Into the third dimension

Three ways to apply UV coating technology to 3-D automotive objects.
Erich Beck.

UV curing of coatings is efficient, but it has largely been limited to flat substrates such as wood panels and paper, where a homogeneous light intensity can be assured. However, there are several ways today in which 3-D objects can be coated with UV curing systems which meet automotive industry needs. These include the use of carbon dioxide inerting, dual cure coatings and pre-coated thermally formable films.

UV curing allows a liquid to be cured instantly into a hard material. Applications - mainly coatings on wood, paper and some plastics - classically run on flat lines for high volume production, using no or low amounts of volatile diluents and curing at ambient temperatures. This results in a highly efficient technology with low process and investment costs. This has been confirmed in an eco-efficiency analysis on the industrial coating of doors [1]. The UV coating resin market shows one of the highest growth rates in the coatings field, at about 9% per year.

UV curing still has significant limitations

Despite its benefits, the market penetration of UV coatings is less than 5% of the industrial coatings market. To achieve growth in different applications, improvements are necessary, mainly in the UV curing of surfaces of 3-D objects, of pigmented coatings and of short production runs. The development of UV curable clear coatings with improved scratch resistance has been a key focus in recent years, particularly for the automotive industry. Current UV applications on vehicles are mainly the coating of plastic parts such as lenses and reflector houses for headlamps, exterior and interior parts, wheel covers, acrylic tail lights, housings for fuel injection pumps, primers for SMC body parts and refinish coatings.

Carbon dioxide inerting

A UV curing process has recently been developed [2] which demonstrates improved potential for curing the coated surfaces of 3-D objects. This uses a carbon dioxide atmosphere to improve the surface cure. (In air, a process known as ‘oxygen inhibition’ reduces the conversion of the reactive double bonds at the surface.) It also broadens the conversions for formulations and decreases for radically induced curing, providing broader application parameters and improved coating performance.

Lower light intensity and cheaper UV sources required

Carbon dioxide has a density about 1.5 times higher than nitrogen or air and can be filled into a container to provide an oxygen-reduced atmosphere. The container (see Figure 1) significantly reduces oxygen effects and improves surface curing.

Coated 3-D objects can also be cured at greater distances from lamp to substrate or even by radiation reflected from the aluminium surfaces of the container into shadow regions. These highly efficient conditions can use lower light intensities and therefore also cheaper UV lamps.

The first example of a continuously running pilot plant was at Rippert GmbH in Germany. A simulation tool is used to optimise the operation by calculating the oxygen level as a function of the geometry of the inert gas facility, the location and power of the heat source, the location of the inert gas inlet and its flow and the movement and size of the object.

Based on simulations with this tool, the construction of a curing facility for a high volume series production for chairs was recently presented by Tikkurila and BASF AG [3].

Dual cure systems

High quality clear coatings for the plastic parts of vehicles are based on two-component polysisocyanate/polyalcohol chemistry (2K PU). This chemistry is also used on metal parts of the car body [4], usually applied over coloured basecoats.

A starting point for the development of UV curable clearcoats for vehicles was the demand for increased scratch resistance, as well as the benefits of efficient curing. Because of problems with UV curing on 3-D substrates in air, most developments started with coating systems that used 'dual cure' coatings - UV combined with thermal curing for the shadow regions. Figure 2 shows that the network structure of polyurethanes may be built up from different raw materials and curing technologies. These include classical two pack isocyanate/polyol systems, a UV monourethane route with urethane acrylates or different options combining isocyanate/alcohol and acrylic ester crosslinking chemistry in a dual cure form.

Increased thermal reactivity

As the acrylate groups do not react in shadow areas, acrylate compounds without thermally reactive groups cannot be bound into the film and may cause migration problems. In an ideal case, therefore, all the acrylate compounds also bear thermally reactive isocyanate or hydroxyl groups on each molecule. Following this reasoning, an aliphatic isocyanate-functional acrylate [5] was developed with a low viscosity of 1200 mPAs which meets the OECD definition for polymers (see Figure 3).

Coatings for plastics: Thermal curing at 80°C

Some of the important requirements for UV coatings for plastic parts of automobiles are to match the properties of conventional coatings in terms of weathering and chemical resistances, adhesion, elasticity, gloss etc. Compared to coatings on metal, the curing temperatures used for plastics are lower due to their lower thermal stability. A typical maximum temperature is 80°C. Additionally, UV coatings should show advantages such as a higher scratch resistance and an economic curing process, and especially a shorter curing time.

In the development of a coating for the “Smart” car, the curing of a dual cure coating containing the above isocyanato acrylate, a polyol and 40% of a volatile solvent was investigated with real time infrared spectroscopy (RTIR) [5]. In an optimised formulation the decrease of isocyanate groups and the conversion of double bonds versus reaction time were recorded. At 80°C the thermal curing reaction and drying were complete after 10 minutes. After that, the UV curing step lasted 30 seconds, and curing then continued in a carbon dioxide atmosphere (see Figure 4).

100% UV automotive coatings without solvent are still an ambitious goal

The curing conditions of a typical conventional two-pack PU coating for automotive plastics are heating at 80°C for 40 minutes after allowing seven minutes for degassing and levelling (see Table 1). The dual cure coating (DC) saves 30 minutes heating time but needs the short UV curing step.

In an ideal case, mono cure coatings (MC) do not need a
heating step if they are applied without solvent. This is an ambitious goal for further development. Currently solvent is still necessary to meet automotive requirements. Fortunately, for both types of UV coatings the solvent content is reduced to about 30% compared to the conventional 2K PU coating with 50% solvent.

The conditions for the UV curing in carbon dioxide atmosphere allow curing of the surfaces at a greater distance. Consequently, a wide range of 3-D objects may be coated. Mono cure coatings are preferred, since they are single-pack systems and can be recycled. The amount of coating required is lower and even their disposal cost is lower.

**Good mechanical and chemical performances are confirmed**

Scratch resistance, chemical resistance and impact behaviour are considered very important properties. The scratch test method used is the "Amtec Kistler" test [6] which simulates car washing. Scratches on the surface are measured in terms of gloss reduction. In the test, storing at 80°C for 2 hours should simulate conditions for reflow. The results in Figure 5 demonstrate significant reflow with the current polyurethane coating, while both UV coatings show a high level of scratch resistance without the need for reflow.

Chemical resistance is checked with a test method specified by Daimler Chrysler [7]. Water based solutions of sulphuric acid, sodium hydroxide, pancreatin, tree resin and pure water are applied to coated test panels, which were heated for 30 minutes on a gradient oven at temperatures between 30°C and 80°C.

The degree of resistance is determined by eye after removing the solutions. Figure 5 shows the temperatures at which the chemicals start to etch the coating. All systems provided good quality.

A special test for plastic coatings is the impact test [8]. A bolt impacts an original plastic substrate coated with all layers - in this case basecoat and clearcoat on a polycarbonate blended with polybutylene terephthalate (PC-PBT). The maximum force \( F_{\text{break}} \) and height of deformation \( h_{\text{break}} \) at the point of break are measured. The force value of 6000 N or the \( h_{\text{break}} \) of 12mm, which is met by all coatings, meets the requirements for bumpers, for example.

Both types of UV coatings are mainly suitable for general requirements of plastic coatings for vehicles (and also in terms of their weathering, adhesion etc, which are not presented in detail here). A choice between a mono cure coating and the two-component dual cure coating will depend mainly on the structure of the substrate in relation to sufficient illumination and cure. The inert gas UV curing process in carbon dioxide helps to reduce the number of critical object geometries.

**Formable foils - a novel, versatile finishing technology**

Paint shops working with liquid coatings need special and costly equipment to obtain high quality surfaces under environmentally friendly conditions. The different parts of a car body are produced and coated in different factories, not all under the same conditions. Therefore, slight differences in colour effects between the different parts are likely.

**No need for a paint shop at the OEM**

These factors provide a reason to develop dry film technologies, where a uniformly coloured film is produced and different parts suppliers will be able to apply the film under much simpler and less critical conditions without the need for a paint shop. This is an important step towards a modular production concept for cars at different locations. The foil carries conventional colour effects, based for example on a base coat/clear coat concept. All the layers are solid, so to produce a storage-stable film, but are thermoplastic or elastomeric so as to be formable under heat or at room temperature.

After the film forming step, the surface of the composite is cured by UV radiation. Even here, inert conditions as mentioned above improve the quality of the surface and are especially helpful for 3-D objects. Oxygen inhibition can be avoided by the use of a protective transparent film on top of the clearcoat. This may have several functions: as a carrier foil, as protection during storage, during film forming, against oxygen ingress and during transport of the finished part.

The foils may be applied after forming and UV curing of back moulding [9] or back foaming processes. Below the basecoat, a foil carrier layer is used which comes in contact with the material prepared for moulding or foaming. Foils can also be made with an adhesive layer for direct laminating to different substrates. These are only a few examples of potential application scenarios. The simplest one should also be mentioned: a single layer foil, colourless or coloured, to improve the general resistance of surfaces.

The materials for the UV curable layer, especially for automotive applications, are the same as those already mentioned: urethane acrylate chemistry either as mono cure or dual cure systems.

In the case of a mono cure system, a solid urethane acrylate, dissolved in a solvent or water, is coated onto a basecoat film applied on a transfer foil. The material of the transfer foil is the intermediate layer between basecoat and the injection mould material. After drying and optionally laminating with a protective foil (Figure 6) the film can be stored. The film is formed via a deep drawing step into a mould with the help of heat and vacuum. After cooling, the separated 3-D foil will be UV cured. Then the injection moulding process follows to build up a more stable plastic part.

**Dual cure systems on foils**

Dual cure systems open up different perspectives (Figure 7). The two pack resin system may be solid or liquid and low in viscosity to save volatile solvents. Both components will react and become solidified or gelled. A slightly crosslinked film provides an elastomeric character, which can easily be deformed at room temperature even by hand and be laminated directly to a substrate.

To obtain similar elastomeric properties for the basecoat, it is useful to take a dual cure formulation similar to that of the clearcoat, but completed by the colouring pigments. Optionally, an adhesive layer on the foil base coat or on the object is possible. As already described, the transfer foil can also be used as an oxygen barrier. Examples are polyolefin foils, which show deformable behaviour at room temperature and are removable after UV curing.

An example of a dual cure formulation forming an elastomeric UV curable film after thermal crosslinking is based on the above mentioned isocyanato acrylate and a mixture of the polyols trimethylolpropane and propane diol (Table 2). The amount of alcohol is calculated for a molar ratio 1:1 of hydroxyl to isocyanate groups.

**Eco-efficiency and high quality for new UV applications**

The eco-efficiency and high quality of UV cured coatings will be extended into new applications such as the coating of more plastic parts and less critical conditions without the narrow lamp to surface distance can be overcome.

An important step here is the development of practicable technologies for UV curing of three dimensional surfaces.
under inert gas atmospheres such as carbon dioxide.
The improvement of dual cure systems also helps to provide excellent surface qualities and save solvent and energy.
A low viscosity isocyanato acrylate was recently developed for such uses. New mono cure coatings should give still higher efficiency, and also yield highly scratch resistant 3-D plastic surfaces.
Curing on demand is an ideal scenario for UV curable multilayer foils as back forming foils or adhesive foils, resulting in high quality surfaces without the use of 'wet' coating technologies in the final application.

REFERENCES
[8] Test PBODC 371 (Daimler Chrysler AG)

Results at a glance
- In order to extend the use of UV cured coatings into new applications, their curing capabilities on 3-D surfaces must be improved.
- The use of inert gas atmospheres such as carbon dioxide or dual cure systems which cure thermally in shadowed areas increases the range and economy of use of UV systems.
- A low viscosity isocyanato acrylate has recently been developed which allows high quality UV coatings to be produced with low solvent contents.
- Multilayer foils, coated in advance but UV cured at the time of final application, provide an alternative means to produce high quality surfaces without the need for 'wet' coating technologies in the final application.

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- Dr. Erich Beck, born in 1953, studied chemistry at University of Erlangen-Nürnberg, Germany, and received his PhD at Technical University of Munich. In 1985 he joined the polymer research division at BASF AG in Ludwigshafen. He is now responsible there for the development of radiation curable raw materials.
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Figure 1: UV curing in carbon dioxide atmosphere.

Figure 2: Polyurethane-polyacrylate networks: using different processes to obtain the same product.

Figure 3: Structure of a new, low viscosity isocyanato acrylate. Properties: NCO value: 15% by wt, double bond content: 2 mol/kg, molecular weight: 800 g/mol, solids content: 100%, viscosity: 1200 mPa s (23°C), iodine colour: 0, residual HDI monomer: < 0.5%, no odour.
Figure 4: Two-stage curing monitored by real-time infrared spectroscopy, with conversion of NCO and carbon-carbon double bonds shown separately. 1st curing step: thermal, 10 min at 80°C, 2nd curing step: UV, 2 kW, CO₂-atmosphere, 30 s, without heating.

(a) Relative residual gloss [%]

(b) Temperature (°C)

- Without
- After reflow

Results for 2K PU, DC, and MC.
Figure 5a - c: Comparison of properties of thermally cured polyurethane with dual cure and mono cure UV coatings: a) Scratch resistance: Amtec-Kistler test, relative residual gloss without and with reflow (2h at 80°C), b) Chemical resistance: gradient oven, 30 min, base coat: silver, testing after 24 hr, c) Impact test: substrate PC PBT with primer, black base coat plus clear coat.

Figure 6: Layer structure and curing of urethane acrylate coating for formable foils.

Figure 7: Dual cure UV systems for coating formable foils.
Table 1: Curing conditions required for various scratch-resistant coatings for plastics

<table>
<thead>
<tr>
<th>Coating type</th>
<th>Solids content</th>
<th>Flash off/thermal curing</th>
<th>UV curing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard 2K PU</td>
<td>50%</td>
<td>7 min ambient + 40 min 80°C</td>
<td>n/a</td>
</tr>
<tr>
<td>Dual cure UV</td>
<td>65%</td>
<td>5 min ambient + 10 min 80°C</td>
<td>CO₂ atmosphere, 2% residual O₂,</td>
</tr>
<tr>
<td>Mono cure UV</td>
<td>70%</td>
<td>5 min ambient + 5 min 80°C</td>
<td>medium pressure mercury lamp 5J/cm² at 50 cm, temp 60°C</td>
</tr>
</tbody>
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Table 2: Example of a dual cure formulation suitable for coating formable plastic foils

<table>
<thead>
<tr>
<th>Component</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isocyanato acrylate (16.0% NCO content)</td>
<td>80.6%</td>
</tr>
<tr>
<td>Trimethylolpropane</td>
<td>4.7%</td>
</tr>
<tr>
<td>1,2-Propane diol</td>
<td>8.2%</td>
</tr>
<tr>
<td>Dibutyl tin dilaurate, 1% dissolved in butyl acetate</td>
<td>2.0%</td>
</tr>
<tr>
<td>1-Hydroxy-cyclohexyl-phenyl-ketone (photoinitiator)</td>
<td>3.5%</td>
</tr>
<tr>
<td>2,4,6-Trimethyl-benzoyl-diphenyl-phosphine-oxide (photoinitiator)</td>
<td>0.5%</td>
</tr>
<tr>
<td>Surface conditioning additive</td>
<td>0.5%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0%</strong></td>
</tr>
<tr>
<td><strong>Viscosity at 23°C</strong></td>
<td>1.0 Pas</td>
</tr>
</tbody>
</table>