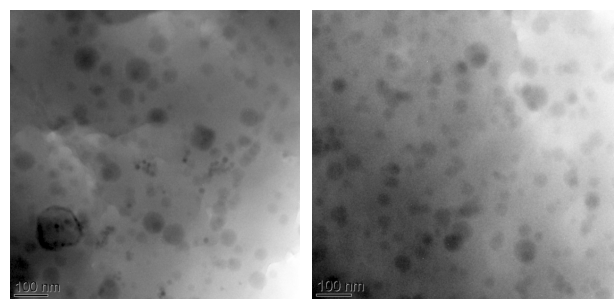


Fig. 6. Transmission electron micrographs (TEM) of thin ultramicrotomed films of the dried resin dispersion with 1 wt.-% 30 nm silica nanoparticles (left: simple mechanical stirring; right: high speed ball mill).



Fig. 7. Coated steel samples after bending test (180°, 8 mm mandrel) and subsequent neutral salt spray test (48 h), left: unmodified polymer resin, middle: resin with 10 wt.% unmodified silica, right: resin with 20 wt.% organo silane modified silica as representative samples.

also has been performed for the nanocomposites with different degree of filling with silica and in dependence on the kind of particle surface modification. Some representative samples are shown in fig. 7.

From fig. 7 it can be derived that after bending and subsequent salt spray test no corrosion in the bended area is observed. This result shows that the flexibility of the polymer matrix is not influenced by the addition of the nanoscaled particles. It seems that the compositions created have the potential to be used in practical applications. An important point in this direction is furthermore the influence of the nanocomposite formation on the evolution of the wear resistance of the coatings. The results of the wear tests according to the description in section 3 are shown in fig. 8.

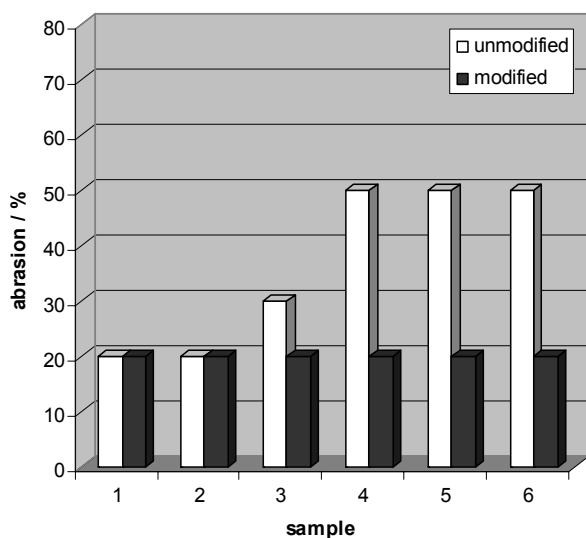


Fig. 8. Results of the wear test on coatings containing unmodified silica (30 nm) and modified silica (30 nm); denotation: sample 1 = 0 wt.-%, 2 = 10 wt.-%, 3 = 20 wt.-%, 4 = 30 wt.-%, 5 = 40 wt.-%, 6 = 50 wt.-%.

It is obvious from the results in fig. 8 that the wear resistance could not be improved with the addition of silica particles to the resin dispersion. The unmodified particles even decreased the resistance compared to the unfilled resin. The observed behavior might be due to the lack in chemical bonding between unmodified nanoparticles and matrix resulting in a decreased possibility to allow controlled crack propagation to occur. This means that the dispersion of nanoparticles in a polymer matrix without interfacial adhesion leads to increasing embrittlement with increasing filler content, which is generally known to occur especially for particles with spherical shape. On the other hand the wear resistance of the nanocomposites with surface modified nanoparticles at least remains constant. This indicates that chemical bonding between the inorganic particulate phase and the polymer resin matrix should play a significant role as already expected. Nevertheless the wear resistance is not increased compared to the unfilled resin even if very high loadings of surface modified silica are dispersed. The reason for this might be that the pin-on-disc type wear test leads to an unfortunate load combination of scratching and frictional components. In order to separate different parameters that might influence the result of this wear test, the coatings were further characterized by micro hardness indentation measurements. Fig. 9 shows diagrams of the universal micro hardness HU_{plast} as a measure for the resistance of the surface against plastic deformation and the elastic fraction of the deformation work.

The hardness increases with raising SiO_2 content, with slightly lower hardness for the modified particles. On the other hand the elastic fraction of the deformation work is nearly the same for all filled coatings and lower than that of the unfilled resin. As a conclusion, it seems that the wear test not only addresses to the hardness of the surface which should increase with increasing filler con-

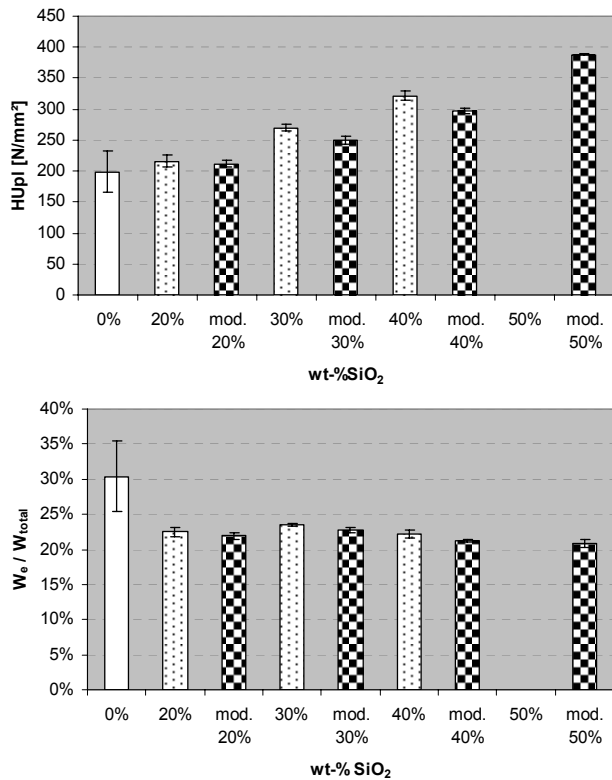


Fig. 9. Plastic micro hardness (HU_{pl}) and elastic fraction of the deformation work (W_e/W_{total}) of the nanocomposite coatings with different content of unmodified (dotted) and GPTES modified 30 nm silica (checked) respectively.

tent but also addresses to the strength of the coating. This means that in case of high friction forces and some brittle behavior of the coating the coating layer will be abraded within very short time. The measurement of the strength of such coatings would be of high interest for future work in order to understand the whole mechanical behavior of such type of composite systems.

5. Conclusions

From the main results it can be derived that with the structural materials concepts a significant improvement in wear resistance could not be achieved. One critical point seems to be the homogeneous distribution of the inorganic nanoparticulate silica additives over the organic resin matrix. Even high shear forces during the dispersion step seem to have almost no effect on improvement of the situation mainly because the organic resin is present as internally cross-linked particles where the inorganic nanoparticles not easily penetrate in. The result is the formation of nanoparticle agglomerates in the dried nanocomposite film having no positive effect on the scratch resistance

because they are not leading to intensive cross linking. Even the silica nanoparticles with the extended organo silane hybrid shell did not show any improvement. A solution for this unfortunate situation could be the use of resin dispersions with smaller particle size in the range of the size of the inorganic nanoparticles and making the resin particles themselves cross linkable with nanoparticles having appropriate functionality. This approach should lead to a more homogeneous distribution of organic and inorganic phases and to more intensive cross linking. A second important point for the improvement of the wear resistance of the layers seems to be the installment of the right tribological behavior. If a low coefficient of friction could be achieved without destroying other important properties of the coatings this would have a very positive effect on the wear resistance because the frictional shear stress on the coating normally leading to failure would be dramatically reduced.

Acknowledgments

The financial support of the work by POSCO Company is gratefully acknowledged.

References

1. KR 2003054375 A, KR 2003053764 A, KR 2003053762 A, KR 2002032735 A, POSCO Co.
2. K. Hackbarth, WO2003022945 A1, Henkel AG, 11.09 (2001).
3. D. Kasper, WO2002040604 A2, WO2003046090 A2, Henkel AG, 20.11 (2000).
4. C. Huang, US 2006/0110537 A1, Hon Hai Precision Industry CO., LTD., 21.11 (2005).
5. B. Oermann, EP 0832947 B1, BASF Corp., 30.09 (1996).
6. B. Munro, EP 1478704 B1, PPG Industries Inc., 20.02 (2002).
7. H. Wiese, EP 1216262 B1, BASF AG, 08.09 (1999).
8. V. J. Tramontano, M. E. Thomas, and R. D. Coughlin, Synthesis and Coating Properties of Novel Waterborne Polyurethane Dispersions. King Industries, Inc., Specialty Chemicals, Science Road, Norwalk, CT 06852
9. Werner J. Blank, Formulating Polyurethane Dispersions, King Industries Inc., Norwalk CT
10. Z. W. Wicks, Jr., F. N. Jones, S. P. Pappas, D. A. Wicks., Science and Technology, p. 261, Third ed., Wiley (2007).
11. Su Chen, Jianjun Sui, Li Chen, John A. Pojman, J. Polym. Sci. A : Polymer Chemistry, **43**, 1670 (2005).
12. H. Schmidt, WO 99/52964, INM gGmbH, 08.04 (1999).
13. B. Standke, DE 4443824 A1, Huls AG, 09.12 (1994).
14. B. E. Yoldas, EP 0263428 B2, PPG Industries Inc., 30.09 (1987).