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 polyurethane systems 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 dependent 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 PUI 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 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 solvoborne 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 has been done on both the resin, or hydrophilic polyol portion, as well as the 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.

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Figure 1—Standard hydrophobic polyisocyanate in polyol dispersion.

Figure 2—Hydrophilic polyisocyanate in polyol dispersion.
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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 blooming. 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 trimmer.

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 properties 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 characteristics wherever possible. Performance advantages from 2K waterborne polyurethane formulations are:

- Low VOC < 1 lb/gal to as low as < 50 g/L
- User friendly application and clean up
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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 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.

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Above photo courtesy of Bayer MaterialScience AG.

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properties of the final coating. The nonfunctional hydrophobic polymer used to modify the starting polyisocyanate is incorporated into the water dispersible crosslinker through an aliphatic linkage instead of a urethane (Figure 4). This allows the use of less polymer, while obtaining a higher level of dispersibility. Correspondingly, this reduces the water sensitivity of the final film because there is less polymer incorporated. Finally, the crosslinker has a higher functionality, resulting in better chemical resistance and hardness, with faster curing 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 vs IPDI
  - Speed of cure, flexibility, low VOC—HDI
  - Hardness, fast drying, long potlife—IPDI

Figure 3—Water-dispersible polyisocyanate—polyurethane modification Generation 1.

Figure 4—Water-dispersible polyisocyanate—polyurethane aliphatic modification Generation 2.

- Low viscosity
  - Easier to disperse, better appearance
- Higher functionality/NCO
  - Chemical resistance, higher crosslink density, adhesive strength development
- Hydrophobic versus hydrophobic
  - Easy to disperse, emulsion stability, high appearance—hydrophobic
  - 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, polycrystallines 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 pigment.
- In this guide formulation, NCO/OH=3.0. The formulator is encouraged to test different indexing ratios of polyol and polycyanate 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 sprayed onto a flat glass specimen. This coating also demonstrated excellent resistance to chemicals such as 10% aqueous hydrochloric acid. Grail resistance was demonstrated by ease of removal of Blue Sharpie after it was allowed to dry for one hour on the coating (<0.3 mil, 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 implemented 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 hydrophobic HDI-Trimmer (1st Generation isocyanate) gave moderate performance, which made them suitable for decorative flooring, but this system was not as resistant 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

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

Figure 6—Polyisocyanate product line overview.

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fter it was allowed to dry for one hour on the coating (<0.3 mil, air-dried for three days at 25°C). 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 waterborne, which yielded a very soft feel and good chemical resistance. However, one of the biggest drawbacks to waterborne 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
properties of the final coating. The multifunctional hydrophilic polyester used to modify the starting polyisocyanate is incorporated into the water dispersible crosslinker through an aliphatic linkage instead of a urethane (Figure 4).

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Table 1—Comparison of Waterborne and Solventborne Crosslinker Formulations for Flooring

<table>
<thead>
<tr>
<th></th>
<th>Waterborne Crosslinker</th>
<th>Solventborne Crosslinker</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOC</td>
<td>200 g/L</td>
<td>400 g/L</td>
</tr>
<tr>
<td>Gardner Circles</td>
<td>6 hr</td>
<td>1.5 hr</td>
</tr>
<tr>
<td>Dry Time (70°F/50%RH)</td>
<td>90 min</td>
<td>2 min</td>
</tr>
<tr>
<td>Tater abrasion (US-1, 125 g/m²)</td>
<td>34 mg</td>
<td>25 mg</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>very good</td>
<td>very good</td>
</tr>
<tr>
<td>Glos</td>
<td>adjustable glossy</td>
<td>glossy</td>
</tr>
</tbody>
</table>

*1/1 Chemical solvent systems based on lasurine, straw 10% sol- china, 10% hy- drophobic ester, 15% amine hydrochloride, 35% liquid hydrochloride, 5% mineral oil. 2. Waterborne coatings: Pinttrer & Miller; solvent-based coatings, before and after,
Figure 7—Spray application formulation.

Table 1—Comparison of Waterborne and Solventborne Topcoat Formulations for Plywood

<table>
<thead>
<tr>
<th>Test</th>
<th>Waterborne Topcoat</th>
<th>Solventborne Topcoat</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOC</td>
<td>20 g/L</td>
<td>400 g/L</td>
</tr>
<tr>
<td>Gardner pencil hardness</td>
<td>6 hr</td>
<td>1.5 hr</td>
</tr>
<tr>
<td>Dry film thickness (100% solids)</td>
<td>34 mg</td>
<td>25 mg</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>very good</td>
<td>very good</td>
</tr>
<tr>
<td>Gloss</td>
<td>adjustable glossy</td>
<td>glossy</td>
</tr>
</tbody>
</table>

Note: Gardner pencil hardness is based on the rate of hardness development at 25°C and 50% relative humidity. Chemical resistance is evaluated using the following: A) boiled water, B) 5% NaOH, C) 10% ethyl alcohol, D) 2% acetic acid, and E) 5% white spirit. Gloss was measured using a 60° geometry specular glossmeter.

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

<table>
<thead>
<tr>
<th>Property</th>
<th>One-Pack</th>
<th>Two-Pack</th>
<th>Two-Pack Msi/Chlorane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Touch-dry (h)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Hardness</td>
<td>5/7/10</td>
<td>9/10/12</td>
<td>5/7/10</td>
</tr>
<tr>
<td>Acetone solubility</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>BHRR</td>
<td>88</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Transparency</td>
<td>Clear</td>
<td>Cloudy</td>
<td>Clear</td>
</tr>
</tbody>
</table>

Note: 0 = no damage, 10 = destroyed.

A combination of this polysiloxane with a high-gloss component A produces a clear, highly resistant, high-gloss waterborne 2K polysiloxane 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 reactants and polysiloxanes 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 polysiloxane technology and the enhancements and how each generation has furthered the performance window of 2K waterborne polysiloxane coatings has been presented. Obviously, this is complemented by the ongoing development of waterborne coating systems. However, the enabling technology for this area is the performance of the variety of hydrophilic polysiloxane crosslinkers available. There is a wide range of formulation 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 even more stringent requirements and legislation regarding VOC and HAPS, and market needs for improved performance, user friendliness, and "green" characteristics.

ACKNOWLEDGMENT

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