Latest Investigations in Formulation and Processing

of Pigmented UV-coatings

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Introduction

The technology of Radiation Curing is well established in the field of clearcoats. This technology is unique due to the combination of features like curing within a fraction of a second, the possibility to formulate coatings without any organic solvent and the outstanding quality of these coatings. Nonetheless, in order to enter into further market segments some restrictions have to be overcome. One major challenge is the UV-curing of pigmented coatings. Raw material supplier, coating producer and the end-user are working together intensively to extend the UV- technology also in the field of coloured UV- coatings.
In this paper an overview is given about several ideas how to produce pigmented, UV-polymerised films with good through curing properties and an excellent hiding power at the same time. The presentation touches the right choice of pigments on the one side but also discuses different ways in processing of a pigmented UV-coating.

UV- Monocure

In principle UV coatings are formulated by combining an unsaturated binder with reactive diluents and a photoinitiator. The exposure to UV- light cleaves the photoinitiator into radicals, which start the radical polymerisation.
The ideal way to cure coloured UV- coatings would be to find pigments, which are absorbing the visible light (400 nm – 700 nm) thus providing a good hiding power. At the same time the coating should be transparent for the UV- light in order to initiate the polymerisation at the bottom of the film. In this case the curing mechanism of radical polymerisation induced by UV-light would be sufficient to transfer the liquid coating to a solid film.

Unfortunately many pigments exhibit an insufficient transparency in the UV- region. Thus not enough photons are able to reach deeper layers of the film. In consequence the rate of radical formation is to low. The result is a film, which is polymerised at the surface but not at the bottom.

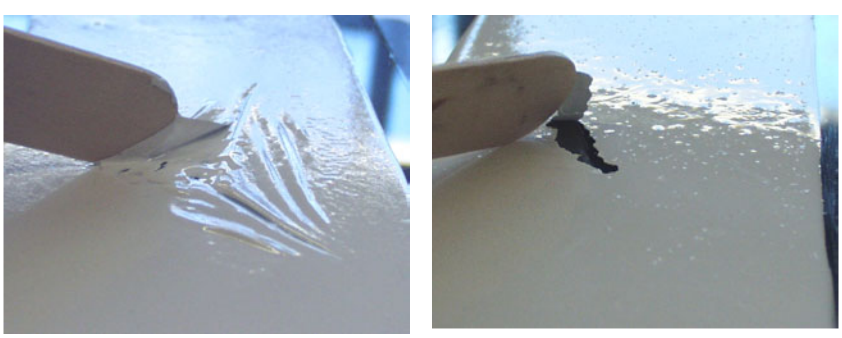

Fig.1: White pigmented UV Coating with bad and good through curing properties

For white pigmented UV- coatings a solution for this problem could be found by developing the class of acylphosphine oxides as photoinitiators by BASF- AG in the 70th. Acylphosphine oxides absorbs UV- light between 380 – 410 nm. In this range titanium dioxide is transparent, which enables the photons to reach the photoinitiator at the bottom of the film. Especially the anatas modification of titanium dioxide is suitable for UV- curing systems. Thus white pigmented UV coatings can be formulated with good hiding power and satisfying through curing properties.

Unfortunately the majority of coloured pigments don't exhibit this desired transparency in the relevant UV- area. The competition between pigments and the photoinitiators for the UV- light very often leads to insufficient through curing properties. The result can be a coating, which polymerises at the surface but not at the bottom.

In order to achieve optimal curing properties the photoinitiator has to be chosen accurately. Fig. 2 shows the transmission of a coating based on a polyether acrylate containing different photoinitiators.

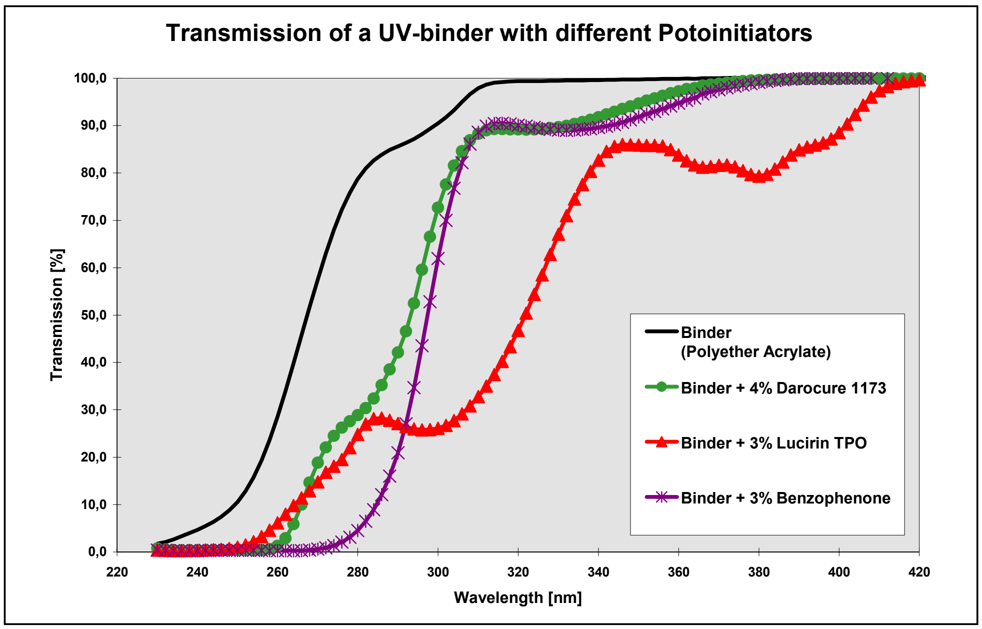

Fig.2: Transmission of a coating based on a polyether acrylate containing different photoinitiators

Due to the absorbance of Acylphosphin oxides (Lucirin® TPO) in the field of 380 – 410 nm the use of such acylphosphine oxides increases the usable UV- wavelength area and leads to improved through curing properties. Since the binder itself absorbs almost all energy below 300 nm short wavelength absorbing photoinitiators act in particular at the surface of the film. Acylphosphin oxides are the preferred initiators to cure pigmented UV- coatings due to their absorption characteristic.

The absorption spectra of some pigments can explain some basic curing properties:

Red: Relatively high transmission between 380 – 420 nm but a high concentration of pigment is necessary in order to achieve a good hiding power. As a consequence the UV- absorption is increased and the coatings are difficult to cure.

Blue: Blue pigments are characterized by a high transmission in the relevant UV-area and high hiding power. Thus relatively good curing properties can be achieved.

Yellow: Yellow pigments have a low transmission level in the UV- area. Additionally these pigments have a poor hiding power. Through curing properties are usually poor.

Green: The green pigments have the lowest transmission level. Thus green pigmented UV-coatings with a good hiding power are hardly curable.

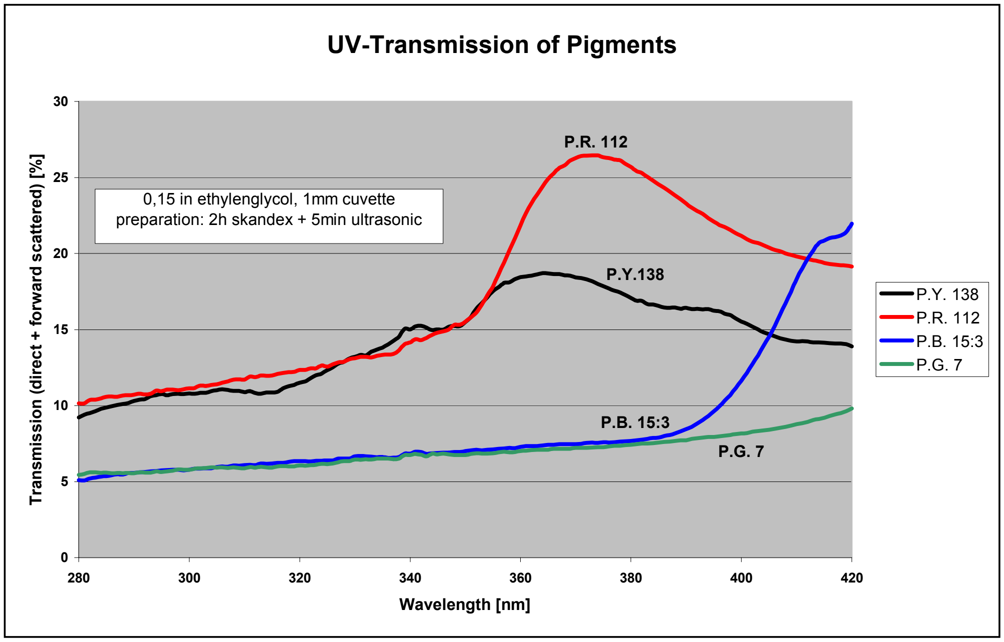

Fig.3: Absorption spectra of some pigments

So far the absorption spectra of a pigment doesn't allow an exact forecast concerning the curing properties of an UV- coating since the hiding power of the film has to be considered. Consequently the pigment concentration plays an important role. In our trials the maximum concentration of a pigment which allows a satisfying curing of the film in a thickness of 30µm was determined. Therefore the pigmented UV coatings have been formulated with increasing pigment concentrations. These coatings were applied on a substrate (aluminum + adhesion primer) in a thickness of 30 µm and the adhesion after the curing was measured by cross cut. The maximum pigment concentration, which can be used in order to achieve a good adhering coating, was determined. The adhesion was taken as a measurement for the through curing properties.

These coatings - with the maximum pigment concentration - were applied on a black and a white substrate for 4 times on the top of each other layer. After each application delta E between both films (white resp. black surface) was measured. The results confirm the practical experience. Green and yellow pigments are much more difficult to cure with a satisfying hiding power compared to blue or white pigmented UV- coatings.

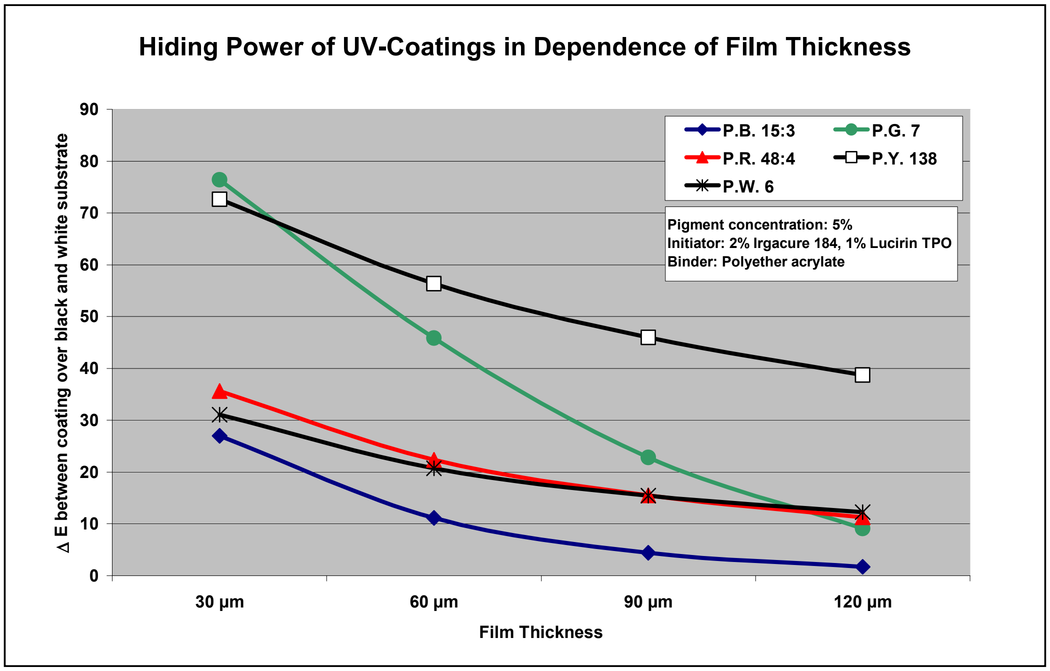

Fig.4: Hiding Power of pigmented UV Coatings

In order to achieve a certain color shade several combinations of pigments can be used. On the example of blue pigments a method was developed, which allows the determination of the most suitable pigment.

Therefore the pigmented UV- coatings were applied on a black and a white substrate in a film thickness of 30 µm. The pigment concentration, which led to a $\Delta E = 5$ between both films was determined in order to have a comparable hiding power.

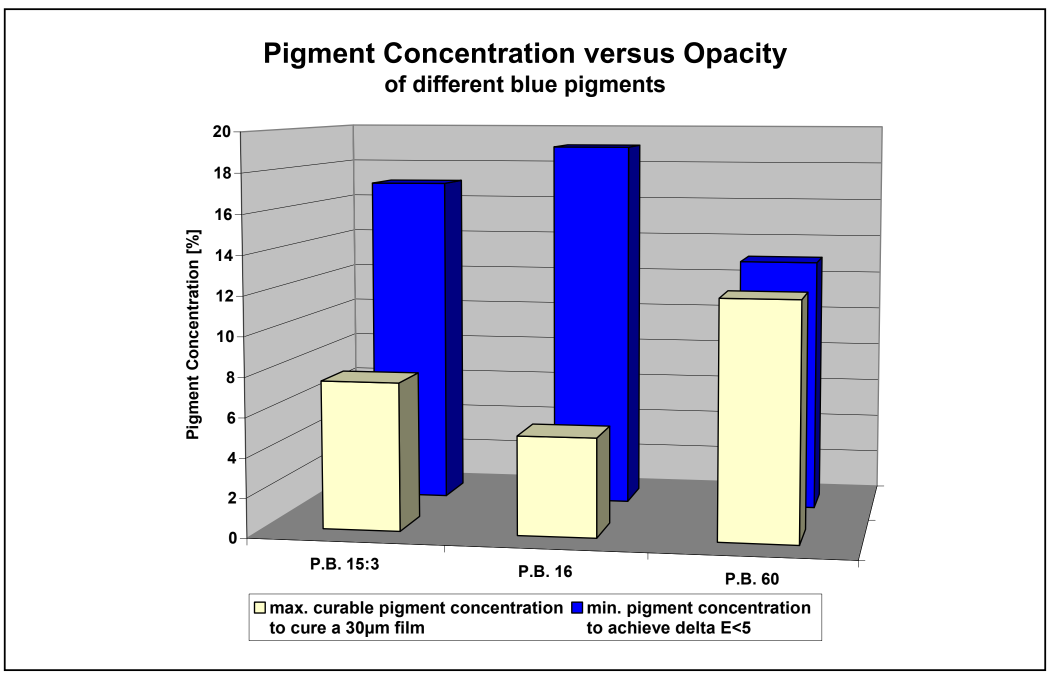

Fig.5: Pigment Concentration for hiding coating (with $\Delta E=5$) / max. curable pigment concentration

Only the P.B. 60, which is a Indantrone blue pigment, exhibits comparable values for both, the max. pigment concentration and the concentration leading to $\Delta E=5$. For the P.B. 16 as well as for the P.B. 15:3, which are phalocyanine resp. Cu- phalocyanine pigments, the maximum curable pigment concentration is below the concentration, which is necessary to achieve good hiding power. Therefore the Indantrone P.B. 60 pigment would be preferred in UV- coatings.

The UV- energy emitted by the UV- lamps has to match to the absorbance of the photoinitiator. Compared to a conventional mercury lamp, gallium- and iron doped mercury lamps emit UV- energy in a longer wavelength region. Thus these lamps lead to improved through curing properties in combination with Lucirin® TPO.

UV- lamps emitting only UV-A and UV-V are also available as so called "sun- tanning lamps". Unfortunately these lamps can't induce the polymerisation of an UV- coating under conventional circumstances due to the strong oxygen inhibition. Under inert atmosphere - and thus in the absence of oxygen - such lamps are useful to cure UV coatings. The UV-A lamp used in the following trial was a Philips HB 406- sun tanning lamp with a total power of 400 W. In order to reduce the oxygen inhibition the coatings have been cured in an atmosphere of carbon dioxide. This process – Curing of UV- Coatings under an atmosphere of carbon dioxide - is patented by BASF- AG under the name Larolux™.

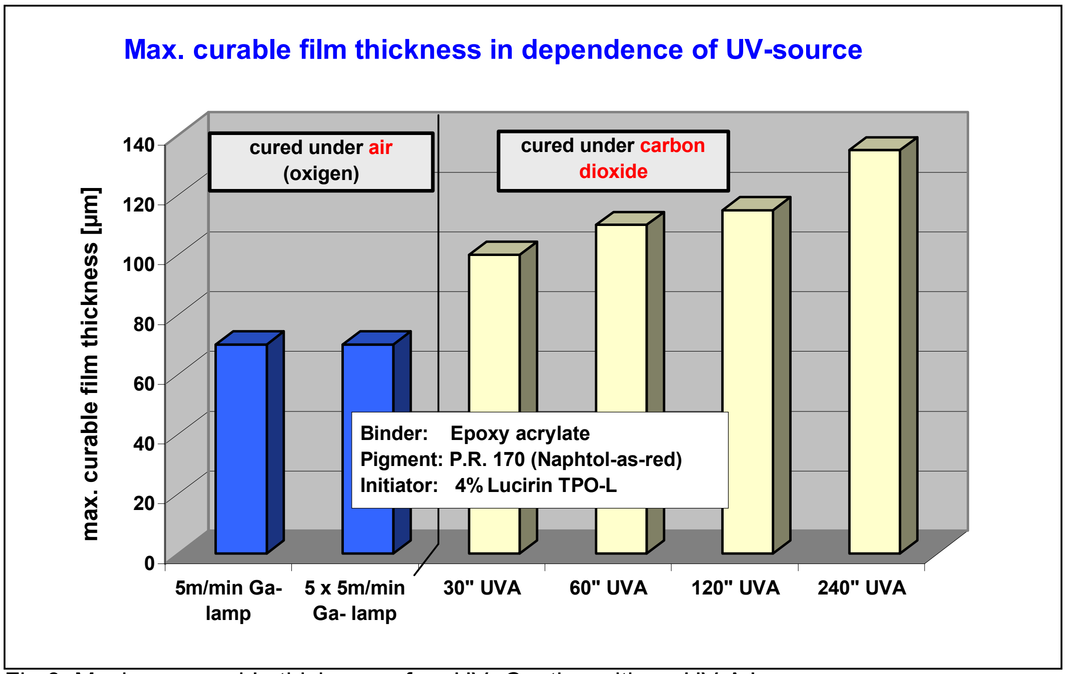

Fig.6: Maximum curable thickness of an UV- Coating with an UV-A lamp

A significant increase in maximum curable thickness of the used coating could be observed by using this UV- A lamps. The curable thickness of the coating cured with a conventional mercury lamp led to a maximum of ca. 70 µm. With the UV-A lamp significant higher curable film-thickness could be measured. Probably this is due to the higher penetration of UV-A light into the film.

UV- Dual Cure

An other approach to cure pigmented UV- coatings is to combine the UV- technology with a second curing mechanism. Especially the formulation of Dual Cure systems where the photo initiated radical polymerisation is combined with a polyaddition reaction can offer a solution. The idea is to combine OH- functional acrylic esters with polyisocyanates where the UV-curing leads to a very rapid curing at the surface whereas the reaction between OH groups of the UV-binder with polyisocyanate leads to a lower crosslinked but solid film at the bottom.

Since the polyaddition reaction is not as fast as UV- polymerisation the full performance of those films can be achieved only after some hours or days. Nevertheless, dependent on the processing parameter (temperature, film thickness, ratio between functional groups,…), such coatings can be handled directly after the UV- exposure but might have a rather short pot life.

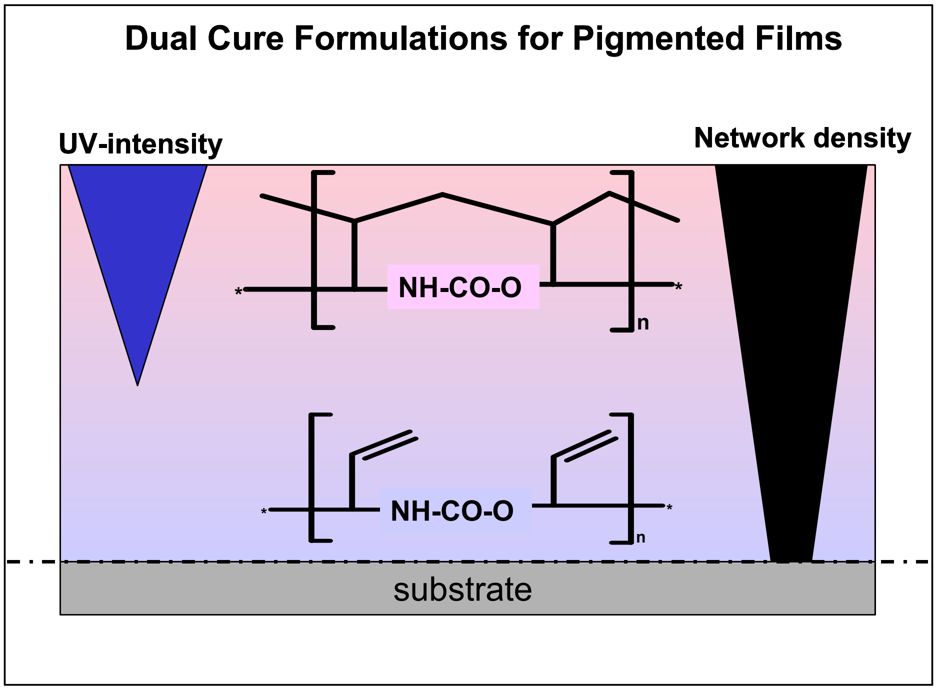

Fig.7: Functioning of an UV- Dual Cure Coating

Both functionalities – unsaturated acrylic group and the NCO group - can be combined in one molecule. This allows the formulation of Dual Cure coatings where the UV / NCO binder can be combined with Polyols in order to formulate PUR coatings with the benefit of polymerising the surface of the film using UV- light.

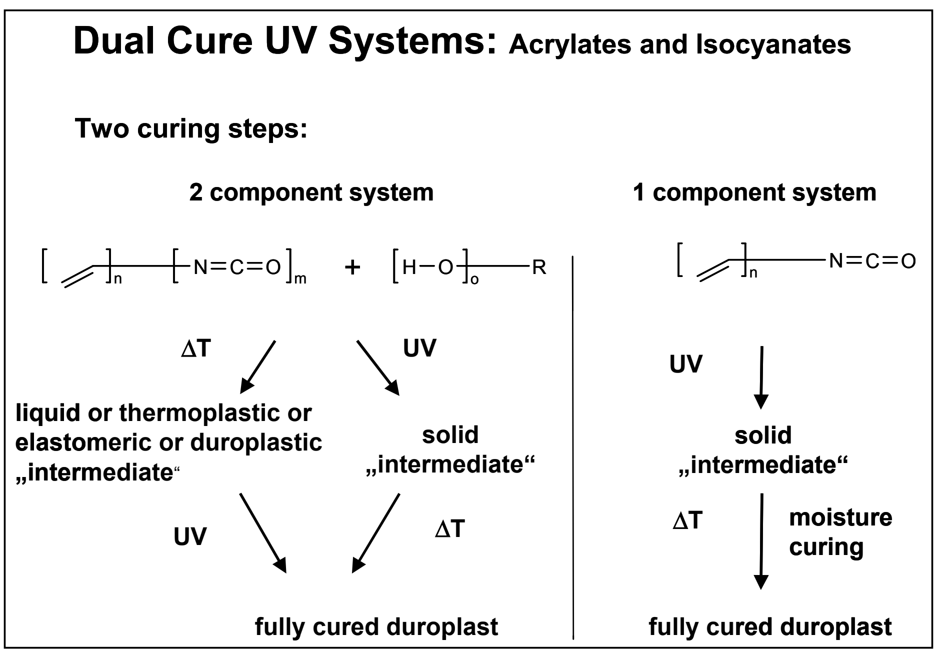

Fig.8: UV- Dual Cure, curing steps

As mentioned above Dual Cure means the combination of two independent curing mechanisms. Thus not only the combination of polymerisation and polyaddition can be considered by formulating dual cure coatings. The combination of physical drying and UV curing is a second approach. Therefore UV- dispersions can be used together with pigments. The photo-induced polymerisation of such coatings will generate a gradient of double bond conversion. At the surface of the coating the sum of physical drying and UV-curing will lead to a high resistance. Although in deeper layers the radical polymerisation is minimized good adhesion is provided due to the physical drying.

Conclusion

In this paper an overview about different approaches to come to full hiding, coloured UV-coatings is presented.

The most convenient way would be to work with an UV- Monocure system where the pigment is able to absorb the visible light (responsible for full hiding power) but not the relevant UV-light (good curing properties). In order to optimise the utilization of pigments in UV-coatings, BASF AG started a project where pigments are being investigated concerning their behaviour in UV-coatings. The target is to offer a solution to formulate pigmented UV- coatings with both, an optimal hiding power and satisfying through curing properties.

By using the UV Monocure technology it isn't possible to formulate every colour shade with a full hiding power and excellent through curing properties at the same time. For these cases the Dual Cure approach has been developed. The combination of radiation curing and a second curing mechanism will generate new applications and higher market shares for UV coatings in the future.