Waterborne UV-curing Polyurethane Dispersions for Clear and Pigmented Coatings on Wood

Christoph Irle, Martin Bayona, Bob Wade, Michael Dvorchak

Waterborne UV-curing coatings for furniture have now enjoyed significant market acceptance for a number of years, in particular in industrial furniture coating. Their most significant improvement over the conventional state of the art, besides their low VOC content, is their high productivity. Recent developments show that UV-curing coatings formulations can also be used very effectively with pigmented coatings and not just with clear varnishes. The products discussed here combine very rapid drying with high property levels. The effects of adding water-dispersible polyisocyanates to such coatings are also presented.

Wood and Furniture Coatings – World Market

Solvent-based polyurethane paints and coatings represent largest volumes in today's coatings market for industrial furniture and professional hardwood flooring. Worldwide, the most widely used coatings are solvent-borne systems based on polyurethane and nitrocellulose lacquers. Of the 1.85 million tons of wood coatings produced in 2002, 42 % were solvent-based polyurethane coatings. Polyurethane (PU) coatings are the coatings of choice in the southern European and Asian wood coatings markets. The People's Republic of China accounts for the largest volume of sales of PU coatings.

The outstanding property profile of PU coatings is acknowledged worldwide. Nevertheless, end users e.g. the United States, prefer not to work with free polyisocyanates. One of the primary reasons is stringent legislation on the use of aromatic polyisocyanates that limits the use of coatings systems containing polyisocyanate.

However, recent developments include environmentally friendly coatings offering a combination of advantages that meet current and future market requirements: A pre-formed urethane polymer that is rapidly crosslinked via UV radiation – our basic idea of waterborne UV-curing coatings – combines high productivity and environmental friendliness and requires very little or no solvent and no polyisocyanate. A major portion of our work over the last few years has been to transfer the advantageous properties of polyurethane coatings to waterborne and UV-curing systems.

Radiation-curing dispersions

A broad variety of products have been commercialized in the wood coatings market. The available UV-curing dispersions follow different chemistries – mostly on a polyacrylic or polyurethane basis. The most promising technology of these various systems are UV-curing PU dispersions. The chemical structure of UV-curing polyurethane dispersions is quite similar to that of long-established polyurethane dispersions. They consist of hard and soft segments, and the broad toolbox available for the design of each segment allows optimization of a huge variety of properties. In most cases, high performance soft segments contribute a certain flexibility, while isocyanates and short chain diols contribute hardness and resistance. Several routes for the introduction of acrylic double bonds have been reported[1]. In our experience, the best-suited method is to introduce double bonds along the polyurethane chain, rather than to attach acrylic units to only the end of the chain or to mix polyurethanes with acrylic monomers or oligomers.

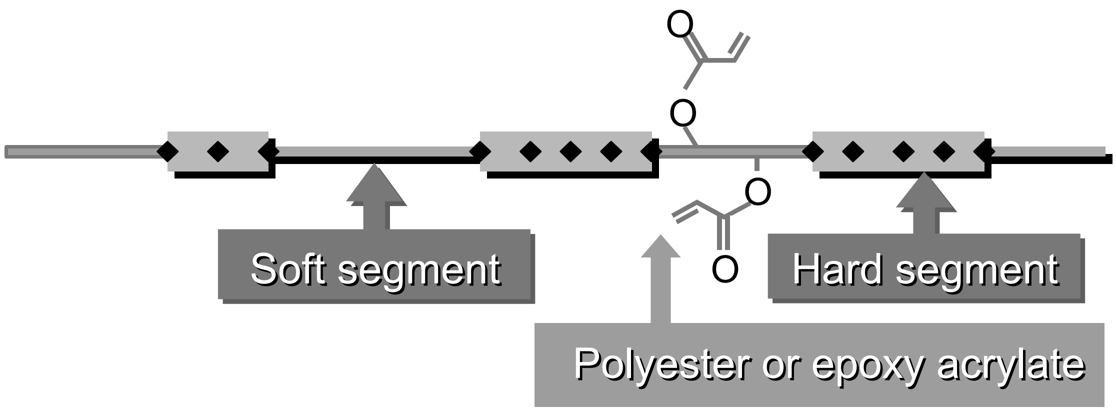


Fig. I: Building blocks of UV-curing polyurethane dispersions

Coatings based on these exhibit the highest growth rates in today's world market. The key property of this type of coating is its similarity to conventional PUR coatings – similar objectives can be achieved using similar application methods, at similar or faster drying times.

As with 100 % urethane acrylates, the polyurethane molecule is formed in the raw material producer's plant. That means the polyurethane network is formed during polymer synthesis, not after application on the substrate. The end user applies a polyurethane coating without having to mix polyol and polyisocyanate.

UV-curing aqueous dispersions have a molecular weight that is many times higher than that of traditional systems consisting of an unsaturated acrylate and a reactive thinner - a very important advantage. This is why the waterborne systems need much less radical crosslinking to obtain the desired properties. And this is why these high molecular weight polymers have less environmental impact than do traditional UV systems consisting of acrylic oligomers.

Tailor-made solutions must be developed to fully translate the advantages of this chemistry into economical and ecological advantages for the end user. As with conventional coatings, the variation of the A and B components yields a broad spectrum of possible properties, enabling the optimization of key properties such as

- Drying speed
- Hardness
- Re-emulsification of overspray

before curing and

- Chemical resistance
- Hardness
- Flexibility

after curing.

Resin design parameters are available that are quite similar to the toolbox available for conventional coatings. These are:

- Content of polyisocyanate incorporated into the polymer
- Structure and properties of the polyisocyanate compound
- Structure and properties of the resin backbone

as well as dispersion parameters such as

- Content of hydrophilic groups
- Mean particle size as well as the production process.

We found that the use of the acetone process is advantageous in this case. Using the acetone process, a chain extension in a thinned organic solution is possible. The acetone used for polymer synthesis is stripped off afterwards. The benefits are raw materials with no cosolvent content and a linear, highly reproducible molecular structure. Drying is reduced to flash off of water, as no or very little cosolvent is used. To further increase productivity, equipment for re-use of overspray can be used. During the past several years, many techniques have been developed for the collection and recycling of overspray lacquer. By using modern equipment such as the dry air oven and recycling processes for overspray, it is possible to achieve very high productivity at moderate cost (cost/square meter).

UV-curing coatings have already entered the market for industrial furniture production, mainly being used as clearcoats. Pigmented UV-curing coatings have always been a challenge, as high pigment concentrations often result in low curing conversion, especially at high film thickness.

To facilitate through cure, the toolbox available for designing UV-curing waterborne coatings offers interesting pathways to optimize curing of coatings:

- If properly designed, PU-based UV-curing dispersions demonstrate fast physical drying. High glass transition temperatures, hardness and mechanical resistance can be obtained even without UV curing.
- By adding a water-dispersible isocyanate crosslinker, the chemical and mechanical resistance of such coatings can be further increased.

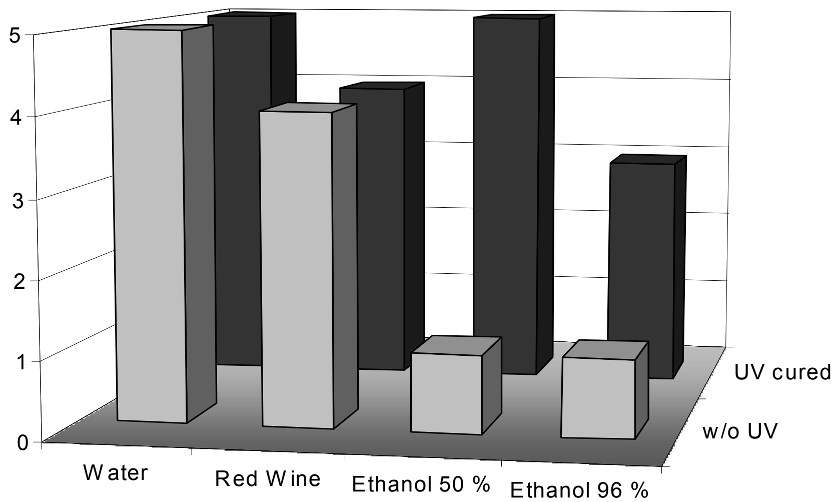
- Optimizing the chemical structure of the polyurethane using the toolbox outlined above allows us to further enhance critical parameters, such as chemical resistance.

Physical Drying

With the basic principle outlined above, it is possible to design very hard and tough polyurethanes that, even without UV-curing, exhibit high hardness and comparatively good chemical and mechanical resistance. This results in an acceptable property level even under poor curing conditions (high pigment content, high film thickness, shadow areas). We compared (Fig. II) chemical resistance and hardness of a white pigmented coating based on a polyurethane dispersion bearing acrylic double bonds under different curing conditions.

Chemical resistance
Beachwood
2 x 90 µm wet

0 = destroyed
5 = no change



Hardness
Glass
2 x 90 µm wet

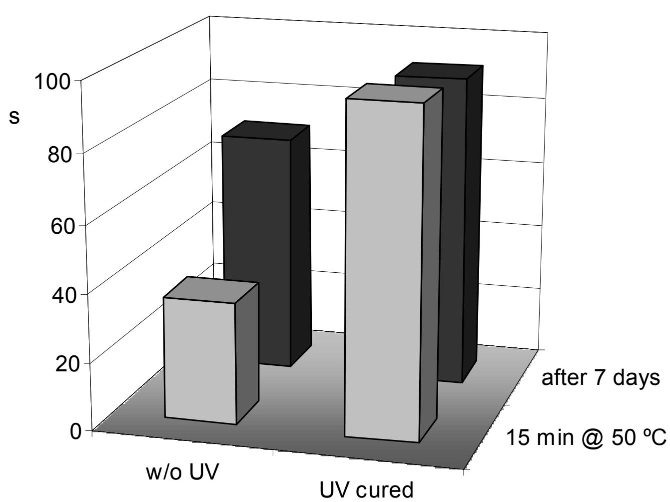


Fig. II: Chemical resistance and hardness of PU dispersion-based, white pigmented coating with and without UV-curing.

The results illustrated in Fig. II indicate that basic properties even without UV-curing reach a fairly high level. Thus, basic protection of the substrate is achieved in shadow areas. Water-resistance and staining resistance (red wine) to a high extent are influenced by the polymer backbone of the PU dispersion. Solvent resistance, such as ethanol resistance, is significantly increased after UV cure. Thus, the fully UV-cured coating exhibits excellent chemical and mechanical resistance.

Fast physical drying – clear coats

Especially in clear coatings, fast physical drying in some cases has a negative effect: caused by trapped water in deep wood pores these pores appear whitened. We found that drying behavior can easily be adjusted by blending the UV curing material with physical drying dispersions. Many polyurethane dispersions and in some cases also polyacrylate dispersions are well suited to give a quick drying, perfectly appearing finish. Results:

- Optimum results are achieved by blending with physically drying, hard, elastic PU dispersions.

  - Final properties are not impaired - chemical, mechanical resistance remain on a high level.

  - Final hardness can be even increased.

- Some PAC dispersions also allow faster drying, especially self-crosslinking types.
- High Tg PAC dispersions tend to have a negative influence.
- Further synergistic effects by adding small amounts of cosolvent – e. g. 5 % of ethanol or i-propanol.

Adding water-dispersible polyisocyanates – waterborne dual cure coatings

As previously reported[2] the addition of water-dispersible polyisocyanates significantly increases the property level of waterborne coatings – even if the “A component” is not isocyanate reactive. The water-dispersible isocyanate forms an independent network by reaction with humidity. Thus, chemical and mechanical resistance and also adhesion can be enhanced.

We tested (Fig. III) white pigmented formulations based on a physical drying, UV-curing polyurethane dispersion with two different species of water-dispersible polyisocyanates:

- A highly hydrophilic, non-ionically modified type (Polyisocyanate A) and
- A medium hydrophilic, anionically modified type (Polyisocyanate B).

Blending ratio was 90:10. The drawdowns were cured at 5 m/min under 1 Hg and 1 Ga lamp

(80 W). The influence of isocyanate blends on hardness, chemical resistance and gloss was followed as a function of time before application (pot life) and time after curing.

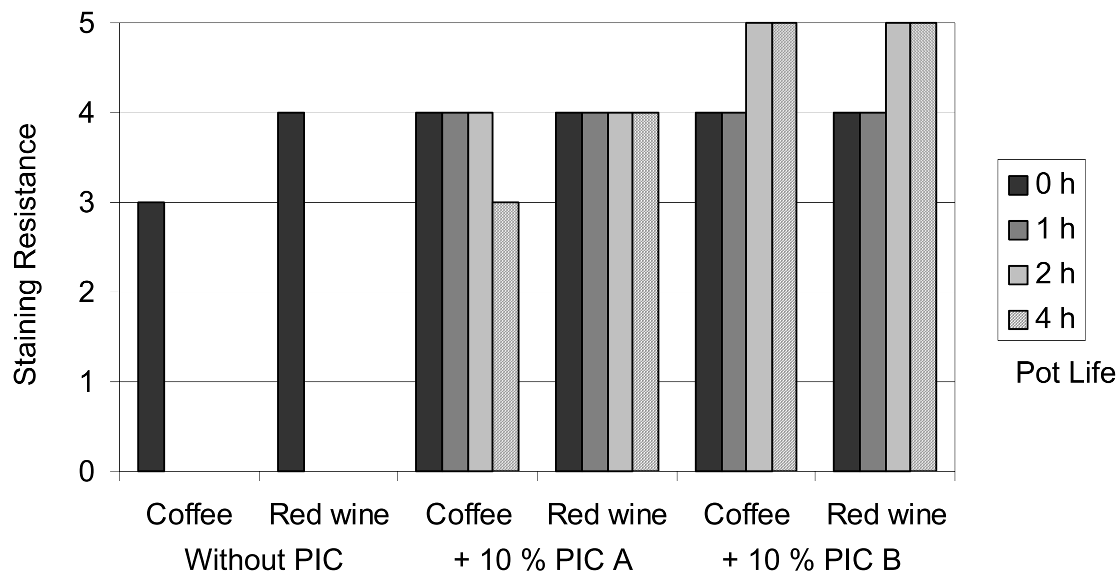


Fig. III: Staining resistance of dual cure waterborne UV pigmented coatings DIN 68861 1b, 5 = pass, 0 = fail

Results:

- Chemical resistance is increased (Fig. III). In particular, the resistance against staining liquids such as red wine or coffee is increased using Polyisocyanate B. The positive influence of these new generation crosslinkers on chemical resistance has already been reported[3]. A slight increase in resistance, furthermore, is observed during the pot life.

- Pot life of the systems varies between 4 and 6 hours as a function of isocyanate and concentration. In most cases, viscosity remains stable after that time. End of pot life is indicated by a decrease in gloss and final hardness.

- The final hardness of the coatings is increased (Fig. IV). Although Polyisocyanate A softens the film, which can be seen in slower hardness development after 1 day, the final hardness is slightly higher, even when crosslinked with PIC A. The final hardness of those films crosslinked with the anionically hydrophilized Polyisocyanate B exhibit significantly enhanced hardness, as compared to Polyisocyanate A.

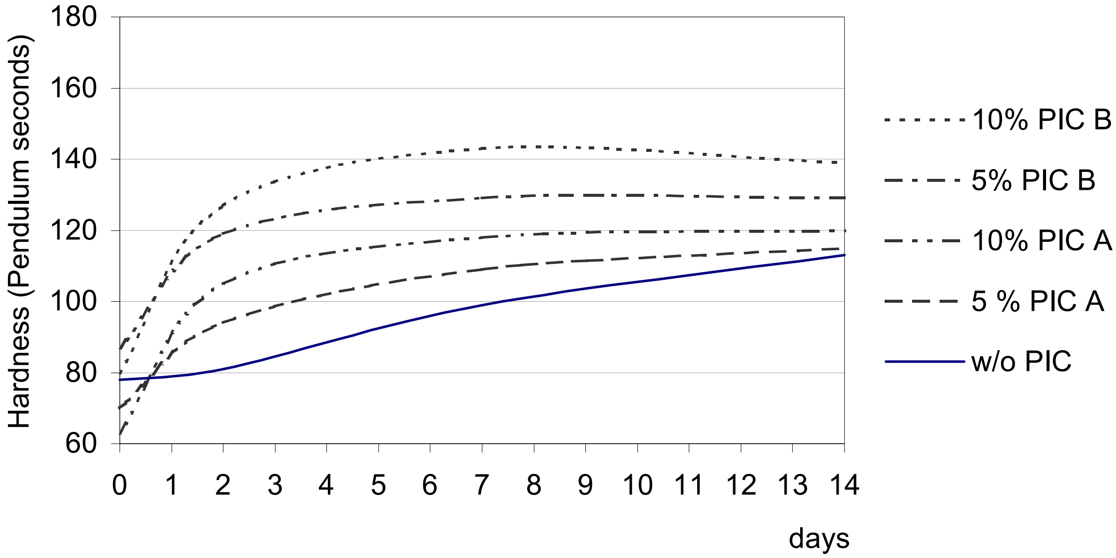


Fig. IV: Hardness development of dual cure waterborne UV pigmented coatings

Summary

Solvent-based polyurethanes have a significant share of today's wood coating markets. This is mainly due to their high property levels and ease and versatility of application. Following the same basic principle, UV-curing polyurethane dispersions represent a low VOC and very effective follow up technology. Using the entire toolbox of polyurethane chemistry enables us to further optimize properties:

- The structure of polyurethanes contributes to high hardness and resistance even without UV curing.

- Further enhancement can be achieved by post-crosslinking UV-cured coatings with water-dispersible polyisocyanates. In pigmented coatings, chemical resistance in particular is increased.

- To adjust drying properties, blening with physically drying, Polyurethane or Polyacrylate dispersions is recommended.

[1] See e. g.

EP 753531, Wolff Walsrode AG **1995**.
M. Gerlitz, R. Awad, Proc. 28th Int. Waterb., High-solids & Powder Coat. Symp., New Orleans **2001**.
W. Fischer, E. Lühmann, D. Rappen, J. Weikard, Proc. European Coatings Symp., Nürnberg **2001**.

[2] Ch. Irle, W. Kremer, E. Luehmann, R. Roschu, European Coatings Conference “Parquet Coatings”, Berlin, **2000**.

[3] Ch. Irle, R. Roschu, M. Bayona, M. Johnson, Proc. 30th Int. Waterborne, High-solids & Powder Coatings Symp., New Orleans, **2003**.