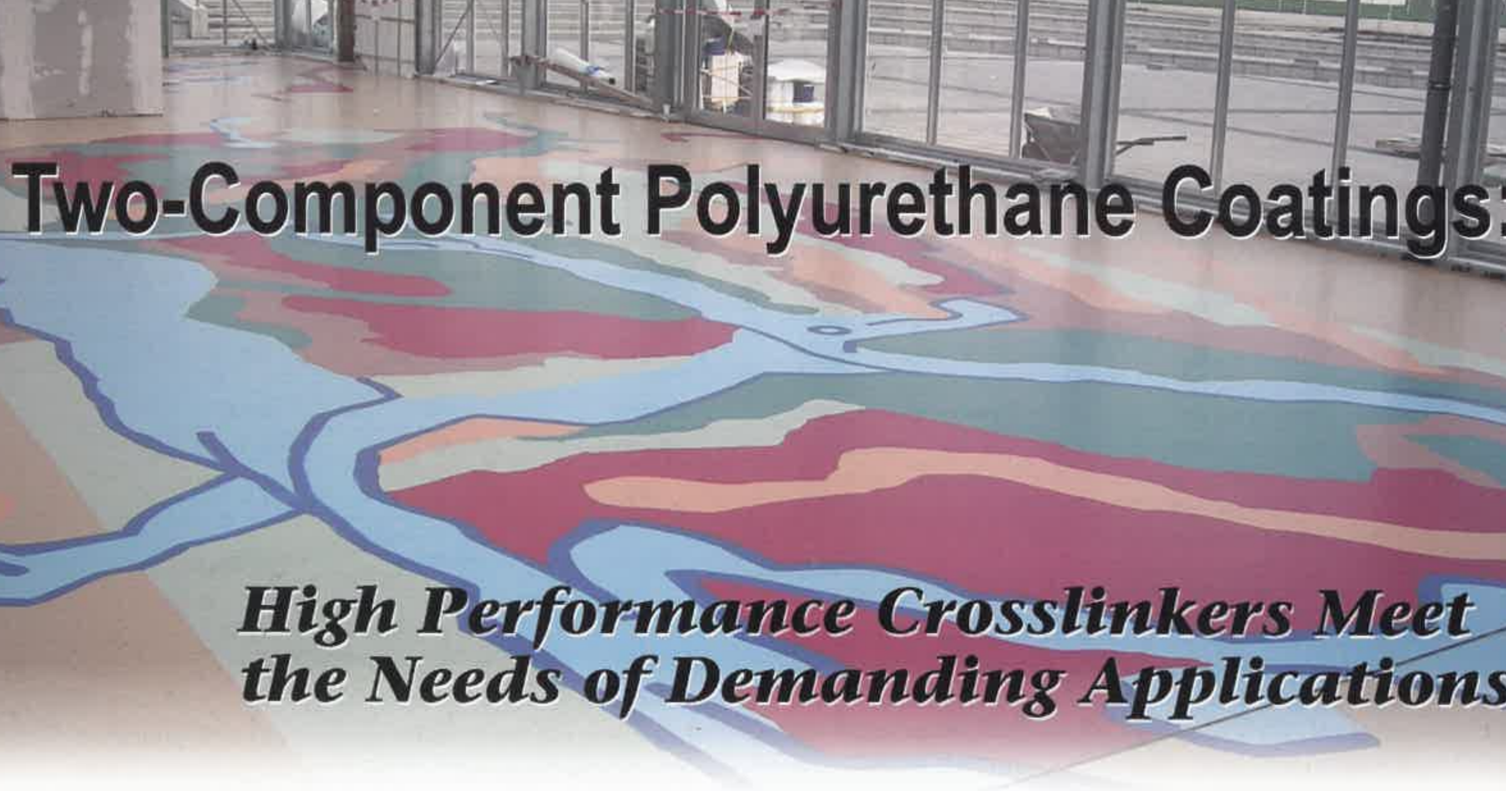


# Two-Component Polyurethane Coatings:

## *High Performance Crosslinkers Meet the Needs of Demanding Applications*

by Myron Shaffer, Raymond Stewart, Kathy Allen, Amy Wylie, and Aaron Lockhart
Bayer MaterialScience LLC*

Two-component (2K) solventborne polyurethanes are the benchmark standard for high performance coatings in the majority of coatings markets. For the formulator the advantages include:

- Wide formulation latitude due to the variety of co-reactants and crosslinkers available
- High quality appearance
- UV stability and weatherability using aliphatic polyisocyanates
- Chemical and solvent resistance
- Hardness, flexibility, and toughness due to the urethane and urea linkages

However, there have been many market and legislative forces pushing formulators to consider waterborne systems. Traditionally, PUDs (polyurethane dispersions) have been used to obtain the benefits of urethane properties in a waterborne system. These systems are dependant on hydrogen bonding, physical entanglement, and coalescence to obtain their physical properties. Typically, these thermoplastic systems have not been able to obtain the same high level of properties as a crosslinked 2K solventborne system.

From the introduction of 2K waterborne PU systems in the early 1990s, market drivers have undergone a transformation. Initially, the drivers were achieving low VOC, low odor, and easy application and clean up. The uniqueness of this chemistry and the ability to meet these demands resulted in Bayer MaterialScience being awarded an EPA Green Chemistry Award in 2000. As the markets have matured, ever higher demands have been placed on these systems and the challenges have been met by ever-improving systems. Most recently, the dominant driver has been to match 2K solventborne

Presented at FutureCoat! 2008, sponsored by FSCT, October 15-16, 2008, in Chicago, IL.
*100 Bayer Rd., Pittsburgh, PA 15205-9741.

Above photo courtesy of: Bayer MaterialScience AG characteristics wherever possible. Performance advantages from 2K waterborne polyurethanes are:

- Low VOC: < 1 lb/gal to as low as < 50 g/L
- User friendly application and clean up
- Low odor and emissions
- Multiple market specific properties: feel (haptic), graffiti resistance, dry time, abrasion/mar resistance, etc.
- Typical solventborne properties mentioned above
- Robust technology platform for meeting today's challenges

Today's waterborne polyurethane systems show equal, or sometimes even better, overall performance than comparable solventborne systems.

Extensive resin design has taken place to allow 2K waterborne polyurethane systems to reach their current state of performance. Work had to be done on both the resin, or Bayhydrol® polyol portion, as well as the Bayhydur® polyisocyanate crosslinkers. Either research thrust would make for interesting reading. However, the focus of this report is to discuss the chemistry and development of the polyisocyanate crosslinkers that have been introduced from the early 1990s until today.

There are a number of properties important to coatings formulators. One of the important properties of coatings is their clarity and overall appearance. The importance of effectively dispersing an isocyanate crosslinker can be easily demonstrated simply by observing the appearance of two similar systems.

## DEMONSTRATION OF IMPORTANCE OF DISPERSIBILITY

In the first example, shown in *Figure* 1, it can be seen that a standard hydrophobic polyisocyanate is not properly dispersed in the polyol dispersion when using a hand mix application. In the electron microscope picture on the right of the figure, the undispersed domains of polyisocyanate in the polyol matrix are plainly visible. On the left, an actual film is laid over the top half of the system label. The poor dispersion of the polyisocyanate is demonstrated by the opacity of the film.

In the second system (*Figure* 2), a hydrophilic polyisocyanate is hand mixed with the same polyol dispersion as the first example. In this system, the electron microscope picture shows a uniform surface and even dispersion in the film (*Figure* 2). Again, on the left an actual film is laid over the system label. In contrast to the first example, this film has high clarity and good appearance due to the excellent dispersibility of the hydrophilic polyisocyanate chosen. Gloss readings as high as 95 are now routinely available. This clearly demonstrates the importance of a good dispersion on coating properties.

## WATER-DISPERSIBLE CROSSLINKER CHEMISTRY

Different approaches using both internal and external emulsifying agents have been tried in the market for supplying water-dispersible polyisocyanates. In our study, the decision was made very early on to focus on internal emulsifying agents. It was felt that using external surfactants could lead to problems such as blistering, decreased water resistance, and blushing. This is mainly due to the inevitable migration of an external surfactant through the coating to the surface.

Initial development work was focused on modifying HDI polyisocyanates with monofunctional hydrophilic polyethers as the emulsifying agent. These were incorporated into the standard hydrophobic polyisocyanate crosslinker through a urethane linkage. This was the first generation of hydrophilic products (see *Figure* 3). The generic structure shown is based on an HDI isocyanurate trimer.

Generation 1 products based on HDI have a good overall blend of properties. They are relatively easy to disperse and form stable emulsions. They have good reactivity and can be used in a wide range of formulations. It is also possible to use lower viscosity starting polyisocyanates to get a lower viscosity water-dispersible crosslinker, which improves dispersibility. Another feature of this product line is the ability to tailor the products for adhesive applications, having higher functionality and less water sensitivity. Even today the majority of development effort has been done with HDI-based products.

Generation 2 products were developed with an eye toward making a step change increase in the overall

Figure 1—Standard hydrophobic polyisocyanate in polyol dispersion.

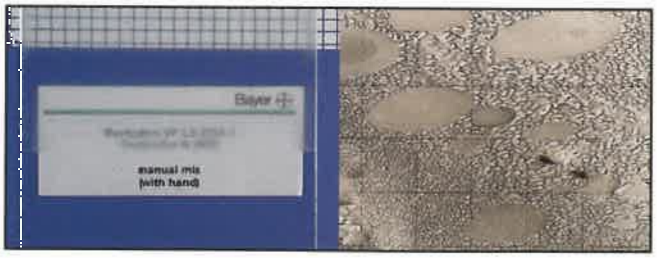
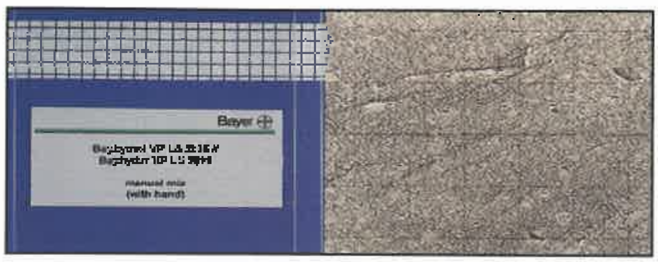



Figure 2—Hydrophilic polyisocyanate in polyol dispersion.



properties of the final coating. The monofunctional hydrophilic polyether used to modify the starting polyisocyanate is incorporated into the water dispersible crosslinker through an allophanate linkage instead of a urethane (*Figure* 4).

This allows the use of less polyether, while obtaining a higher level of dispersibility. Correspondingly, this reduces the water sensitivity of the final film because there is less polyether incorporated. Finally, the cross linker has a higher functionality, resulting in better chemical resistance and hardness, with faster property development.

In the most recent developments, the use of ionic emulsifiers has been pioneered. Using a unique sulfonic acid, ionic emulsifiers are reacted into the resin backbone using a urea linkage. The urea linkage provides additional hydrogen bonding, contributing to the overall properties of the system. This combination results in improved dispersibility combined with higher hardness and comparable, or even improved, chemical resistance relative to the Generation 2 products. In addition to a higher NCO content, these products also give lower water sensitivity relative to the non-ionic emulsified crosslinkers. Similar to a polyurethane dispersion, the neutralization amine shown in *Figure* 5 evaporates, leaving a lower residual hydrophilicity in the final coating.

Polyisocyanate product line overview:

- HDI versus IPDI
  —Speed of cure, flexibility, low VOC—HDI
  —Hardness, fast drying, long potlife—IPDI
- Low viscosity
  —Easier to disperse, better appearance
- Higher functionality/% NCO
  —Chemical resistance, higher crosslink density, adhesive strength development
- Hydrophilic versus hydrophobic
  —Easy to disperse, emulsion stability, high appearance—hydrophilic
  —Low water sensitivity, chemical resistance, high shear dependence—hydrophobic

## GENERAL INDUSTRIAL SPRAYABLE APPLICATION

When developing a formulation, it is necessary to start from a good base and choose the polyol and polyisocyanate carefully. For industrial coatings, polyacrylates are a good starting point for the polyol portion due to their (1) crystal clear color; (2) hardness and flexibility; (3) reactivity; (4) light and heat stability; (5) durability; (6) resistance to solvents, water, chemicals; (7) drying and cure; and (8) pigment dispersing ability.

On the polyisocyanate side, the formulator can choose a Generation 3 crosslinker, which is characterized by (1) ease of mixing, (2) reactivity, (3) durability, (4) compatibility, and (5) formulating flexibility.

To illustrate, a formulation was developed for spray application (*Figure* 7).

There are some general observations that should be made about this formulation:

- Although it contains no pigment, VOC amount is less than 1.0 lb/gal. One would anticipate an even lower VOC depending on the choice of pigmentation.
- In this guide formulation, NCO/OH=3.0. The formulator is encouraged to test different indexing ratios of polyol and polyisocyanate to obtain desired properties.
- Usable pot life will vary, depending on environmental conditions and choice of components, such as pigments, to be used in the formulation.

To illustrate, *Figure* 8 shows the rapid development of this coating when spray applied onto a flat glass specimen.

This coating also demonstrated excellent resistance to chemicals such as 10% aqueous hydrochloric acid. Graffiti resistance was demonstrated by ease of removal of Blue Sharpie

Figure 3—Water-dispersible polyisocyanate—polyether urethane modification Generation 1.

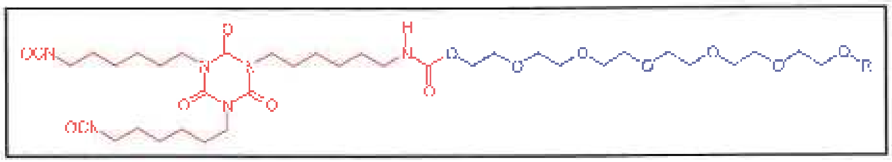



Figure 4—Water dispersible polyisocyanate—polyether allophanate modification Generation 2.

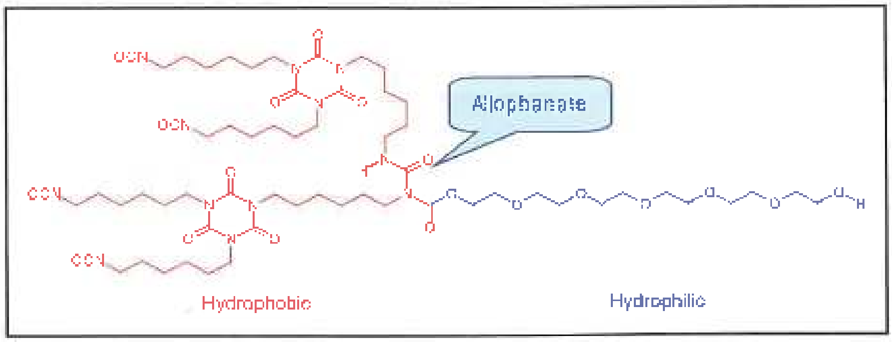
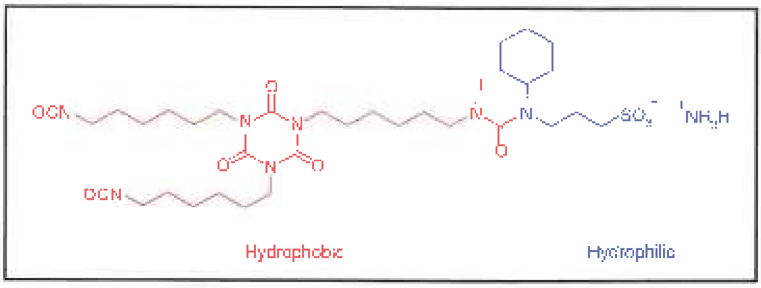


Figure 5—Water-dispersible polyisocyanate: ionic urea modification Generation 3.




after it was allowed to dry for one hour on the coating (~50 microns, air-dried for three days at ~25°C).

## CONSTRUCTION TOPCOAT FOR FLOORING

For construction flooring, a standard solventborne topcoat formulation has a VOC content of about 400 g/L. Over the past few years, an increasing trend in the construction industry has been to promote a healthier environment by requiring "greener" technology. Proof of these trends comes in three major areas: stricter Federal regulations of VOCs, increased communication of environmental issues impacting consumers, and increased sensitivity to solvent odor from solventborne technology currently being used in the market. Changes made by California to its VOC regulations are expected to be adopted by other states. Parts of California instituted a 50 g/L limit for residential flooring applications and 100 g/L limit for commercial applications in 2006. These limitations severely restrict the coating systems that can be used in the flooring market.

To respond to the increasing demand for low-VOC topcoats, a waterborne polyurethane topcoat resin was introduced into the market years ago. Coatings based on hydroxyfunctional polyester dispersions in combination with a hydrophilic HDI-Trimer (1st Generation isocyanate) gave moderate performance, which made them suitable for decorative flooring, but this system was not equal to the solventborne system in terms of chemical resistance, durability, and ease of application.

The R&D work during the past few years has included the search for new resins and isocyanates that have physical properties equal to solventborne along with low odor and ultra low VOC. Our worldwide developments have been completed with three hydroxyfunctional polyacrylic dispersions, and on the isocyanate side, a low-viscosity 3rd Generation polyisocyanate HDI-trimer. Because of the low viscosity of the isocyanate, the addition of solvent was not needed, allowing formulators to achieve a low odor and an ultra low-VOC coating. Testing was done comparing the new waterborne system with the solventborne system. A sample of the results are shown in *Table* 1.

An advantage of the new 2K waterborne system over previous waterborne and solventborne systems is that the final gloss can be tailored. Depending on the blend ratio of the polyol dispersions, the clearcoat formula can be customized to achieve any gloss level. *Figure* 9 depicts the relationship of the gloss level to polyol dispersion blends.

## SOFT-TOUCH COATINGS

One of the biggest markets currently utilizing soft-touch coatings is the automotive industry. Automotive companies have been applying soft-touch coatings to the interiors of cars since the early 1990s. The initial soft-feel coatings were solventborne, which yielded a very soft feel and good chemical resistance. However, one of the biggest drawbacks to solventborne systems is the VOC level. Governmental regulations have pushed formulators to search for more environmentally friendly technologies. Therefore, the coatings industry has seen soft-touch coatings shift towards 2K waterborne chemistry, utilizing polyurethane dispersions (PUD) and water-dispersible isocyanates.

A typical waterborne soft-touch formulation consists of an OH-functional PUD, a non-functional PUD, and a water-dispersible polyisocyanate. The formulator's choice of dispersions and crosslinker can yield a variety of softness and resistance levels. Choosing an isocyanate that would result in a higher crosslink density coating often leads to a coating that is less soft. The

Figure 6—Polyisocyanate product line overview.

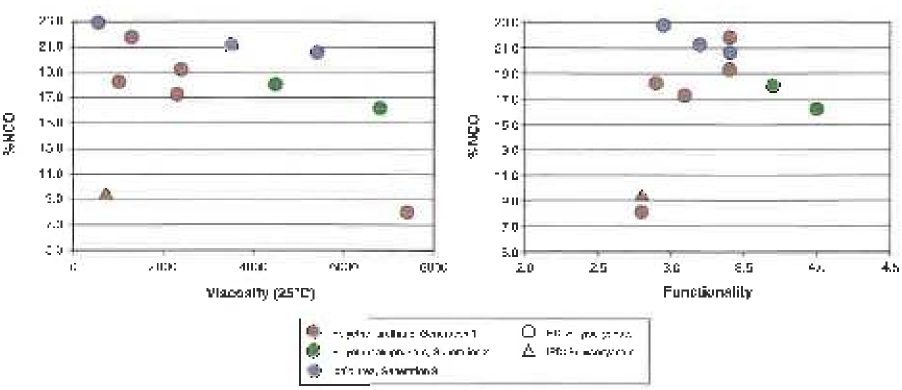


Figure 7—Spray application formulation.

**2K Clearcoat - NCO:OH=3.0/1.0**

| Raw Material | Weight | Volume | Weight Solids | Volume Solids | Supplier |
|---|---|---|---|---|---|
| *Component I* | | | | | |
| Polyacrylate dispersion[a] | 36.15 | 4.08 | 18.08 | 1.91 | Bayer Corporation |
| Water, DI | 7.4 | 0.89 | 0 | 0 | Fisher Scientific |
| Baysilone Paint Additive VP AI 3468 | 0.23 | 0.02 | 0.23 | 0.02 | Lanxess/Borchers |
| Tego Foamex 822 | 0.09 | 0.01 | 0.02 | 0 | Goldschmidt Chemical Corporation |
| DSX 1514 (8% in DI water) | 1.73 | 0.21 | 0.08 | 0.01 | Cognis Corporation |
| Subtotal I | 45.6 | 5.21 | 18.41 | 1.94 | |
| *Component II* | | | | | |
| Hydrophilic polyisocyanate[b] | 31.45 | 3.24 | 31.45 | 3.24 | Bayer Corporation |
| Butyl glyrol | 5 | 0.66 | 0 | 0 | Fisher Scientific |
| Subtotal II | 36.45 | 3.91 | 31.45 | 3.24 | |
| *Component III* | | | | | |
| Water, DI | 22.95 | 2.75 | 0 | 0 | Fisher Scientific |
| Subtotal III | 22.95 | 2.75 | 0 | 0 | |
| Total | 105 | 11.86 | 49.86 | 5.18 | |
| Spray Viscosity 26 sec DIN #4 Cup | | | | | |

**Theoretical Results**

| | | | |
|---|---|---|---|
| Weight solids | 47.49 | Wt/gal | 8.85 |
| Volume solids | 43.72 | Mix ratio (vol) | 1.33:1:0.70 |
| P/B | 0 | NCO:OH | 3 |
| PVC | 0 | Theoretical VOC | 0.91 |

(a) Polyacrylate dispersion: hydroxy-functional acrylic resin dispersed in water; 50% resin, 40% water, 1% Dowanol PnB; equivalent weight as supplied = 640 g/mol.
(b) Hydrophilic polyisocyanate: HDI-based, aminosulfonic acid modified; 100% solids as supplied; equivalent weight = 182 g/mol.

challenge for the formulator is to obtain a soft touch formulation that is highly resistant while maintaining softness. One can also vary the isocyanate choice to generate a coating with haptics that range from a suede or velvety feel to more of a rubbery, grabby type feel. This variety in feel is a benefit because different areas of the world define softness differently.

Much work has been done to significantly improve the performance of water-dispersible isocyanates for soft-feel coatings. Additional work has been dedicated to exploring how the improvements made have enhanced adhesion, resistance, haptic, and application properties.

## SITE-APPLIED WOOD FLOORING

Waterborne systems are a well established technology in the site applied wood floor coatings market. The primary reasons for this are the significant reduction in VOCs, low odor, and ease of application. High molecular weight, co-solvent-free PUDs offer rapid drying

Figure 8—Hardness development of 2K clearcoat.

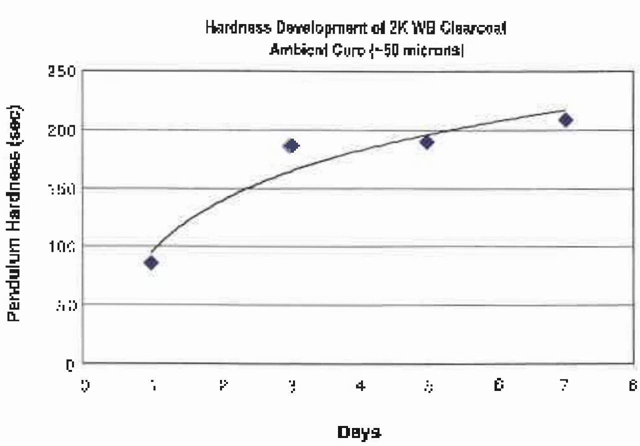



Figure 9—Gloss modification using blending of acrylic dispersions.

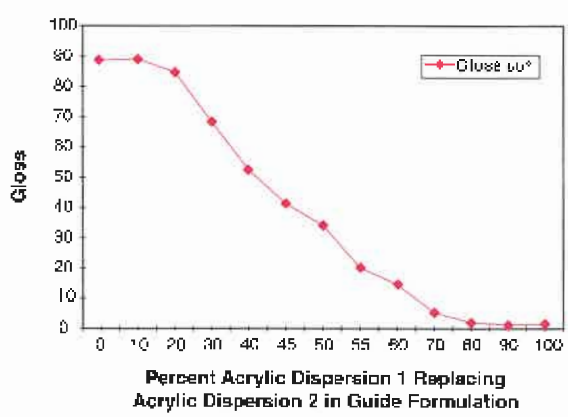


**Table 1—Comparison of Waterborne and Solventborne Topcoat Formulation for Floors**

| Test | Waterbased Clearcoat | Solventbased Clearcoat |
|---|---|---|
| VOC | 0-20 g/L | 400 g/L |
| Gardner circular | 6 hr | 1.5 hr |
| Dry Time (70°F/50%RH) | | |
| Taber abrasion | | |
| (CS-17, 1000 cycles) | 34 mg | 25 mg |
| Chemical resistance[a] | very good | very good |
| Gloss | adjustable | glossy |

(a) Chemicals tested by a spot test included 10% acetic acid, 10% sulfuric acid, 10% hydrochloric acid, 10% ammonium hydroxide, 50% sodium hydroxide, isopropanol, methyl ethyl ketone, DI water, Betadine, 10% bleach, and gasoline. Skydrol and brake fluid were tested by immersion.

**Table 2—Performance Enhancement of Site-Applied Wood Floor Coatings with Generation 1 and Generation 2 Water Dispersible Polyisocyanates**

| | One-Pack | Two-Pack PIC/Urethane | Two-Pack PIC/AlloPhanate |
|---|---|---|---|
| Touch-dry (h) | 1.5 | 1.5 | 1.5 |
| Hardness (s) 1d/7d | 104/137 | 57/130 | 59/127 |
| Acetone 10s[a] | 4 | 0 | 0 |
| BHMR[a] | 4 | 0 | 0 |
| Gloss (60°) | 88 | 49 | 88 |
| Transparency | Clear | Cloudy | Clear |

(a) 0 = no damage; 5 = destroyed.

while low mean particle size leads to high wet film transparency and wood warmth. The selection of polyurethane dispersion also determines a coating's overall hardness and drying rate. However, water reducible polyisocyanates are added to 1K coatings for on-site wood floor applications that require a higher level of chemical and mechanical resistance properties. Examples of such enhancements are resistance to household reagents (nail polish remover, household cleaners) and resistance to scuffing by shoe soles, called Black Heel Mar Resistance (BHMR). Other key factors for the acceptance of a 2K system are ease of mixing, ease of application, and acceptable potlife.

For 2K site-applied applications, it is essential that the curing agent can be easily incorporated into component A. When designing a crosslinker for waterborne coatings, an optimized level of hydrophilic character must be identified to achieve target properties. In short, an elevated amount of hydrophilic groups simplifies incorporation of the crosslinker while an excessive content of hydrophilic groups, on the other hand, impairs the chemical resistance and increases water sensitivity.

The first generation of waterborne 2K polyurethane parquet sealers consisted of a combination of component A and a Generation 1 polyisocyanate. In these systems, the crosslinker does not become sufficiently homogenized during manual mixing, and the parquet finish frequently turns out rather cloudy. This limited the use of this technology to matte and semi-gloss finishes. This was overcome by utilizing a Generation 2 water-dispersible polyisocyanate that could be easily incorporated under practical conditions, thus yielding a more finely dispersed polyisocyanate having an optimal level of hydrophilic modification.

This modification to the crosslinker structure improves the dispersability so greatly that it can be easily incorporated simply by shaking the container after addition to component A. Resultant particle sizes are in the range of approx. 100 nm, which are also the typical values for polyurethane dispersions. Therefore, for the first time, thorough mixing under practical floor refinisher conditions is now possible.

A combination of this polyisocyanate with a high-gloss component A produces a clear, highly resistant, high-gloss waterborne 2K polyurethane coating, as seen in *Table* 2.

Upon incorporation of the crosslinker, the coating system has a pot life of about five hours and still yields consistent properties. After this period of time, the most significant change is gloss reduction.

## CONCLUSIONS

It is clear that we have come a long way from the early skepticism that this technology was greeted with when it was first introduced. There has been a great deal of developmental effort put into optimizing both the coreactants and polyisocyanates necessary to make this technology feasible and allow it to reach the high standards of performance that we have come to expect from polyurethane coatings.

In this work, a quick overview of waterborne polyisocyanate crosslinker development and how each generation has furthered the performance window of 2K waterborne polyurethane coatings has been presented. Obviously, this is complemented by the ongoing development of waterborne coreactants. However, the enabling technology for this area is the performance of the variety of hydrophilic polyisocyanate crosslinkers available. There is a wide range of formulating expertise that allows the tailoring of properties for a multitude of applications for coatings, adhesives, and sealants. As we expand upon this, it will allow us to continue to meet ever more stringent requirements and legislation regarding VOC and HAPS, and market needs for improved performance, user friendliness, and "green" characteristics.

## ACKNOWLEDGMENT

Dr. Christoph Irle for technical support and discussions and Chad Quatman for application and testing of the industrial coatings.