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UV Curable Electrodeposition Systems

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Summary: This article reviews the development of a UV curable electrodeposition system. Tailor-made acrylic functionalized polyurethane resins, which have been designed, are described and basic properties of the final e-coat system are shown. In addition several fundamental studies have been performed in order to analyze as well the homogeneity of the deposition as the efficiency of the UV curing process.

Keywords: coatings, irradiation, UV, electrodeposition, polyurethane

Introduction

UV-radiation curing has become a well-accepted technology which, because of its distinct advantages, has found manifold industrial applications, mainly as fast-drying protective coatings, printing inks and adhesives.[1] A liquid resin can be transformed almost instantly into a solid polymer material by simple exposure to UV light at ambient temperature, without emission of volatile compounds.

With respect to the application of coatings, electrodeposition is ecological and economical the most efficient method. The objective and therefore an innovative challenge was the development of a electrodeposition and UV-curing process, which combines the advantages of both techniques.

Urethane-acrylates have been selected as telechelic oligo- and polymers, because of their known overall balance of properties, in particular the superior resistance to abrasion and scratching, and the high impact and tensile strength of the cured polymer. As these compounds are not soluble in water, ionic groups had to be introduced into the polymer backbone to obtain stable dispersions.

Experimentals

Principles of anodic electrodeposition (AED)

Electrodeposition offers high corrosion protection, low cost, and compliance with

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environmental regulations. It is used for coating of articles of various sizes including steel building trusses, car bodies, furniture, appliances, toys, and details.[2, 3] The current success of electrodeposition is due to the water-dispersible, synthetic, electrodepositable macro ions as filmformers. The process is most frequently called electrocoating, though various names, such as electropainting, elpo, e/coat, etc, are in use. Electrodeposition combines many advantages of other painting methods with new and desirable features:

- Formation of films in highly recessed areas such as cavities, box sections, creases, and flanges results in excellent corrosion protection.
- Use of water as continuos phase virtually eliminates the fire hazard and environmental pollution and reduces the cost of control equipment.
- Low viscosity of the bath facilitates agitation and pumping and allows fast entry and drainage of workpieces.
- Freshly deposited coats are composed of nearly 95% non-volatile substances and therefore allow immediate gentle handling; there is no tendency to sag or wash off during cure.
- A second coat, usually a color coat, of waterborne or solvent-borne spray paint can be applied directly over the uncured electrocoat.
- Approximately 95% of the applied paint is utilized because the liquid paint, which adheres or fills the cavities of freshly coated pieces, is rinsed back by ultrafiltration into the coating tank.
- Overall savings, accounting for materials, labour, capital investment, energy, etc. are 20-50% compared to spray, electrostatic-spray, or dip-coat painting.

The plating cell contains a solution or dispersion of ions, which provide the electrical conductivity. Two electrodes, which have to be made of conductive materials like metal or graphite, are placed into the bath.

When the electrodes are being used in a direct-current system they are referred to as the *anode* and the *cathode*. The anode is the one, which is connected to the positive pole of the power source, and the cathode is the one, which is connected to the negative side of the power source.

Within the cell, the electrolyte is a solution or dispersion of positively and negatively charged ions – the electrolyte. When electricity is applied to the cell the electric field draws negatively charged ions towards the anode and the positively charged ions towards the cathode. Negatively charged ions are therefore known as, *anions* and positively charged ions as, *cations*. The current within the electrolyte solution is carried by these ions. The electrons can carry the current as far as the surface of electrode and no further. So at the surface of the electrode, which is immersed in the solution, there has to be some way of transferring the conduction process across the boundary of the electrode.

In the bulk of the solution, the composition is kept more or less homogenous by mechanical agitation. Because of the viscosity of the solution this agitation does not extend right up to the surface of the electrode, thin layer of solution exits over the surface of the electrode which is essentially free of convection. This is known as the *Nernst diffusion layer*. Any movement of reactants towards the electrode, or products away from it, is therefore either by *diffusion*, following Fick's laws, or *electrical migration.*

Drying and UV-curing

The coating is applied in several process steps. In the first step the conductive substrate is electrocoated using voltages of 100 – 200 V and bath temperatures between 25 and 30 °C (the determination of this application window is described below).

Then this electrocoagulated film is washed and pre-dried. It can be dried by using an air stream or additionally by using temperatures of 60 – 80°C for some minutes. The residual water is nearly quantitatively removed during this step.

The resulting film is UV cured using 2 passes on a Fusion UV-lamp system (Hg-emitter at max. 240 W/cm) at a belt speed of 5 m/min. For the UV curing a typical photo-initiator (α-hydroxyketone type) has been added to the formulation.

Basics in binder chemistry

Aqueous polyurethane dispersions have been gaining increasing importance in a wide-range of applications, due to their excellent properties.[4] These include:

- Adhesion to various substrates
- Resistance to chemicals, solvents and water
- Abrasion resistance
- Flexibility and toughness
- Fast dry
- Outstanding flexibility and impact resistance
- Low volatile organic content = less pollution

Conventional polyurethane resin systems usually contain a proportion of volatile organic solvents. At the end of the 1970s, the manufacturers of polyurethane resins developed processes that permitted the synthesis of low-solvent or solvent-free aqueous polyurethane dispersions. The increased use of polyurethane dispersions is attributed not only to the above-mentioned profile of properties but also to pressures from coating industry and environmental legislation for raw materials with a low organic-solvent content.

Central to the utilisation of polymers in aqueous media is the fact that certain polar functional groups are capable of conferring water solubility or water dispersibility to otherwise water-insoluble polyurethane. Best known are carboxylic acid groups, sulphonic acid groups, and tertiary amine groups. The concentration of such functional groups in the polymer highly influences its solubility or dispersibility in an aqueous environment. Thus, at high concentrations, the polymer may be water soluble, and at lower concentrations the polymer may be water dispersible, provided its molecular weight/viscosity is not excessive. At even lower concentrations, the polar group may be capable of providing charge or steric stabilisation to a dispersion of the polymer in water.

A range of synthetic routes is available for the preparation of waterborne polymer systems. The polymers can differ widely in terms of (1) the nature and concentration of the polar solubilizing group, (2) molecular weight, and (3) the hydrophobic/hydrophilic characteristics depending on the units in the polymer chain. As a result, aqueous polymer systems with a wide range of different morphological and physical characteristics can be obtained.

Special binders for UV-ED-Systems

Aqueous polyurethane dispersions (PUD‘s) are of special interest. They offer a good balance between mechanical properties like abrasion, hardness or tensile strength. The properties of polyurethanes can be modified in a wide range by varying the composition of the typical building blocks, such as polyols and polyisocyanates or chain extension chemistry. The most common way to synthesize polyurethanes is the formation of a medium molecular weight isocyanate terminated prepolymer by the reaction of polyols with polyisocyanates. In the case for use the polyurethanes for anodic electrodeposition, it is also necessary to incorporate acid functional groups into the polymer backbone. After the prepolymer is formed, functionalization and / or chain extension can take place to form the final polyurethane.

The main route for the synthesis in this work is described as follows:

A polyester polyol of hexanediol, neopentylglycol, adipic acid and isophthalic acid is reacted with dimethylolpropanoic acid and isophorone diisocyanate at 80°C for ca. 5 h until the isocyanate is consumed to form the polyurethane prepolymer. The acid number is adjusted to

30 and the NCO/OH ratio of 1 to 1.5. The primarily synthesis route is shown in figure 3:

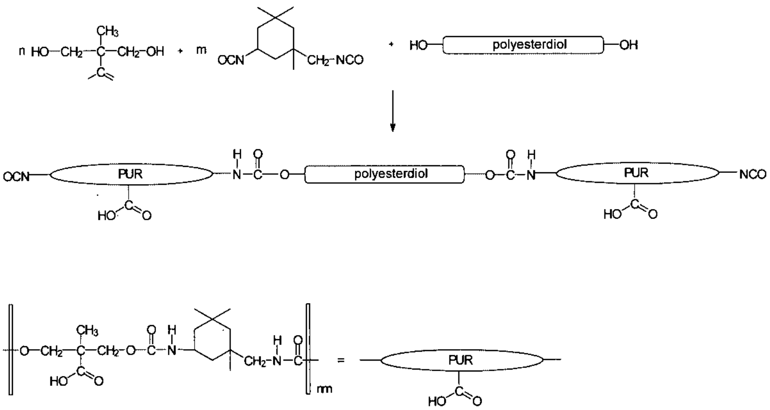

Figure 3. Schematically formation of a acid functional, isocyanate terminated polyurethane prepolymer.

Due to the need to prepare UV-curable resins, the above shown prepolymer is then functionalized with hydroxy ethylacrylate to give a acrylic functional polyurethane, shown in figure 4.

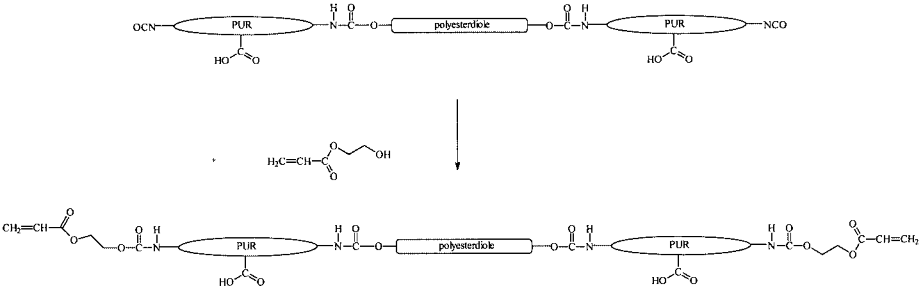

Figure 4. Acrylic functionalized polyurethane

Linear acrylic functional polyurethanes are very important to adjust overall mechanical properties, but with concideration to achieve also good solvent and / or chemical resistance, there is the need to use other UV-active cobinders to enhance crosslinking density and thereof chemical resistance of the final coating.

Results and discussion

Water content

In contrast to conventional electrodeposition coatings the UV system is not heated up to temperatures above 80°C during the whole application process. Although this offers more opportunities regarding the substrates which can be coated, it on the other hand becomes crucial to exactly control the water content of the deposited layer.

During the electrodeposition process most of the water is expelled from the coagulated coating film. However, it is well known, that the residual water content of the deposited film is still in the range of 5 – 10 % w/w. In a standard electrocoat this water is removed during the baking process very easily at temperatures well above 150 °C. In the new UV system this has to be ensured at temperatures of 60 – 80°C. If there is still water in the film when the fast UV curing takes place, it cannot evaporate but would be entrapped in the solid polymer network. The technological properties like hardness, gloss, resistance of the resulting coating film would significantly suffer. Consequently the water content of the deposited film has been determined as a function of the deposition parameters.

By means of a DoE the results have been collected and a response surface has been modeled. Figure 5 shows the water content of the deposited film as a function of T/°C and U/V. It can be clearly seen, that the water content increases significantly with increasing bath temperature and voltage.

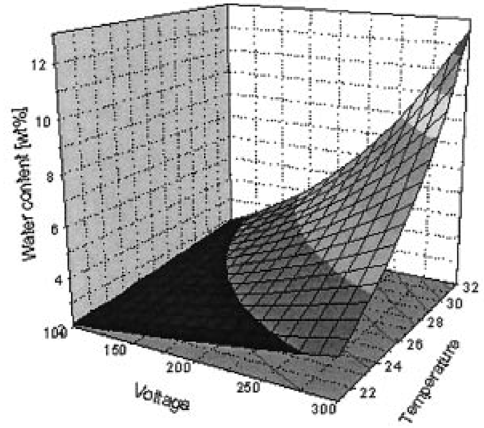

Figure 5. Water content of the deposited coating film as a function of bath temperature and voltage.

Based on these results, the application windows for the deposition process was defined. The usable voltage was limited to approximately 150 V, the bath temperature was varied from 26°C to 30°C. In this case it was shown, that after pre-drying for 10 min. at 60°C the residual water is quantitatively removed from the film. The UV cured coatings showed excellent technological properties.

Stability

A critical issue of electrodeposition coatings is the stability of the resulting bath materials. Since an e-coat bath in operation is refilled permanently, the dispersions have to be very stable.

In order to evaluate and improve the static stability of the system, a special test equipment LUMiFuge® which combines a centrifuge with an optical detection system was used.[5]

The homogeneous dispersion is placed into a measuring cell, which is then rotated with up to 3000 rotations per minute. This correlates to an accelaration of up to 1200 g , which significantly accelerates the migration of the particles within the dispersion.

The transmission is synchronously measured by an infrared flash along the whole length of the cell.

Zones of well distributed dispersions scatter and adsorb the light, so transmission is low. In contrast, any clarification allows more light to reach the CCD-lines: transmission raises.

The larger the particle size, the faster the demixing. The boundary between the light adsorbing sediment and the clear water phase can be detected as a function of time.

Due to this accelerated migration and fully automatic detection, the stability/instability of the dispersions could be assessed on a very short time frame. The sample is analyzed in user defined intervals over a whole measuring time of up to 24 hours. The corresponding transmission profiles are automatically collected and can be analyzed separately. Figure 6 shows an example for a typical transmission profile, which shows a creaming of the dispersed particles.

The red curves relate to the beginning of the test run. You can clearly see the air/dispersion interface, which is characterized by a strong drop of the transmission intensity. The well-dispersed material is scattering and adsorbing the test beam quantitatively. However, as a function of time, the dispersed particles start to cream. This can be detected by a shift of the boundary layer toward the top of the measuring cell (on the left hand side of the diagram). At the end of the test run (green transmission profile) you can see the floated material, which is located at the top of the cell, and an increased transmission through the rest of cell, which

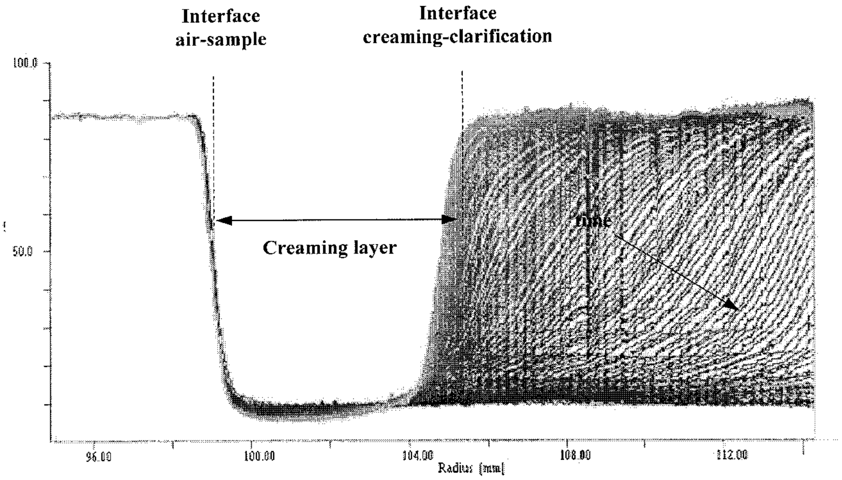

Figure 6. Example of a transmission profile with creaming.

relates to a clarification of the system.

In order to quantify these results, you can follow the clear/turbid interface as a function of time and thus get values for the sedimentation velocity (measured in µm/s). We have shown, that these data are correlating well with standard stability values determined in test cylinders. The main reason for the improved stability was the adjustment of the compatibility of the two resins. In order to achieve this the type and amount of the hydrophilic diole component within the synthesis of the crosslinker was varied and optimized. The dispersions, which are based on these resins, have a small mean particle size of approximately 100 nm and thus show nearly no sedimentation.

Conversion of the unsaturated acryloyl groups

An advantage of the electrodeposition process is the early water-free coagulated film directly after the deposition, as already shown before. As a consequence only moderate heating is necessary to remove the residual water from the film and to proceed with the fast UV curing step. However, it is well known, that the conversion efficiency of UV curable systems strongly depend on the mobility of the polymers, which are engaged in the process.[7-9] If the viscosity of the polymeric matrix is very high it becomes more difficult to achieve a quantitative through-cure of the material, due to the immobility of the acrylic groups. Working at low temperatures could therefore possibly lead to an insufficient conversion of those groups. The influence of the substrate temperature on the conversion of the double bonds was investigated as a function of the applied UV dose. The extent of polymerization was calculated from the distinct band at 810 cm^{-1}, which can be assigned to the twisting mode of the acrylate double bonds.[6] Figure 7 shows the residual amount of double bonds as a function of the UV dose at two temperatures (room temperature and 80°C).

It can be clearly seen, that the substrate temperature has a significant influence on the conversion during the UV curing process. Whereas approximately 10% of the unsaturated double bonds remain unreacted at room temperature, a nearly quantitative conversion can be reached at a temperature of 80°C and a UV dose of 1 J/cm^2.

Therefore, in order to obtain cured films with good ageing and weathering stabilities, during this study the UV curing was done at increased temperatures (60 – 80°C) and with UV doses of > 1 J/cm^2.

Technological properties of the UV/EC coatings

The UV curable electrodeposition system, which has been developed within this project, can be in principal deposited on any conductive substrate. However, all tests have been performed on regular steel panels, which have been coated with a film thickness of approximately 20 microns. The films showed an excellent optical appearance and very good hardness. Critical issues like adhesion to the substrate and resistance against solvents (e.g. acetone) have been tested and compared to standard thermal cured e-coat systems (see Table 1).

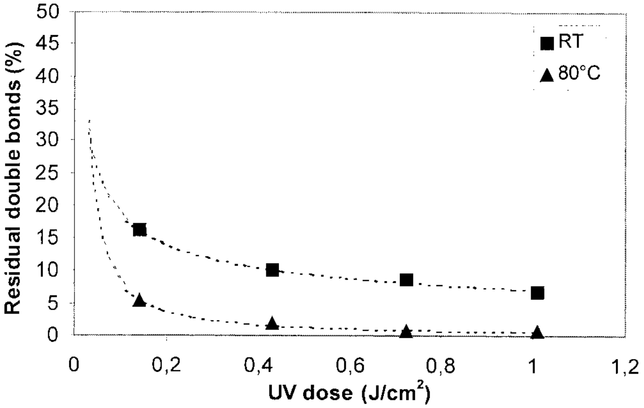

Figure 7. Relative amount of residual double bonds as a function of the applied UV dose.

Table 1. Technological properties of the UV/EC system compared to standard thermally cured electrodeposition systems

	UV/EC system	**Classic thermal cured systems**	
		Melamine	**Isocyanate**
Gloss @ 60°	>90	70-75	80-85
Cupping test (Erichson) (mm)	8,7	5,0	5,1
Acetone resistance 60s	Passed	Passed	Passed
Pendulum hardness (osc.)	145	110	130
Cross hatch test	0	1	0-1

The UV/EC system shows a superior gloss and hardness compared to thermally cured e-coat materials. In addition it still is not brittle, but shows an elasticity of 8,7 mm Erichson indentation. The material also passes the acetone and MEK tests, which proves the high crosslinking density resulting in a very good chemical resistance.

Conclusion

Waterbased polyurethanes have been identified as a powerful system for UV curable electrodeposition coatings. With respect to the mechanical and technological film properties a combination of two different resin components has been developed. In order to achieve an excellent performance of the final coating, the linear, acryl functional polyurethane is preferably used for adjusting the mechanical properties whereby the oligourethane is used to adjust the crosslinking density and therefore to increase the chemical resistance.

The resulting waterborne dispersions show very good stability and can be deposited very homogeneously. The coating can be applied on different conductive substrates and for example exhibits good adhesion on steel panels.

Dependent on the temperature during the curing process, a nearly 100% conversion of the double bonds can be realized.

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