TECHNOLOGY FORUM

Weather-Stable Low-Gloss Powder Coatings

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Manufacturing weather-stable powder coatings with a matte surface and consistent quality is a challenge to the powder coatings industry. Technically acceptable results are achieved using the dry blend process, but one-shot formulations based on polyurethane raw materials or the use of a bifunctional polyurethane matte hardener offer interesting alternative solutions. Investigation of the powder coating films using a perthometer and an electron microscope provides a deeper understanding of the matte powder coating systems.

INTRODUCTION

Weather-stable coatings that yield matte films are an important application field for powder coating systems in Europe, as well as in the U.S. market. Because of their outstanding weather stability and excellent flow and surface properties, polyurethane powder coatings are among the systems used, for example, in the coating of wall cladding elements, garage doors, door and window profiles, and car accessories.[1]

Compared with wet coatings, it is more difficult to produce matte surfaces with powder coatings. Moreover, the same methods cannot be used. In wet coatings, the pigments and extenders migrate to the surface of the film during drying. The roughness created by these particles results in the desired gloss reduction. In contrast, powder coatings contain no solvents and reach relatively high melt viscosities during baking. The transition from a low-viscosity phase to the solid state does not occur. There is a far lower accumulation of matting agents at the surface of the film.

METHODS OF MATTING POWDER COATINGS

Matting Additives

Powder coatings can be matted to a certain extent by the addition of extenders, such as Aerosil, silicas, talc, and barium sulphate. However, too large a quantity of mineral matting agents or pigments results in poorer mechanical properties.

The addition of the metal salts of polymers yields gloss values down to 40%.[2] Additives, such as micronized waxes, cellulose derivatives, and thermoplastic cellulose esters are not compatible with the other components of the coating formulation and, thus, also reduce the gloss.[3] The resultant coatings exhibit uniformly distributed precipitation of these components; however, just slight modifications to the extrusion conditions influence the size of the particles which are incompatible with the overall system. This makes it difficult to reproduce the desired gloss level.

Dry Blend Process

By manufacturing two powder coatings of the same shade using different binders in separate processes and then mixing them together in their dry state, i.e., not in the melt, matte coatings can be produced as long as suitable components are selected.

The problem with these powders, apart from the high manufacturing costs, is the reproducibility of an exact gloss level. In overspray recycling, signs of demixing were observed. Nevertheless, this process is very significant in practice and is described using polyurethane systems as an example.

One-Shot Matte Formulations

Progress in the manufacture of matte powder coatings has been achieved with the "one-shot" process. In contrast to the dry blend process, all the components of the formulation are subjected to a joint extrusion process. From both the production and handling aspect, this process is simpler. As described in the following, polyurethane powder coating systems provide interesting options for producing matte coatings by this method.

Powder Coating Raw Materials with Different Functional Groups

The use of bifunctional powder crosslinkers or resins also makes it possible to achieve low-gloss values.[4] The easy reproducibility and comparatively slight influence of the manufacturing and baking conditions on the gloss level are what make these powder coatings attractive.

EXPERIMENTAL

Materials

The materials used are commercially available powder coating raw materials. A number of the following types of polyester resins with various OH numbers were used: Uralac· (DSM Resins), Crylcoat· (UCB), Additol· (Vianova Resins), and Albester‰ (McWhorter). The polyurethane crosslinkers used were Crelan VP LS 2147, Crelan VP LS 2181/1 and other Crelan–types (Bayer AG, Germany). Other powder coating raw materials, used in concentrations of only a few percent, were: flow promoter Modaflow P III (Solutia Inc.), degassing agent Benzoin (Aldrich), catalyst Crelan KE 9594 (Bayer AG, Germany), and carbon black (Degussa-Hüls, Germany). Titanium dioxide (Kronos Titan GmbH, Germany) was added in 35% b. wt. in all

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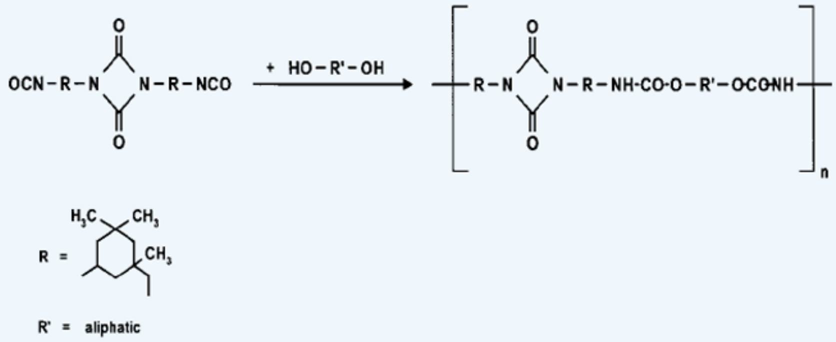

Figure 1—Idealized structure of a polyuretdione crosslinker. The dimerized diisocyanate has to be prepolymerized with a diol to yield solid products. Molecular weight may be controlled by adding definite amounts of monoalcohols to block the chain ends irreversibly.

formulations. A polyester resin and crosslinker were generally used in stoichiometric ratio.

Processing

Each formulation consisting of a hydroxyl-bearing polyester, polyurethane hardener, pigment, extender, flow promoter, and benzoin were mixed separately for three minutes in a Prism Pilot III high-speed mixer (Prism, UK) operated at 2,000 rpm. The mixture was transferred to an extruder. Extrusion was carried out either on a twin-screw extruder "Megacompounder ZSK 25" (Werner & Pfleiderer, Germany) operated at 90/100/90°C and a speed of 180 rpm or on a Buss PLK 46 co-kneader (Buss AG, Switzerland) operated at 100/120°C at a speed of 100 rpm. The hot extrudate was allowed to cool down, crushed to small, brittle chips, and ground to a mean particle size of approximately 35 µm in an ACM-II air separation ball mill (Hosokawa Micropul, Germany).

Application, Curing, and Testing

Powder coatings were applied on 0.8 mm aluminum panels (yellow chromated Bonder-panels) using a corona gun (Wagner, Germany) operated at 80 kV. The coatings were cured 10 min at 200°C (objective temperature) in an electrical oven; the film thickness was adjusted to 50-60 µm.

Mechanical testings such as Erichsen indentation and reverse impact resistance, as well as chemical resistance versus acetone were checked one day after curing. Gloss was determined with a Micro-TRI-gloss detector (BYK-Gardner, Germany).

Additionally, the topography of the coatings discussed was analyzed by using a "Perthen S 8 P" perthometer (Mahr Perten, Germany or Mahr Corp., Cincinnatti, OH) and a "D 3100 Multimode" atomic force microscope (Digital Instruments, USA). The perthometer records the surface structure by using a non-contact laser technique according to DIN EN 4287.

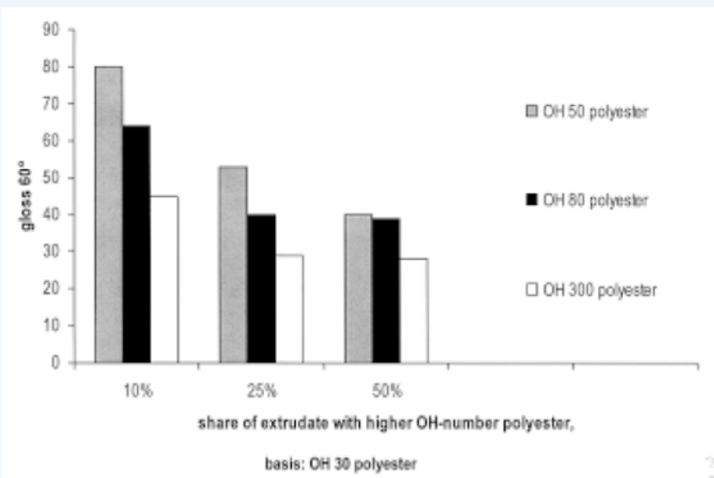

Figure 2—Differences in the OH-number and the mixing ratio of both powder systems are main factors to determine the gloss level in the dry blend process. For example, with a 25% share of an extrudate based on OH 50-polyester the gloss is approx. 55%, whereas a 25% share of an extrudate based on OH 300-polyester yields a gloss of approx. 30%.

DISCUSSION

Dry Blend Process with Polyesters of Different Hydroxyl Numbers

In the dry blend process, mixed polymer systems are used which crosslink at different speeds. The wider the difference in reactivity of the two systems, the lower the gloss level. During baking, the more reactive powder coating particles crosslink first although they are unable to coalesce properly. They form a network which partially protrudes above the melted coating. Later in the baking process, the less reactive particles crosslink. They polymerize and shrink on the network already formed. The protrusions form a surface structure which is responsible for the gloss reduction.

In the investigations described, hydroxyl-bearing polyesters are crosslinked with a non-emissive polyuretdione hardener[5-7] (*Figure* 1). This hardener contains no blocking agent, and has a particularly low melt viscosity. By combination with suitable polyesters with different hydroxyl numbers using the dry blend process, matte coatings with good mechanical properties and excellent leveling are produced.

In the first test series, the extrudate based on a polyester with a low hydroxyl number of 30 and the polyuretdione crosslinker is mixed before milling with a second extrudate based on a polyester with a higher hydroxyl number and the same hardener. Both the mixing ratio of the two extrudates and the difference in the hydroxyl numbers of the polyesters used have a significant influence on the gloss. *Figure* 2 shows that the higher the difference in the hydroxyl numbers of the polyesters in the two extrudates, the lower the achievable gloss. A polyester combination with hydroxyl numbers of 30 and 80, for example, yields a gloss of 40%, whereas a combination with hydroxyl numbers of 30 and 300 reduces the gloss to 30% if a 1:1 mixture of both components is chosen.

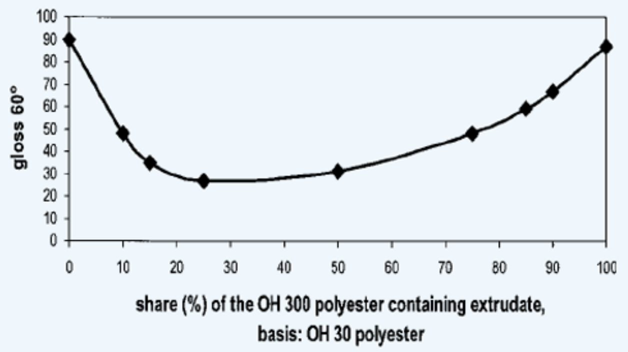

Figure 3—A dry blend mixture of 25% extrudate based on OH 300-polyester and 75% extrudate based on OH 30-polyester yields a minimum gloss of 30% in this system.

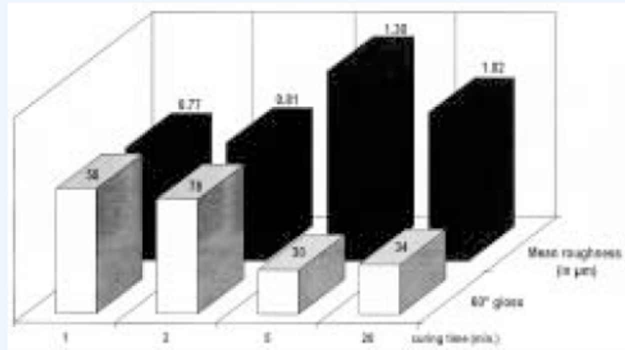

Figure 4—In a dry blend system, based on polyuretdione crosslinker/OH-polyester, the final gloss level is formed during the whole curing period. Mean roughness corresponds in an acceptable way.

Influence of OH 300 Polyester on Coating Properties

We examined the influence on the powder coating properties by increasing the content of the extrudate with the OH 300 polyester. The reactivities of such powders increase with the content of OH 300 polyester as this resin provides more reaction centers for the uretdione hardener. The 60° gloss passes a minimum at a mixing ratio of approx. 1:3, i.e., 25% extrudate with the OH 300 polyester (*Figure* 3). A higher content of the more reactive component increases the gloss again. Thus, on one hand, the maximum possible difference in the hydroxyl numbers and the reactivity of the two powder coatings, which are mixed together, results in a low-gloss value. On the other hand, the system must have enough time to form the two-phase polymer structure during baking, which is responsible for the matting effect.

After baking under the selected conditions, all of the systems display good resistance to acetone. With increasing content of the OH 300 polyester and the resulting higher crosslinking density of the polymer network, there is a trend towards a further improved chemical resistance. The Erichsen indentation after crosslinking under the selected baking conditions is 7 to 9 mm. The values yielded by the reverse impact test are between 20 and 80 in.-lb, depending on the polyester used. They can be optimized, if necessary, by specific catalysis.

Investigations of the Surface Structure during Baking

It was of special interest to determine how the surface structure of a matte powder coating changes during baking and at what point the matte effect produced in the case of the dry-blended powder coating is completed.

Therefore, the topography of a matte powder coating produced by the dry blend process was examined under the perthometer after different baking times. This is a non-contact test method in which the surface of the coating is scanned with a laser and the roughness profile recorded.

- After one minute, an orange peel structure with a depth in the millimeter range becomes apparent. In contrast, the microroughness of the surface is only slight and the gloss of the coating is correspondingly high.
- After two minutes, the surface in the millimeter range is less irregular. The 60° gloss is still very high. Crosslinking has largely not yet occurred, as shown by the low Erichsen indentation values.
- After five minutes, the micro-roughness has more than doubled and the gloss has decreased considerably. The reaction between the binder and hardener produces a significant increase in the microroughness, thus yielding the desired gloss reduction.
- After 20 min, the surface has become somewhat smoother again, and the gloss has increased slightly.

Figure 4 shows the values for the mean roughness measured with the perthometer and the gloss as a function of the baking time. The gloss reduction during the curing reaction and the associated increase in roughness can be seen clearly.

One-Shot Matte Formulations

Both the manufacture and the application of a matte powder coating are easier and less expensive if all the raw materials can be mixed and extruded together. Further processing yields a homogeneous powder in which two poly-

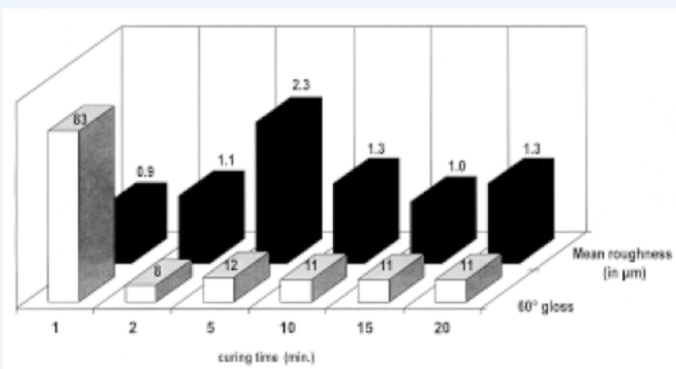

Figure 5—The one-shot system on the basis of a polyuretdione crosslinker and two OH-polyesters of different OH-numbers yields gloss levels of approx. 10%. The final gloss is formed quite quickly. Mean roughness does not correlate very well presumably due to leveling effects.

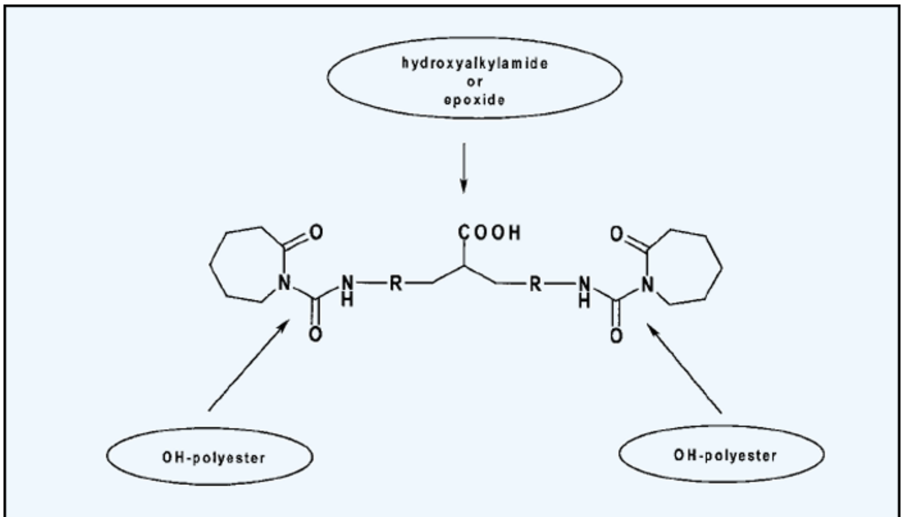

Figure 6—Bifunctional matte hardener is a blocked polyurethane with an additional carboxyl group. The crosslinking takes place by the reaction of isocyanate with OH-polyester and a parallel reaction of the carboxyl-group with an epoxide or hydroxialkylamide.

mer systems of widely differing reactivity are finely distributed.

Even when using a one-shot process, two hydroxyl-bearing polyesters can be combined with a uretdione crosslinker to produce a powder coating of outstanding quality with 60° gloss of 10 to 15%. The ratio of the two polyesters is around 5:1. In our example, an OH 30 polyester is used with an OH 300 polyester to ensure an adequate difference in reactivity, because the gloss value is again depending on the difference of OH numbers of the polyesters used as described previously.

The coating yielded has excellent flow, very good mechanical properties, and good resistance to acetone.

Again, the degree of matting as a function of curing time was examined (*Figure* 5). Surprisingly, the final gloss level is reached after two minutes and is nearly constant for the rest of the curing time. The microroughness in this example does not correlate very well to the gloss values. It can be supposed that beside the formation of microstructure, the leveling has an impact on the roughness.

Our investigations show that the one-shot technique described allows the quantities of raw materials to be varied in a very narrow range so as to achieve an adequate degree of matting. If one of the polyesters is too dominant in the formulation, there is a significant increase in the gloss. Additionally, the processing conditions have to be kept precisely in order to obtain reproducible results.

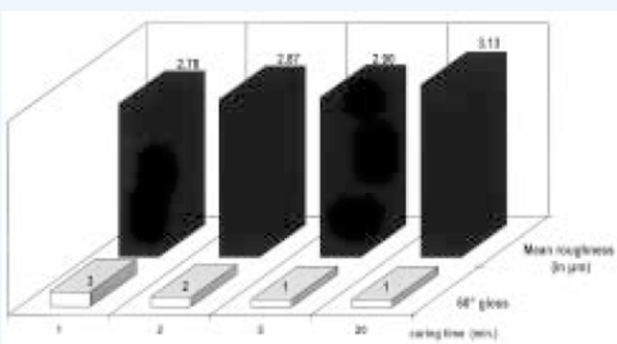

Figure 7—Bifunctional matte hardener yields coatings with a comparatively high mean roughness and a very low gloss. This gloss level is reached immediately after the start of curing.

Crosslinkers with Two Different Functional Groups

This section describes an unusual hardener which, because of the two different functionalities in the molecule—an isocyanate and a carboxyl function—allows two parallel curing reactions (*Figure* 6). A hydroxyl-bearing polyester is again used as the co-reactant for the ε-caprolactam blocked NCO groups and hydroxyalkyl amide or epoxy functional crosslinkers as the co-reactant for the carboxyl groups. The choice of the OH-polyester—normal durable or super durable, lower or higher OH-number—has a strong impact on the coating properties, but not so much on the gloss level of the coating.

The degree of matting is, therefore, virtually unaffected by the baking time and, as was found, by the baking temperature. This robustness is a key advantage of this powder coating system.

Immediately after the start of the curing, a very low gloss is apparent. The microroughness in this system is nearly unaffected by the curing time. Compared with the matte coatings described previously, the level of roughness is significantly higher, fully in accordance with the extremely low gloss (*Figure 7*).

If the surface structure of the coating is observed during baking using the electron microscope, chain-like polymer structures with a width of approximately 5-10 µm become apparent after baking for one minute at 180°C. These become more pronounced as baking progresses and cover the surface of the coating like a network. Nevertheless, after just one minute, the surface is dull and matte. In terms of the measurable gloss, this does not change with the progression of the baking process.

Applications for the Matte Hardener

The formulation described is largely unaffected by the conditions which prevail during the manufacture and application of powder coatings. Very similar properties are achieved if epoxies are used instead of hydroxyalkyl amide as the co-reactants for the carboxyl group. Many conventional hydroxyl-bearing polyester resins are suitable as the binder component for reaction with the isocyanate groups. The leveling, the mechanical properties, as well as the chemical resistance of the coating, are excellent.

Nevertheless, in industrial applications a slightly higher gloss level is usually required. If the bifunctional matte hardener is combined in various ratios with blocking agent free uretdione crosslinkers, the variation of gloss between 1 and 85% is easily possible (*Fig-*

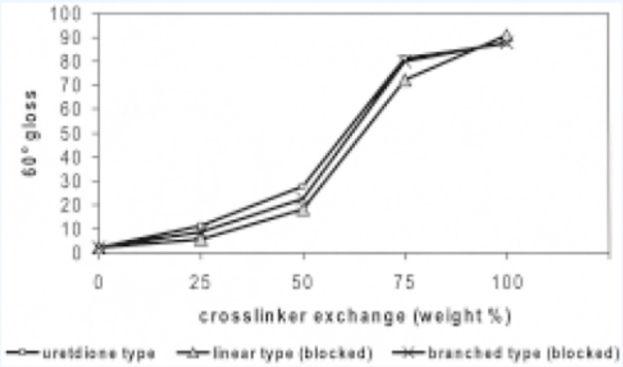

Figure 8—Very low gloss of a powder coating system based on the bifunctional matte hardener can be adjusted to any desired gloss level by using a crosslinker mixture with a polyuretdione or a blocked polyurethane hardener.

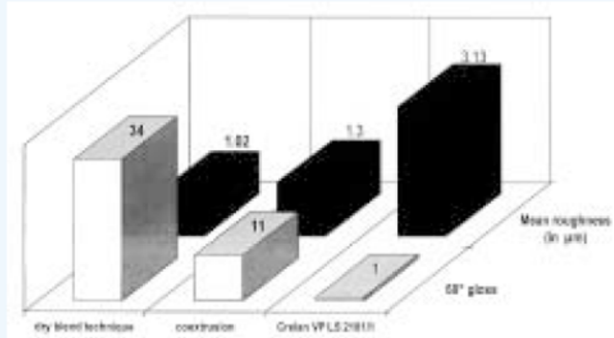

Figure 9—Minimal gloss levels achievable using the different matting techniques are plotted. The values are fully in accordance with the mean roughness of the coatings.

ure 8). The gloss can also be varied as required by combining the matte crosslinker with blocked PUR hardeners. The gloss curves obtained with these combinations are at a slightly lower level. In these cases, the recipes have to be modified to ensure stoichiometric ratios between the polyester resin and both crosslinkers.

Correlation Between Surface Roughness and Gloss

Figure 9 plots the roughness values against the 60° gloss values. There are clear differences between the matte powder coatings manufactured by the various processes. The reciprocal relationship between surface roughness and gloss can be seen clearly. It can be pointed out that the minimum gloss value achievable by the alternative methods is dependent on the homogenity of the two different systems. In the case of dry-blend technique, different solid particles of approx. 35 µm in diameter are mixed. The achievable gloss level by using this technique is only 20-30%. The dispersion in the one-shot process is significantly higher; the raw materials form a nearly homogeneous mixture if the extrusion process is optimized. In this case, 10-15% gloss is easily achievable. Using the bifunctional matte crosslinker, the different functional groups definitely appear in the same ratio in every molecule. The dispersions with regard to the two different reactions are nearly perfect. Here the gloss level is by far the lowest. One to three percent gloss is easily achievable. The option of increasing the very low-gloss level to any required value by using an individual mixture of the bifunctional hardener and a blocked or blocking agent free PUR crosslinker is a key advantage of this system.

SUMMARY

Matte films with gloss values of around 30% can be obtained by combining two powder coatings, each consisting of a hydroxyl-bearing polyester and a polyuretdione hardener. Matting is dependent on a significant difference in the reactivity of the two hydroxyl-bearing polyesters with the polyisocyanate hardener.

Low-gloss coatings can also be produced by coextruding powder coating raw materials based on two polymer systems with very different reactivity. This one-shot process of matte polyurethane powder coatings offers technical and economical advantages for the manufacturer.

The most elegant method of producing dull matte coatings with gloss values significantly lower than 10% is to coextrude a bifunctional matte poly-urethane hardener with a hydroxyl-bearing polyester and hydroxyalkyl amide or epoxy. This crosslinker contains blocked isocyanate and carboxyl functions in one molecule. Through careful formulation, any gloss value can be yielded reproducibly. The powder coatings are extremely robust during manufacture and application.

References

(1) Brand, D., *Proc. DFO Congress on Powder Coating Applications*, in Boppard, Germany, 107 (1998).
(2) Loar, D.F. and Verlé, F., *Welt der Farben*, 13 (1995).
(3) Schülde, F., *DEFAZET*, 33, 46 (1979).
(4) Meyer, F.V., Dhein, F., Rudolph, H., and Kreuder, H-J., *Farbe & Lack*, 91, 1118 (1985).
(5) Thometzek, P., Basten, H., Köhler, K., and Meier-Westhues, H.-U., *Farbe & Lack*, 104, 22 (1998).
(6) Meier-Westhues, H.-U., Thometzek, P., and Laas, H.-J., *Farbe & Lack*, 103, 140 (1997).
(7) Freudenberg, U., Meier-Westhues, U., and Laas, H.-J., *Eur. Coat. J.*, 9, 804 (1997).