# 100% solids aliphatic polyurethane coatings—from dream to reality

By Dr Shiwei Guan, Research and Development Manager, Madison Chemical Industries Inc., Milton, Ontario, Canada

Polyurethane coatings which are 100 percent solids have become one of the most important families in the coatings industry today. These polyurethane systems are effective because of their outstanding life expectancy and performance. Features include resistance to aggressive corrosive environments, high abrasion and impact resistance, curing capability at temperatures as low as -40°C, strong adhesion, high film build and fast application. All this is coupled with compliance with the most rigorous regulations on volatile organic compound (VOC) emissions.

Existing 100% solids polyurethane technologies have been confined mainly to aromatic polyurethane systems, made by reacting aromatic isocyanates, such as methylene diphenyl diisocyanate (MDI) or toluene diisocyanate (TDI), normally with polyether polyols.

When exposed to UV light such systems oxidise much more easily than do polyurethanes prepared from aliphatic isocyanates. Aliphatic isocyanates reacted with either polyester or acrylic polyols have thus become indispensable in the formulation of high-performance weatherable coatings. They present the industry with its first durable ambient curing, thermosetting protective coating with long term gloss and colour retention.

Traditionally, aliphatic polyurethane coatings incorporate high molecular weight (MW) compounds which, typically, require high levels of solvents to make them usable in spray applications. These levels of solvent will not be permitted in the near future due to increasingly stringent environmental and safety regulations coupled with consumer demands for ecologically more benign materials.

## Towards higher solids

The 1990 US Clean Air Act imposed stringent controls upon air emissions and restricted the amount of organic solvents (the primary source of VOCs) emitted from a coating system.

Together with powder and water-borne coatings, high solids coatings evolved to meet the demand for reduced solvent levels. In epoxy and aromatic PU systems, 100% solids technology has been successfully developed, but in aliphatic PU systems, this has been rarely achieved by manufacturers.

Some reasons for this are:

- The high MW/viscosity of most commercial 100% solids aliphatic polyisocyanates, polyester and acrylic polyols means high solvent levels are needed to make them usable in spray applications;
- When individual viscosity values are in the right range, different polyisocyanate demands of those 100% solids polyols make it difficult to design a coating system with the right volume mixing ratio and/or balanced viscosities of the two components; and
- Greatly reducing the solvent content makes a major impact on formulation and performance properties and thus becomes a challenge to coatings chemists.

Over the past ten years, three main routes to compliance with high-solids aliphatic PU coatings have been pursued:

- Low MW compounds which have lower viscosity resulting in minimum solvent usage for application[2-3];
- Reactive diluents[4], and
- New PU prepolymers[5].

New technologies have also been developed by the author recently at Madison Chemical which leads to three novel types of system: 100% solids, VOC-free, instant setting; high-solids mix-and-apply; and high-solids one-component.

## Low MW compounds

Higher solids aliphatic PU coatings have been achieved by reducing the MW of the polyisocyanates and co-reactants.

Compared with co-reactants such as polyester and acrylic polyols, it is apparent that the aliphatic polyisocyanates are already the high solids component of the coatings. Commercially, HDI-based isocyanate and biurets are being made to viscosities as low as 500 centipoise.

Acrylic polyols have been favoured for aliphatic PU systems because of their superior weathering, low cost, hydrolytic

## Aliphatic PU chemistry

Very high solids (both aromatic and aliphatic) PUs are usually in a two-component format. One component is a polyisocyanate-rich liquid, and the other is hydroxyl functional co-reactants. The typical aliphatic PU reaction is shown below:

$$R-N=C=O + R^1-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2OH \rightarrow$$
$$R-NH-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2-O-\overset{O}{\overset{\|}{C}}-R^1$$

The rapid exothermic reaction provides PU systems with low-temperature curing ability. This is a significant advantage over many other reactive resin systems used in coatings, such as epoxies.

While there are virtually unlimited arrays of hydrogen donors for preparing PU coatings, hydroxyl based systems are used almost exclusively. In an aliphatic system, PU coatings produced from the reaction of aliphatic isocyanates with a hydroxyl functional coreactant were initially formulated with polyester polyols. These coatings possessed good weathering performance.

With the increased demand for improved durability at low cost, acrylic polyols were then used. These have low isocyanate demands and also give superior hydrolytic stability over polyesters. Both polyester and acrylic polyols tend to be more expensive than polyether polyols, and they are usually more viscous and therefore more difficult to handle. The high viscosity makes it more difficult to develop 100% solids aliphatic PU systems.

Only a few variations are possible with the isocyanates, whether in original or a modified form. The most common aliphatic isocyanates are hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI). The nature of the isocyanate-bearing species will greatly affect reactivity. Aliphatic isocyanates are considerably less reactive than aromatic isocyanates such as TDI and MDI. Differences also exist between individual aliphatics, for example, HDI is faster than IPDI. For the above reasons, commonly available aliphatic PU coatings have a much longer curing time (5-8 h) compared with aromatic PUs (e.g. 10 minutes to 1 hour).

A two component PU system normally has a mixing ratio of 1:1 by volume. Higher mixing ratios are normally used to obtain a coating system whose two components are mixed together just before application. In this case, the pot life of the coating system must be of sufficient length (at least 45 min) for easy application.

The 1:1 mixing ratio is an ideal choice for achieving not only 100% solids, but an instant setting PU system. It is commonly used for most 100% solids aromatic PU coatings. A major problem, however, is to design a 1:1 coating system so that each component has the same viscosity. The equal viscosity helps to simplify set up and maintenance of the spray equipment, and also to avoid many application problems due to mismetering of the two components while using plural component spray equipment[6]. UT stability, and low isocyanate demands. However, their very high MW (10 000-20 000 g/mol) is coupled with high solvent demand, yielding coatings with less than 50% solids at application viscosities.

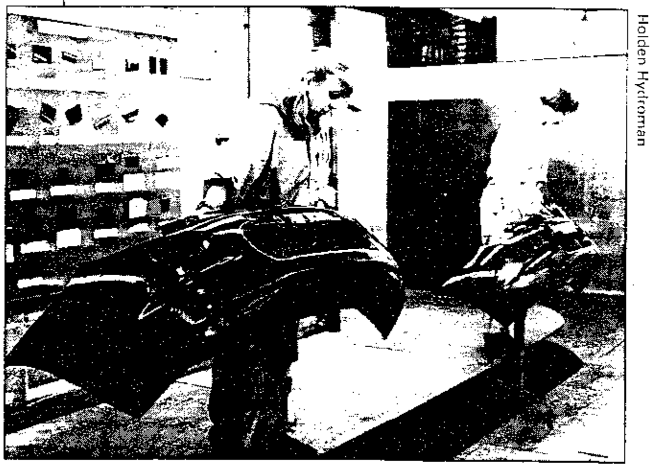
Acrylics have therefore been developed with MWs typically below 2500 g/mol. The functionality of these acrylics, however, has had to be increased to maintain the excellent resistance characteristics of these types of systems. Coatings with solids contents of greater than 75% have been achieved using this approach.

Altering the MW/functionality to obtain compliant coatings results in shorter pot lives and longer drying times. Cure rates can be increased by adding catalysts or increasing the amount of catalysts, which shortens cure times, but also shortens pot lives.

Another problem with the use of low MW components is an increase in the crosslink density of the coating. Too high a level of crosslink density can lead to a decrease in flexibility, impact and mar resistance.

**TABLE 1 EARLIER WAYS TOWARDS HIGHER SOLIDS ALIPHATIC POLYURETHANES**

| Approach | Advantages | Disadvantages | VOC level, lb/gal (g/l) |
|---|---|---|---|
| Low mol. wt polyester/ acrylic polyols | Low cost, low viscosity, hydrolytically stable, no additional chemistry needed | Limited availability, high functionality & crosslink density, short potlife & longer drying | 2.5-3.5 (302-424) |
| Blocked amines | High yield & quick drying when exposed to ambient moisture | Expensive, limited sources, or hydrolysis stability, limited shelf life | 0.98-2.0 (118-242) |
| Reactive diluents | Low viscosity, low MW good hydrolysis stability | Expensive, low functionality, possible performance changes | 2.0-2.6 (242-315) |
| New prepolymers | High MW, low viscosity, low oligomer/residual isocyanate content, easy to achieve 1:1 mixing ratio | Limited availability, longer drying time | 2.8 (339) |



Holden Hydroman

**Off-line painting of automotive components uses a variety of systems, including PU-based ones**

Rather than using low MW polyester and acrylic polyols, blocked amine functional reactants have also been introduced to make higher solids aliphatic PU (or, more precisely, polyurea) coatings. These include aspartic acid esters, ketimines, and aldimines.

Aldimines—a result of the reaction between amines and aldehydes—look the most promising approach here. They show much better hydrolytic stability than ketimines and so can be adapted to actual applications. Experimental formulations with solvent levels at or below 2.0 lb/gal (240 g/l) have been reported[6].

## Reactive diluents

Reactive diluents are low-viscosity co-reactants designed to reduce VOCs in coating systems. While they generally provide the ability to reduce the viscosity of the polymeric composition similar to a solvent, they also react with the polymer. Reactive diluents based on low MW polyester or polyether polyols, castor oil derivatives, oxazolidines and acetoacetate chemistry are commercially available.

Reactive diluents tend to have low reactivity toward isocyanates, low functionality, and relatively low viscosity. This makes them very attractive for use in aliphatic PU systems with long potlife and reasonable drying times. Aliphatic PU systems with VOC levels as low as 2.58 lb/gal (312 g/l) have been reported[4].

Reactive diluents are, however, normally much more expensive than commercially available polyesters, acrylics, and other coreactants, so that end users find the coating systems too expensive. Also, performance properties may change if large amounts of reactive diluents are added, due to their low functionality and low MW.

## Prepolymer use

Prepolymers have long been used in high solids PU coatings systems, especially in aromatic systems. Conventional prepolymer manufacture often results in the production of a significant amount of high-molecular-weight oligomers, which cause high-prepolymer viscosities.

The aim has thus been to develop high-molecular-weight aliphatic PU prepolymer systems with a low oligomer content and less than 1% of residual isocyanates[5]. With the low viscosity, higher-molecular-weight prepolymers as the isocyanate-rich component (often referred as the 'A' side), a significant amount of the high solvent demand polyols from the polyol rich component (the 'B' side) can be avoided. The low oligomer content of these prepolymers also results in the additional benefit of longer pot lives. With the new prepolymer technology, IPDI-based aliphatic PU coatings systems with VOC contents at 2.8 lb/gal (339g/l) have been reported[5].

**TABLE 2: GLOSS RETENTION OF COATINGS**

| System | Initial gloss 60° | Gloss retention |
|---|---|---|
| New 100% solids aliphatic | 92 | 90 |
| Commercial 70% solids aliphatic | 86 | 92 |
| Commercial 100% solids rigid aromatic | 93 | 65 |

Test: 5000 h QUV 3133 (ASTM G53). Gloss values by ASTM D523

Table 1 summarises these approaches towards higher solids aliphatic PU systems. Obtained VOC levels for individual approaches in Table 1 are typical for aliphatic PU basecoat/topcoats.

## 100 % Solids aliphatic

The focus on developing higher solids aliphatic PU systems which can still be applied using conventional field-pressure pot-spray equipment has forced the coatings chemist towards developing an 'ideal chemistry.' This must include all those problems discussed above (hydrolysis stability, short potlives, etc.).

Low MW co-reactants, reactive diluents, and prepolymers have already been successfully used in developing 1:1 mix-

**TABLE 3 : CHEMICAL RESISTANCE OF COATINGS***

| System | 10% $H_2SO_4$ | 5% $HNO_3$ | 25% NaOH |
|---|---|---|---|
| 100% solids aliphatic | No colour change, slightly softened | No colour change, slightly softened | No colour change, slightly softened |
| Commercial 70% solids aliphatic | No colour change, slightly softened | No colour change, slightly softened and blistered | No colour change, Slightly softened |
| Commercial 100% rigid aromatic | Slight colour change | Colour change | Slight colour change |

* Test: ASTM D714; 96 hours chemical exposure

ing, plural component, 100% solids epoxy and aromatic PU coatings.

These systems normally require plural component spray equipment. While the plural component equipment is relatively complicated, successful application of 100% solids coatings is being achieved by numerous end users on a regular basis.

Too much emphasis has also been placed on finding a 'super-ideal resin/co-reactant solution' on an individual basis to reduce solvent levels. However, formulating a good higher-solids PU coating system involves considering many parameters other than solvent demand and MW.

Efforts towards higher solids or 100% solids aliphatic PUs should, therefore, be made in a systematic way, combining all individual possible solutions together.

At Madison, such an approach has resulted in a new 100% solids, VOC-free, instant-setting, aliphatic PU technology. This produces a resilient PU coating film with excellent tear strength, impact and abrasion resistance.

The viscosity values of both isocyanate and co-reactant components were perfectly balanced at 1000 centipoise as per ASTM D2196. Handling characteristics were: end users' choice of initial setting time from 5 to 30 min, cold weather cure ability (-10°C to +65°C), low and high film build, a one-coat system for most general maintenance applications, and non-flammability.

Although application of this 100% solids aliphatic system is currently with plural component (1:1) spray equipment, it is interesting to note that for some coating formulations, conventional one-component spray equipment could be used.

## Performance of new system

Physical and chemical properties of the 100% solids aliphatic PU system, as well as its gloss and colour retention, were all high.

After 5000 h exposure, both the 100% solids and the 70% solids commercial aliphatic PU systems had gloss retention of greater than 90%, compared with 65% for the 100% solids aromatic PU system (Table 2).

Long-term outdoor weathering tests with these systems is currently underway. Initial results for 18 months showed the 100% solids aromatic PU system was chalking and darkened in colour as was expected. Both the 100% solids aliphatic and the 70% solids commercial aliphatic PU systems had gloss retention of greater than 95% and showed no colour changes by a visual examination.

The 96 hours of continuous immersion exposure in the chemical resistance tests is far more than the average duration of a chemical spill. This has become the standard used by some coatings manufacturers as part of the 'extra care' that they take for end users. Table 3 shows typical results obtained for these systems.

No colour changes were found with the 100% solids aliphatic and the 70% solids commercial aliphatic PU systems. They were, however, slightly softened, which is typical for most high solids aliphatic PU systems after immersion. As is to be expected from most of the advanced 100% aromatic PU systems, the aromatic PU coating discoloured without any other physical property changes.

All three PU systems showed good abrasion resistance (Table 4), but it should be noted that the abrasion resistance of a PU system is somewhat related to its rigidity. A PU coating can be designed to be very rigid or very elastomeric, and better abrasion resistance is normally found with an elastomeric system. One cannot therefore conclude from Table 4 that the aliphatic PUs will have better abrasion resistance than the 100% solids aromatic PU.

The adhesion of a coating is generally considered to be a good indicator of its longevity (Table 5). The 100% solids aromatic PU coating showed excellent adhesion up to 2000 psi (13.8 MPa). Both the aliphatic systems had an adhesion value greater than 750 psi (5.2 MPa), which is above normal for an exterior application.

It should be mentioned that the excellent adhesion of the 70% aliphatic PU, also developed by the author, is not commonly seen with most of the high solids aliphatic PUs available in the market today. When applying the aliphatic PUs to very rough substrate surfaces such as ductile iron pipes or concrete structures, an aromatic basecoat under the aliphatic PUs is recommended.

A nationally recognised steel tank manufacturer has used the 100% solids aliphatic coating with good results. This company had been using a commercial high-solids coating on the exterior of their above-ground tanks. This gave a satisfactory finish when cured but, in production, needed too long between coats and drying time was also too long, especially at low winter temperatures. This cut capacity and slowed production considerably.

Bayer AG

**The testing of the durability of coatings simulates likely end-use situations**

With the new 100% solids aliphatic PU technology, however, a number of advantages became immediately apparent. Only one coat was required to completely cover the tank without a primer. The new coating also cured in about 20 minutes at ambient temperature and the tank could be moved out of the painting room very quickly. The new coating dried to a bright and shiny finish which has excellent resistance to UV and weathering. **UT**

**TABLE 4: TABER ABRASION TESTS***

| System | Weight loss, mg |
|---|---|
| 100% solids aliphatic | 40 |
| Commercial 70% solids aliphatic | 60 |
| Commercial 100% rigid aromatic | 75 |

* Test ASTM D4060, 1 kg load CS17 1000 cycles

**TABLE 5 RESULTS OF ADHESION TEST***

| System | Adhesion, psi (MPa) |
|---|---|
| 100% solids aliphatic | 750 (5.2) |
| Commercial 70% solids aliphatic | 1000 (6.9) |
| Commercial 100% rigid aromatic | 2000 (13.8) |

* Test ASTM D4541 when adhered directly to a near white blast (SSPC-SP10) steel

## References


1. Shiwei Guan, "Assuring Quality When Applying 100 Percent Solids Polyurethanes", Journal of Protective Coatings and Linings, 74, December 1995.
2. J. L. Williams, "High-Solids Polyurethane Coatings, Past, Present, and Future", Proc. Twentieth Waterborne, Higher-Solids and Powder Coatings Symp., New Orleans, LA, 1, 1993.
3. S. M. Lee, etc., "Aldimine-Isocyanate Chemistry: A Foundation for High Solids Coatings", Proc. Twenty-Second Waterborne, Higher-Solids and Powder Coatings Symp., New Orleans, LA, 69, 1995
4. G. N. Robinson, etc., "High Performance Polyurethane Coating Systems Utilising Oxazolidine-Based Reactive Diluents", Journal of Coatings Technology, 69, Vol. 66, December, 1994
5. Jeffrey Kramer and Sherri Bassner, "Using Novel Polyurethane Prepolymers in VOC-Compliant, Two-Component Weatherable Topcoats", Paint & Coatings Industry, 42, August, 1994
6. M. J. Dvorchak, et al., "Aldimine-Isocyanate Chemistry: Applications in High Solids Coatings", Proc. Twenty-Second Waterborne, Higher-Solids and Powder Coatings Symp., New Orleans, LA, 78, 1995