

# Waterborne UV Coatings: A New Option for Plastics

Patricia Jacobs\*, Jan Weikard\*\*, Erhard Lühmann\*\* and Stefan Sommer\*\*

*\*Bayer MaterialScience LLC, Pittsburgh, PA, USA*

*\*\*Bayer MaterialScience AG, Leverkusen, Germany*

## **Abstract**

A new generation of waterborne UV-curing polyurethane dispersions is now available that make it possible to formulate coatings for plastics with performance properties that could previously only be attained by two-component polyurethane systems or solventborne UV systems. This paper will discuss the performance of UV-curing polyurethane dispersions in three application areas: hard high-gloss clearcoat over basecoat, single layer metallic coating, and soft-touch coatings.

## **Introduction**

As a result of pressure from state and federal regulators and public environmental concerns, coatings formulators and manufacturers are seeking to implement environmentally friendly “green” coatings technology alternatives that perform as well as or better than conventional mid-to-low solids solventborne systems. Additional driving forces in the industry include the increase in the cost of solvents, energy costs and CO<sub>2</sub> emissions. Water is often the alternative carrier of choice to replace expensive solvents and their attendant VOC and HAPS concerns.

Plastic substrates, in particular, offer some real challenges to anyone trying to switch to more environmentally friendly coatings formulations. One issue with coating plastic is that solvent is often needed to help with adhesion of the coating to the substrate. A second is the flexibility of the plastic and the need to match the flexibility of the coating with that of the part to be coated. And often, in designing a coating to be flexible enough for the target substrate, crosslink density is reduced resulting in inadequate resistance properties. In addition, many plastics have low heat distortion temperatures, thus requiring a coating that can be dried/cured at relatively low temperatures. A final issue is viscosity – plastic parts are most often coated via spray application, requiring fairly low viscosity that may be difficult to attain in a low VOC, low HAPs coating.

In general, polyurethane coatings are a particularly good choice for coating plastic. Polyurethane coatings offer outstanding appearance and resistance properties. They provide excellent adhesion to many plastic substrates. In addition, due the

nature of the urethane linkage, polyurethane coatings offer a unique combination of flexibility and toughness that can be matched through judicious formulating to the target substrate. This is due to the presence of extensive hydrogen bonding that offers effective additional crosslinking that releases and re-forms under strain. (Figure1) And polyurethane coatings can be designed to provide optimum crosslink density under low-temperature cure conditions. But, depending on the raw materials, formulating a low VOC solvent-borne coating can result in a final viscosity too high for spray application.

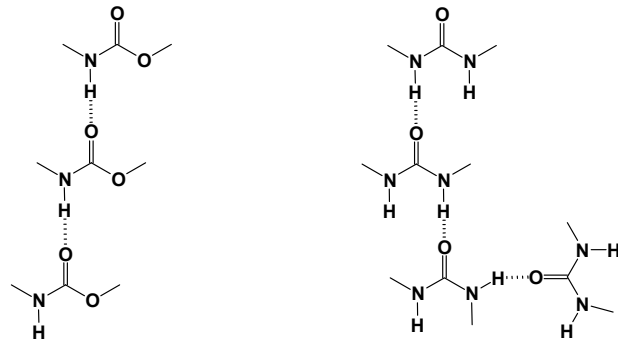


Figure 1. Hydrogen bonding in urethane (left) and urea (right)

Waterborne polyurethane coatings for plastics are well known as a “green” alternative, providing all the advantages of solvent-borne polyurethane coatings. One of the significant advantages of these dispersions is that the viscosity of the product is independent of the high molecular weight of the polymer backbone. This means a low-solvent or solvent-free high-molecular weight polyurethane can be spray applied without difficulty.

However, due to limitations inherent in the manufacturing process, typical one-component waterborne coating formulations may have insufficient crosslink density for high performance applications. Higher crosslink density can be achieved by using a two-component (2K) waterborne polyurethane coating formulation. In some cases, due to limitations of equipment or pot life requirements, the coating applicator may be restricted to use of one-component coatings formulations. In this case, is there a good one-component alternative that meets the performance requirements of plastic parts?

One good solution is the UV crosslinkable polyurethane dispersion (UV PUD). Such dispersions can be prepared with no cosolvent, or minimal cosolvent as needed for leveling and to achieve good adhesion of the coating to the plastic substrate. As illustrated in Figure 2, the polymer backbone is based on the reaction product of (typically) a diisocyanate and a hydroxy functional polyester acrylate, epoxy acrylate, or polyether acrylate, etc., and often, a low molecular weight diol. A hydrophilic group is incorporated to give the resulting polymer dispersion stability in water.

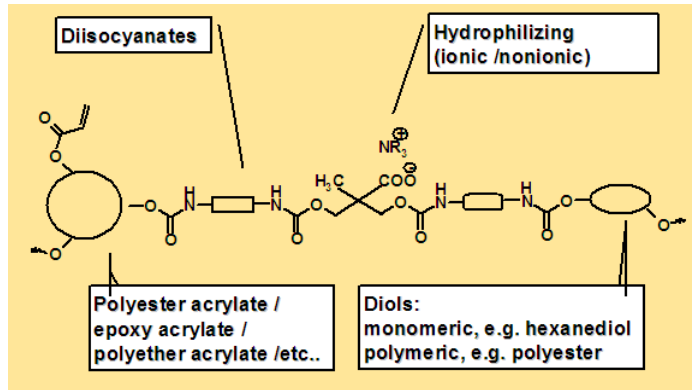


Figure 2. Generalized chemical structure of a UV curable dispersion

A potential drawback of UV cure coatings is the problem of curing in shadow areas for complex shaped parts. In contrast to conventional UV cured systems in which all molecular weight buildup and crosslinking is dependent on the efficiency of the UV cure, the resins in waterborne polyurethanes are already of high molecular weight and the UV reaction provides only additional crosslinking. In areas of the plastic part where the UV cure may not be complete, the polyurethane resin still has the properties contributed by physical dry and partial UV cure. This is also true in pigmented systems where through-cure may not be complete. The physical dry of the polyurethane dispersion in combination with partial UV cure still provides adequate coatings properties. An additional advantage of waterborne UV coatings compared to traditional UV curing coatings is low photoinitiator demand. Higher levels of photoinitiator can result in increased costs and color.

Use of a polyurethane dispersion requires that the water be driven off before UV crosslinking, either via ambient drying, hot air, or IR. Such dispersions consist of particles of polyurethane resin stably dispersed in water. Film formation occurs as the water evaporates and the dispersed particles are forced into contact with one another, finally coalescing to form a continuous film. The UV crosslinking can be completed during the initial cure sequence, or later, long after the physical dry. (Figure 3)

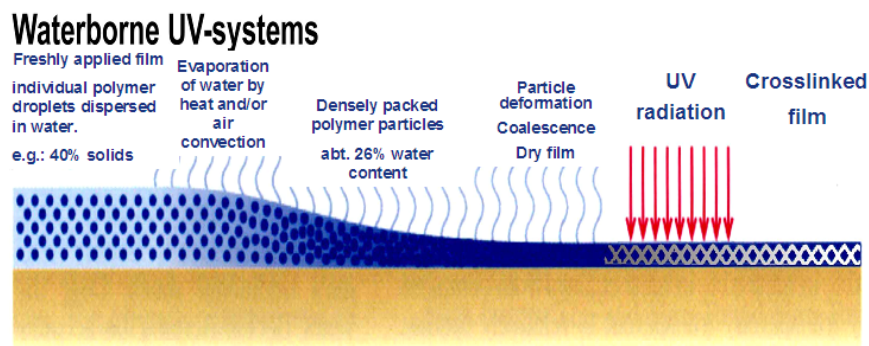


Figure 3. Diagram illustrating film formation and curing of a UV polyurethane dispersion

Coatings formulated with UV polyurethane dispersions can be applied directly to the plastic substrate as gloss or matte clearcoats or as pigmented coatings. They can also be applied over basecoat as matte or gloss clearcoats. In addition these coatings can be designed to enhance the haptic properties of the part as a soft touch coating.

This paper will highlight the performance of UV-curing polyurethane dispersions in three application areas: hard high-gloss clearcoat over basecoat, single layer metallic coating, and soft-touch coatings.

### ***Materials and Methods***

UV-curing polyurethane dispersions were synthesized based on polyester or epoxy acrylates by procedures described elsewhere.<sup>i</sup> For soft-touch coatings, polyether, polyester, or polycarbonate polymeric diols were incorporated.<sup>ii</sup> UV PUDs for hardcoats were synthesized from standard UV PUDs by incorporating high-functional UV-crosslinking monomers through a proprietary dispersion process.

For comparison in the hardcoat development, a commercial UV-curing solventborne formulation based on a blend of oligomers and monomers for mobile phone coatings was used, i.e. the blend Desmolux<sup>®</sup> B175X in combination with the urethane hexaacrylate Desmolux<sup>®</sup> U400 (Bayer MaterialScience). The UV PUD developed for soft-touch coating was compared to a state-of-the-art commercial waterborne 2K polyurethane system based on Bayhydur<sup>®</sup> 3100 (Bayer MaterialScience) and a combination of Bayhydrol<sup>®</sup> (Bayer MaterialScience) hydroxy-functional and non-functional polyurethane dispersions.

Commercial photoinitiators were used: blends like Irgacure<sup>®</sup> 500 (Ciba Specialty Chemicals), Esacure<sup>®</sup> KIP100F, Esacure<sup>®</sup> DP250 (Fratelli Lamberti) or pure products like 2-Hydroxy-1-[4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]-phenyl]-2-methyl-propan-1-one, (Bis-HDMP, Irgacure<sup>®</sup> 127, Ciba Specialty Chemicals) or Bis-acyl-phosphine-oxide (BAPO, Irgacure<sup>®</sup> 819, Ciba Specialty Chemicals) were used as described. Additives for waterborne UV formulations were standard commercial products: Byk<sup>®</sup> 348 (BYK-Chemie) for flow and wetting, Amine AMP<sup>™</sup>90 by Angus<sup>™</sup> to adjust pH, Acrysol<sup>®</sup> RM8 by Rohm&Haas as thickener, Dehydran<sup>®</sup> 1293 by Cognis as anti-foam and dispersing aid for matting agents in concentrations as recommended by the respective suppliers.

Aquamet<sup>®</sup> WPO 6600/60, a phosphorous-organic stabilized grade by Schlenk Metallpulver was used in metallic single-layer UV coatings while a 1:1 combination of Degussa's matting agents Acematt<sup>®</sup> 3200 and 3300 was used in soft-touch formulations.

Substrates for coatings were panels made of ABS, PC or PC/ABS blends.

Flash-off of water and solvents and UV curing was accomplished by a combination of a convection/IR dryer and a UV oven. After application by spray coating, the films remained for five minutes at room temperature. Subsequent flash-off was accomplished by treatment with 60°C hot air for two minutes and, where noted, by additional simultaneous irradiation with infrared light. The surface temperature of the pre-dried coatings could be determined by a temperature sensor immediately before UV cure and was varied between 40° and 80°C. UV cure was accomplished by a

single 120 W/cm mercury or gallium doped lamp. If not noted otherwise a dose of 1000 mJ/cm<sup>2</sup> was applied.

Resistance properties for soft-touch coatings were evaluated as indicated. For clear and pigmented hard-coats testing protocols of mobile phone producers were used. Pencil hardness was determined by Mitsubishi pencils with 1 kg load, 45° angle and flat tip.

Glass transition temperatures were determined by DSC after heating the sample to 150°C. Double bond conversion was measured by FT-IR, analyzing the C=C-band at 810 cm<sup>-1</sup> using an uncured sample as reference for 0% conversion.

### ***UV-PUD Hardcoat for Cell Phones***

To date, the largest application area for waterborne UV polyurethane coatings has been wood coatings. But the same UV PUDs that perform well on wood do not give the desired gloss and brilliance on basecoated plastic. The surface of the dried basecoat has a level of micro-roughness that is telegraphed to the coating surface due to physical drying. Therefore, the clearcoat does not have the high gloss and brilliance that can be achieved with the non-physical drying solventborne UV systems. In wood coatings the primed wood is usually sanded before application of the top coat, hence high gloss is possible with physical drying UV systems. Figure 4 compares the gloss of a physical drying waterborne urethane acrylate designed for wood coatings applied on a smooth surfaced ABS film and over a micro-rough physical drying basecoat. Thus, the use of PUDs developed for wood coatings as plastic coatings in waterborne UV-technology is usually not possible.

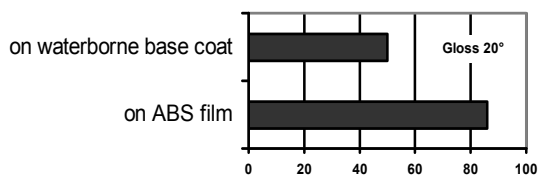


Figure 4. Gloss at 20° angle of a physical drying UV cured PUD for wood coatings on ABS film and on basecoat. The differences in gloss are attributed to the micro-rough surface of the basecoat.

In order to overcome the problem of the down-glossing due to physical cure, dispersions based on those used in wood coatings were modified by incorporation of high-functionality UV monomers. The incorporation of these monomers had two effects. It increased the double bond density of the UV PUD to a level equivalent to or higher than that of a conventional UV clearcoat for cell phones and it reduced the physical dry and increased the gloss of the clearcoat. (Figures 5 & 6)

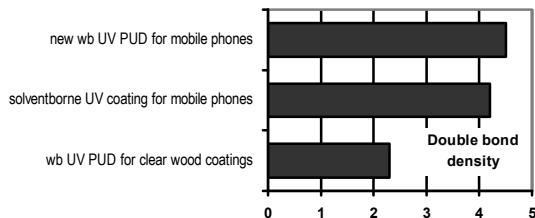


Figure 5. Double bond density of the new waterborne UV system for mobile phone coatings (UV PUD including high-functional acrylic monomer) in comparison to a WB UV system for wood coatings and a commercial solventborne UV coating for mobile phones.

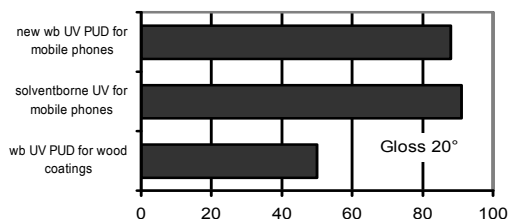


Figure 6. 20° angle gloss on basecoat of physical drying UV PUD for wood coatings, solventborne commercial UV system for mobile phones and new UV PUD (including high-functional monomer) for mobile phones.

Such an addition of monomers to the formulation could have two potentially negative consequences. Because the monomers are hydrophobic, they are difficult to incorporate into water with a hydrophilic resin. Once the mixing is complete, they could affect the stability of the resin particles dispersed in water. Also, in a conventional UV formulation, such an addition could well lead to brittleness of the coating. To overcome the difficulties inherent in blending the high functionality monomers into the dispersion without increasing particle size and negatively impacting storage stability, a new proprietary process was developed. This process resulted in a storage-stable translucent dispersion (100 nm avg. particle size) of a high molecular weight polyurethane that provides films of high double bond density. The inherent flexibility of the polyurethane backbone mitigates any tendency to brittleness.

In further experiments, we studied the effects of various curing parameters on the film properties of the newly developed hardcoat. Initial screening of photoinitiators indicated the superiority of bis-DHMAP as providing the best final film properties with the new waterborne coating. It initially imparts to the film higher than desirable color, but this bleaches out after only a few hours.

Having selected a preferred photoinitiator, a DOE was carried out to determine optimum cure conditions regarding irradiation level, photoinitiator concentration (1.25% and 2.5% on solids), and temperature at cure. Performance was measured as pendulum hardness and pencil hardness. We found, in agreement with other reports, that the hardness correlates with the temperature of cure and level of irradiation, although this dependence is less pronounced at the higher photoinitiator concentration (Figure 7). The same trend was observed in the Tg of the cured film

as illustrated in Figure 8 – the higher the cure temperature and irradiation, the higher the T<sub>g</sub>.

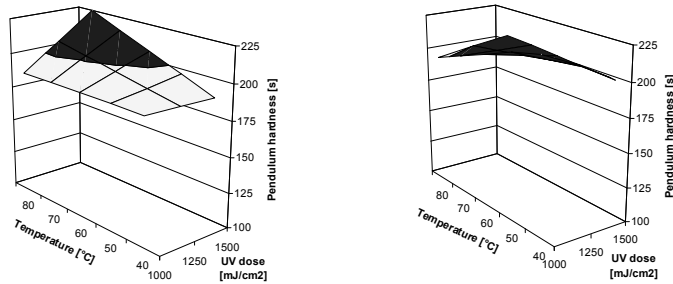


Figure 7. Statistical model for the dependence of pendulum hardness on temperature at UV cure and UV dose for new UV PUD hardcoat. Photoinitiator (bis-HDMP) concentration: left 1.25%, right 2.5% on solids.

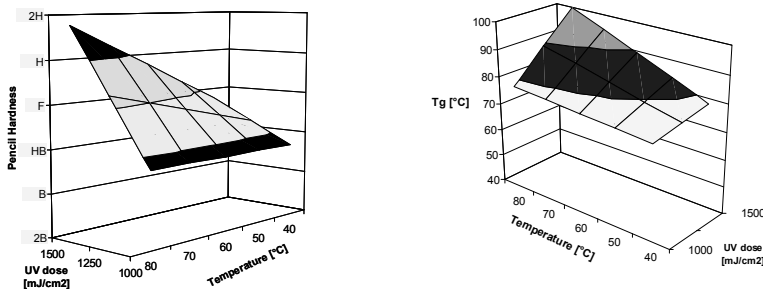


Figure 8. Statistical model for the dependence of pencil hardness (left) and glass transition temperature (right) on temperature at UV cure and UV dose for new UV PUD hardcoat. Photoinitiator bis-HDMP concentration 2.5% on solids.

Using the curing parameters as determined above, we coated polycarbonate mobile phone shells with silver-metallic solventborne TPA or waterborne acrylic or PU basecoats (10  $\mu\text{m}$  dry film thickness) and WB UV hardcoat (20  $\mu\text{m}$  dry film thickness). The coated phone shells were subjected to testing based on protocols specified by several mobile phone producers. The test protocols vary somewhat from one manufacturer to another but are generally similar. The following parameters are common to test protocols required by the producers:

- High gloss
- Pencil hardness H or higher
- Excellent crosshatch adhesion before and after immersion in boiling water
- High temperature/humidity resistance
- Chemical resistance: solvents, suntan lotion (elevated temperature/humidity) cosmetics, and artificial sweat
- RCA and/or Taber abrasion resistance
- Low yellowing after irradiation with lamps that emulate sun light
- Hot/cold temperature cycling resistance

The performance of the new UV PUD varied somewhat depending on the type of basecoat used. Good clearcoat adhesion was achieved on most, but not all types of solventborne TPA basecoats. Excellent results could be achieved with waterborne

basecoats only when they were crosslinked with hydrophilic polyisocyanates or carbodiimides. As long as there was good adhesion between the basecoat and clearcoat and the UV cure temperature was kept high, the new UV PUD passed all the testing outlined above.

### ***Metallic Effect UV Waterborne Hardcoat***

We also explored the applicability of UV PUD hardcoat technology to formulating a metallic effect monocoat. Property targets for the development were good gloss and resistance properties as well as excellent adhesion. Adhesion is dependent on the through-cure that is achievable, which in turn depends on the layer thickness and pigmentation level. We chose a phosphorous-organic treated metallic effect pigment that is stable in waterborne formulations. Following the formulation recommendations of the pigment supplier, we evaluated photoinitiators. In this case, a blend of benzophenone and an alpha-hydroxyketone provided surface-cure, while through-cure was improved when BAPO was added to the formulation. We studied the influence of cure parameters (IR dose or temperature at UV cure, lamp type, UV dose and layer thickness) on the surface- and through-cure by FT-IR spectroscopy on the front and reverse side of free coating films.

Surface cure exhibited only marginal variations in double bond conversion. Under all cure conditions, conversion was well above 90% and could thus be considered as complete<sup>\*\*</sup>. Layer thickness had the greatest effect on through-cure. Figure 9 illustrates the model statistically derived from the data for two series of dry films, 13 µm and 26 µm thick, respectively. For the thin films, the through-cure shows a dependence on high initiator content similar to the pendulum hardness of the non-pigmented system (Figure 7, right hand). For large areas of the experimental space good through-curing was achieved. The thicker layer, however, required optimized conditions. Nonetheless, a conversion of 80% of the double bonds is possible at high temperature and high UV dose. This elevated temperature (70° – 80°C) is best achieved by hot air and infrared irradiation. The influence of the lamp type (Hg or Ga) was statistically not significant.

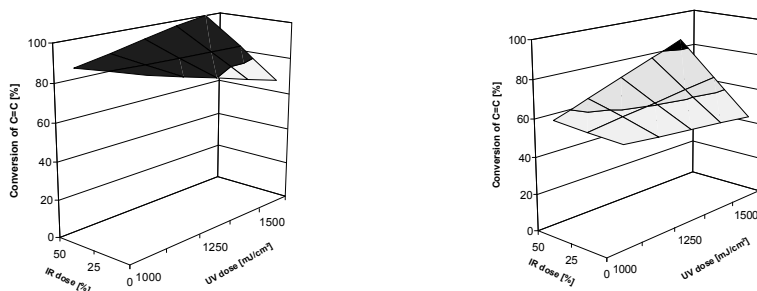


Figure 9. Waterborne metallic pigmented formulation of new hard UV PUD: Statistical model for the dependence of double bond conversion on UV dose and temperature as measured on the reverse side of the coating (variation in infrared radiation: 0% IR results in 50°C; 50% IR results in 80°C surface temperature. Cure with one Hg lamp at 120 W/cm. Pigmentation level: 19% on formulation solids; full hiding power at 16 µm dry film thickness. Dry film thickness: 13 µm left; 25 µm right

<sup>\*\*</sup> Statistically, for a tetra-functional monomer, curing of 80% double bond conversion corresponds to  $0.2^4 = 0.16\%$  of non-polymerized molecules, while curing of 90% corresponds to  $0.1^4 = 0.01\%$  of non-polymerized molecules.



Good through-cure under the optimized conditions were confirmed by application-related testing of the metallic coating on polycarbonate mobile phone shells. The optimized but still basic formulation has good hiding power and a gloss of approximately 70% (60° angle), good adhesion, even after immersion in boiling water for one hour, and excellent resistance against solvents. Resistance against suntan lotion is almost on the same level as the non-pigmented formulation.

### ***Waterborne UV-curing soft-touch coatings***

Often, coatings are applied to plastic substrates not just for protection, but also for haptic properties, i.e., a leather-like or rubbery soft feel. Traditional solvent-borne or solvent-free UV cure coatings formulations cannot achieve a soft touch effect because it is almost impossible in these systems to achieve such a low Tg flexible coating. Soft feel in a coating is normally delivered via two-component solvent-borne or waterborne polyurethane coatings. However, this effect can also be achieved with waterborne polyurethane with the bonus of UV-cure efficiency. The polyurethane backbone in such a dispersion is designed for high molecular weight, a flexible backbone and UV reactive side chains. The unsaturated side chains provide loci for additional crosslinking and better resistance properties.

The haptic properties of soft-touch coating formulations usually come from the combination of a soft binder and small particles (micrometer range) of special matting agents. It is also possible to use additives like wax or silicone to achieve a certain surface slip. In the development of a UV-cure PUD for soft-touch coating, we targeted a low Tg non-blocking polyurethane binder. This PUD was combined with surface-treated silica matting agents known to perform well in waterborne two-component polyurethane coatings. The challenge has been to identify a suitable binder that produces soft coatings but nonetheless has good chemical resistance properties. To date, no measurable physical property has proven suitable for prediction of haptic properties and thus development work remains largely empirical. Therefore, we started with a polyurethane binder based on a polyester acrylate and a higher molecular weight polymeric diol that had suitable haptic properties and then relied on trial and error to optimize the chemical resistance.

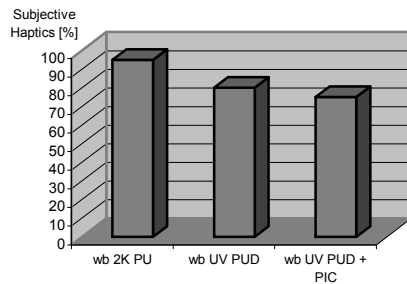


Figure 10. Relative subjective haptic on ABS film of: <sup>1)</sup> a commercial waterborne soft-touch 2K PU system; <sup>2)</sup> new wb soft-touch UV PUD; <sup>3)</sup> new wb soft-touch UV PUD in combination with a hydrophilic polyisocyanate (PIC). Each is in identical formulations with silica matting agents. 100% = best, 0% = worst.

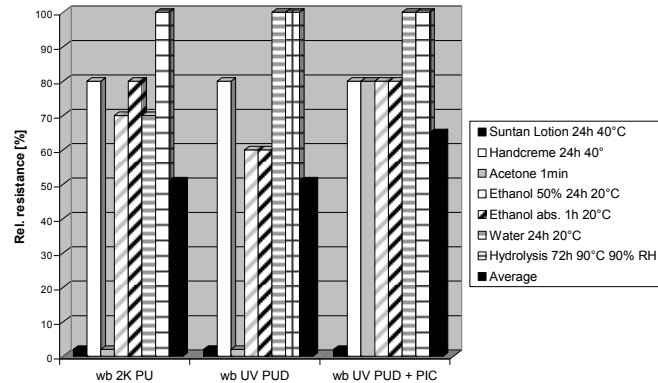


Figure 11. Chemical resistance on ABS film of <sup>1)</sup> commercial WB soft-touch 2K PU system; <sup>2)</sup> new WB soft-touch UV PUD; <sup>3)</sup> new WB soft-touch UV PUD in combination with a hydrophilic polyisocyanate. Each is in identical formulations with silica matting agents. 100% = unchanged, 0% = severe damage.

The results for haptic and chemical resistance of our new development are summarized in Figures 10 and 11. Compared to the commercial waterborne two-component PU system standard in the automotive industry for interior parts, the velvet-like touch was almost matched. In general, the chemical resistance of the UV PUD is on the same level as the 2K polyurethane system. However, neither the commercial 2K polyurethane nor the UV PUD system have adequate resistance to acetone or one of the most aggressive suntan lotions, Water Babies<sup>®</sup> by Coppertone<sup>®</sup>, at elevated temperatures. If the UV PUD is used in a dual-cure formulation<sup>iii</sup>, i.e. it is further crosslinked by a hydrophilic polyisocyanate based on hexamethylene diisocyanate, the acetone resistance is very much improved. The advantage for the coater is obvious. Instead of a drying time of 30-40 minutes at 60°-80°C, the waterborne UV coating requires only about five minutes for water evaporation and one minute for UV curing. With the dual-cure system, chemical resistances are further improved, out-performing the 2K polyurethane system. Of course, with any 2K polyurethane formulation, including dual cure, there are pot-life limitations.

## Conclusions

With a new generation of waterborne UV-curing polyurethane dispersions available it is now possible to formulate coatings for plastics with performance properties that could previously only be attained by two-component polyurethane systems or solventborne UV systems.

The UV coating of mobile phones and other equipment with similar demanding performance requirements is possible for the first time without the use of organic solvents. Waterborne UV technology offers the option to convert the conventional solventborne two-layer film-build to waterborne. The high quality single-layer pigmented systems are a new and economical alternative.

The benefits of one-component formulations for soft-touch coatings are evident: fast curing, little or no organic solvent, with performance and haptics equivalent to 2K waterborne formulations. A further increase in chemical resistance is desirable and subject of ongoing research work for all types of soft-touch coatings, both UV- and non-UV-curing.

Water as solvent is a favorable alternative, economically as well as ecologically and now new waterborne UV coatings products are available for the manufacturers of mobile phones and similar goods made from plastics.

### ***Acknowledgements***

Contributions by Nicole Doenni, Antje Hoffmann, Ulrich Itter, Uwe Klippert, Richard Kopp, Birgit Krueger, Joerg Lederer, Gerrit Woudenberg, Goenuel Yelkaya, Wendy Yu, Amy Wylie, John Zern, and Emery Yuhas are gratefully acknowledged.

---

<sup>i</sup> EP-B 0753531, Bayer MaterialScience AG.

<sup>ii</sup> US 2004/0259970 A1, Bayer MaterialScience LLC.

<sup>iii</sup> US 6,960,639, Bayer AG.