

100% Solids Polyurethane and Polyurea Coatings Technology

The need for corrosion protection has provided a great challenge for today's coatings industry to formulate and to provide coatings products that can meet various combined requirements. These include environmental and safety compliance such as volatile organic compound (VOC) content, cost-effectiveness, appearance and high performance.

The ideal corrosion protection coating system must be environmentally friendly, worker-safe, durable and able to expose little or no metal/substrate surface to the environment while being resistant to environmental, mechanical and chemical damage from the initial stage of handling and installation through its entire service life. It should also come at a reasonable cost in terms of materials, application, repair and operation maintenance. One-hundred-percent solids polyurethane and polyurea coatings technology is regarded as a coating solution that stacks up well against this long list of demands and is the fastest growing technology of choice for a number of industries. The expansion of polyurethane technology into new markets is believed not to be a question of if but when¹.

Currently, there are three 100% solids coating systems available: elastomeric polyurethane, elastomeric polyurea and rigid polyurethane. Each system has unique and outstanding properties. However, there are many misperceptions and much misunder-

standing about the differences among the three systems as well as the advantages and disadvantages of each system's application and performance. A lot of hype also exists, especially with respect to 100% solids elastomeric polyurea coatings, which needs to be put in perspective by providing an accurate gauge to decide whether a polyurea or polyurethane is the best choice for an application.

This paper reviews the basic chemistry and development of three coating systems currently available: 100% solids elastomeric polyurethane, 100% solids elastomeric polyurea and 100% solids rigid (or structural) polyurethane. This paper discusses the differences among the three sys-

tems' structure, properties and application characteristics and provides guidelines on the selection of the three coating systems by highlighting the development of several new systems of 100% solids polyurethane and polyurea coatings technology and their application in high-performance corrosion protection. These new systems include modifications by ceramic and/or anti-microbial additives and the world's first 100% solids, rigid and aliphatic polyurethane coatings.

Chemistry and Development

The history of polyurethane coatings began in the late of 1930s after Otto Bayer and coworkers discovered the diisocyanate addition polymerization

When it comes to corrosion protection, how do these technologies stack up?

By Shiwei William Guan
Madison Chemical Industries

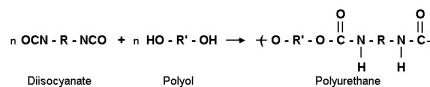


Figure 1: Polyurethane chemistry.

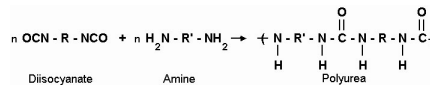


Figure 2: Polyurea chemistry.

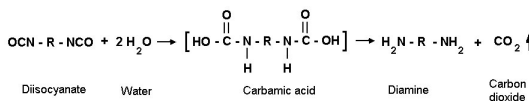


Figure 3: Isocyanate/water reaction.

<i>ASTM description</i>	<i>Type I One-package pre-reacted</i>	<i>Type II One-package moisture cured</i>	<i>Type III One-package heat cured</i>	<i>Type IV Two-package catalyst</i>	<i>Type V Two-package polyol</i>	<i>Type VI One-package non-reactive lacquer</i>
<i>Characteristics</i>	<i>Unsaturated drying oil modified; no free isocyanate</i>	<i>Contains free isocyanate</i>	<i>Blocked isocyanate</i>	<i>Isocyanate prepolymer plus catalyst</i>	<i>Part A – isocyanate rich; Part B – polyols or amines</i>	<i>Fully polymerized polyurethane dissolved in solvents</i>
<i>Main curing mechanism</i>	<i>Oxidation of drying oil; Solvent evaporation</i>	<i>Reaction with atmospheric moisture</i>	<i>Thermal release of blocking agents and then reaction</i>	<i>Reaction of isocyanate with moisture and/or components in catalysts</i>	<i>Reaction between Part A and B; instant curing possible</i>	<i>Solvent evaporation</i>
<i>Polymer</i>	<i>Alcoholysis products of drying oils reacted with isocyanate</i>	<i>Higher molecular weight diols and triols</i>	<i>Prepolymer forms to an adduct with blocking agents such as phenol</i>	<i>Prepolymer similar to Type II but catalysts could contain polyol/ amine</i>	<i>Relatively lower molecular weight</i>	<i>Thermoplastic polymer with relatively high molecular weight</i>
<i>Chemical resistance</i>	<i>Fair</i>	<i>Fair to good</i>	<i>Good to excellent</i>	<i>Fair to excellent</i>	<i>Good to excellent</i>	<i>Fair</i>
<i>Corrosion resistance</i>	<i>Poor</i>	<i>Poor to good</i>	<i>Fair to good</i>	<i>Fair to excellent</i>	<i>Fair to excellent</i>	<i>Poor to fair</i>
<i>Corrosion protective applications</i>	<i>Exterior or interior; non-immersion services; Wood; Concrete; Metal</i>	<i>Exterior or interior; non-immersion services; Wood; Concrete; Metal</i>	<i>Not used for anti- corrosive coatings in the field; Automotive and product finishes</i>	<i>Similar to Type I but the design of catalyst may change the properties; Some suitable for immersion</i>	<i>Used for many substrates; Elastomer for concrete; Rigid concrete; Rigid for metals</i>	<i>Not normally used for corrosion protection; Auto- motive and product finishes.</i>
<i>Special considerations</i>	<i>Better abrasion than most oil paints</i>	<i>Properties and curing affected by humidity</i>	<i>Heat required for cure</i>	<i>Similar to Type II but with speed of curing</i>	<i>Special equipment may be required</i>	<i>VOC limitation</i>

Table 1: Six ASTM polyurethane coatings types.

procedure that resulted in the preparation of many polyurethanes and polyureas^{3,4}. Polyurethane chemistry, based on the exothermic reaction between di- or poly-isocyanates and compounds with hydroxyl end-groups such as polyols, is illustrated in Fig. 1.

It is the exothermic nature of this reaction that provides fast-setting, cold-temperature curing ability and unlimited film build-up of 100% solids polyurethane coatings. Similarly, but often much more quickly, di- or poly-isocyanates can react with compounds with active hydrogen groups such as amines to form polyureas (Fig. 2).

Isocyanates can also react with water, yielding a substituted urea at the end of the process. This two-step reaction is controlled by the much slower isocyanate/water reaction, producing a substituted carbamic acid that breaks down into an amine and carbon dioxide gas. The amine then reacts with further isocyanate to yield the substituted urea (Fig. 3). References to polyurea chemistry usually refer to the one-step reaction shown in Fig. 2 rather than the two-step reaction shown in Fig. 3.

When the production of carbon

dioxide gas provides as a benefit the principal source of gas for blowing in the manufacturing of low-density flexible polyurethane foams, the gas is unwanted in the application of a polyurethane coating. The carbon dioxide causes bubbles or foaming within the coating during cure. If there is a significant number of bubbles in the coating and defoaming has not been taken place, chemical and physical properties of the coating will be diminished. The finished surface of the coating may become dull, and foaming, blistering and bubbling may occur.

The above simple polyurethane or polyurea chemistry provides a great deal of versatility to coatings formulators that no other coatings resin chemistries can provide. There are hundreds of different isocyanates and thousands of polyols and amines available for the formulator to choose from, resulting in millions of permutations and combinations. Examples of isocyanate groups are aliphatic isocyanates (HDI, m-TMXDI, and IPDI) and aromatic isocyanates (TDI and MDI). Examples of polyols include polyethers, polyesters, acrylics and

castor oil derivatives. The amine components can be aliphatic or aromatic amine resins and amine-terminated chain extenders. The selection of different resin types has great impact on the properties of the finished coating. For example, aliphatic isocyanates are recommended to make aliphatic polyurethane or polyurea coatings for exterior and above-ground applications because of their UV and weather resistance. Aromatic coatings are often used for interior or underground applications for their chemical resistance and low cost. When certain types of resins are used, varying the type and the degree of branching of the polyols/amine and isocyanates, as well as NCO/OH ratio, a great variety of coating properties can also be obtained ranging from very flexible to hard and brittle films.

The development of polyurethane coatings technology matches the rate of development and commercialization of polyurethanes science and technology. During World War II and the post-war period, various polyurethane products proved to be of great commercial importance, especially in the production of flexible and rigid foams.

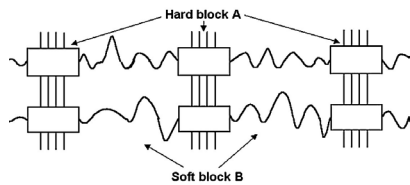


Figure 4: Elastomeric polyurethane coatings.

Since the 1960s, castable polyurethane elastomers have also become widely used, particularly in the automotive industry. Polyurethane adhesives then became accepted in a variety of commercial applications. Finally, polyurethane coatings began to find commercial acceptance but did not enter the mainstream until the 1980s.

As a result, available technology on polyurethane foams is ample and goes back some 50 years. More information is also available with regard to elastomeric polyurethanes. However, developments in polyurethane coatings are relatively recent, and it has been largely up to the coatings manufacturers to develop their own technology, with or without the help of the resin manufacturers.

ASTM has grouped six different polyurethane coating types in the ASTM D16 Standard⁵. Table 1 summarizes the characteristics and properties of the six ASTM polyurethane coating types. Most high solids and 100% solids polyurethane coatings for the purpose of high performance and corrosion protection are designed using the plural component format of the ASTM D16 Type V.

It is not surprising that many earlier or entry-level versions of 100% solids polyurethane coatings have been designed as elastomeric polyurethanes, based on the formulating experiences from castable elastomers and foams that are readily available from polyurethane resin manufacturers, whose main research is focused towards application in automobile and construction industries rather than corrosion protection. One hundred percent solids elastomeric polyurethane coatings are products of

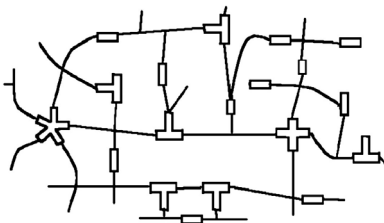


Figure 5: Rigid polyurethane coatings.

the reaction of difunctional isocyanates with long chain difunctional polyols or a mixture of di- and tri-functional polyols, using short-chain difunctional polyols or diamines as chain extenders. The major advantage of 100% solids elastomeric polyurethane coatings is their excellent flexibility, and the major disadvantage is that they are less alkali and solvent-resistant than epoxy, polyester and/or vinyl ester systems⁶. This is often the case as well with other ASTM polyurethane coatings such as moisture-cured polyurethanes, which in general use high molecular weight difunctional polyols and isocyanates. As a result, over a long-term period it has been viewed by some people in the corrosion industry that the general corrosion and chemical resistance of polyurethane is not as great as other corrosion resistant coatings^{6,7}.

Formation of coatings films with superior resistance to abrasion, chemicals and temperature extremes is not impossible. This requires a three-dimensional, cross-linked structure, which can be readily accomplished with the polyurethane technology by employing at least one reactive component that contains three or more reactive groups in the molecule. In many applications, both the isocyanate and polyol reactants can be resins that contain multiple functional groups to form such a highly crosslinked structure. This has resulted in the establishment of 100% solids rigid (or better described as "structural") polyurethane coatings technology.

In North America, 100% solids rigid (or structural) polyurethane coatings were first developed specifically for underground storage tanks in the early 1970s by Madison Chemical

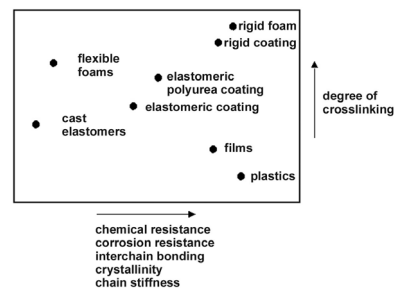


Figure 6: Structure-property relationships in 100% solids polyurethane and polyurea coatings.

Industries, Inc. In 1975, ULC (Underwriters Laboratories of Canada) issued the first listing for cathodically protected steel tanks with a rigid polyurethane coating. In 1981, the same technology was approved for use in the STI-P₃ tank by the Steel Tank Institute (STI). By the late 1980s, 100% solids rigid/or structural polyurethane technology had almost completely replaced coal tar epoxy and other coatings technologies in the North American underground storage tank industry. Since then, this coatings technology has become one of the predominant protective coatings technologies for industries such as water and wastewater pipes, steel storage tanks and large utility power poles.

Because it is not unusual that polyurea linkages would exist in many polyurethane products due to the use of amines either as chain extenders or as resin components to partially or fully replace polyols, the term "polyurethane" or even simply "urethane" is often used to describe any polymer that has been chain extended by reaction with di- or poly-isocyanate including polyurea⁸. As a result, the coatings industry did not differentiate between coating products based on isocyanates/amines and isocyanates/polyols. Coatings systems based on either chemistry or blends were all marketed as "polyurethane coatings." It wasn't until 1989 that Dudley Primeaux of Texaco Chemical Company introduced his concept of 100% solids polyurea spray elastomer coatings⁹, based on Jeffamine polyetheramines from Texaco (now Huntsman).

Since then, the 100% solids polyurea spray elastomers have been promoted as a new coatings technolo-

Resin composition	Elastomeric Polyurea	Class 1 Hybrid Elastomeric	Class 2 Hybrid Elastomeric	Class 3 Hybrid Elastomeric	Elastomeric Polyurethane	Rigid Polyurethane
Isocyanate	Low functional MDI, TMXDI, IPDI or prepolymer	Low functional MDI, TMXDI, IPDI or prepolymer	Low functional MDI, TMXDI, IPDI or prepolymer	Low functional MDI, TMXDI, IPDI or prepolymer	Low functional MDI, HDI, TMXDI, IPDI or prepolymer	Multi-functional MDI, HDI, TMXDI or prepolymer
Main resin	Long chain Di or Tri-functional polyetheramine	Long chain Di or Tri-functional polyetheramine	Long chain Di or Tri-functional polyetheramine	Long chain Di or Tri-functional polyol	Long chain Di or Tri-functional polyol	Multi-functional polyols
Chain Extender	Short chain polyetheramine or DETDA or Unilink	Short chain polyetheramine	Short chain Di or Tri-functional polyol	Short chain polyetheramine or DETDA or Unilink or Clerlink or IPDA	Short chain Di or Tri-functional polyol	Multi-functional polyols
Catalyst	None	None	Yes or none	Yes or none	Yes or none	Yes or none
NCO index	1.05-1.1	1.05-1.1	1.05-1.1	1.05-1.1	1.02-1.20	1.02-1.20
Functionality	2.0-2.2	2.0-2.2	2.0-2.2	2.0-2.2	2.0-2.4	2.4-2.9

Table 2: Chemical compositions of typical 100% solids elastomeric polyurethane, elastomeric polyurea and rigid polyurethane coatings.

gy with the so-called "Polyurea Advantage"¹⁰, and the industry formed its own association as the Polyurea Development Association (PDA) in 2000. PDA is now insisting that for a system to be called polyurea, its amine or polytheramine content must be 80% or more. A product is called a polyurethane when its content of hydroxyl polyol is 80% or more. Between these two parameters, a system can be considered a polyurea/polyurethane hybrid or blend system.

Reddinger and Hillman¹¹ further grouped the hybrid polyurea systems into three different classes: Class 1 or Class 2 hybrid systems use polyetheramine as the main resin component, but use hydroxyl containing polyamine (Class 1) or polyol (Class 2) as chain extenders. Class 3 uses polyols as the main resin component and polyamines as chain extenders.

If these definitions are followed, 100% solids elastomeric polyurea coating products currently available today are almost entirely based on the use of polyetheramines. Jeffamine polyetheramines consist of a family of di- or tri- amine products having repeating polyether back structures such as oxypropylene units, which are functionally terminated with primary amine groups positioned on secondary carbon atoms. Thus, the amine nitrogen is sterically hindered in nucleophilic reactions by the pendant methyl group. Therefore Jeffamine polyetheramines exhibit "moderate" reactivity, which, together with their light color, low viscosity, low vapor

pressure and high primary amine content, provides desirable features in many epoxy and polyurea applications.

Table 2 lists the differences in chemical compositions associated with typical 100% solids elastomeric polyurethane, elastomeric polyurea, and rigid polyurethane coatings.

Structures and Property-Property Relationships

100% solids elastomeric polyurethane coatings. A polyurethane elastomer can be regarded as a linear multi-block copolymer of the type $[AB]_{n>2}$, as shown in Fig. 4. The copolymer has segmented structures consisting of long flexible and rubbery B blocks, known as soft blocks or soft segments (e.g. of polyether or polyester oligomers) joined by the relatively rigid polyurethane-polyurea A blocks, known as the hard blocks (segments) that are mainly made of diisocyanate-extender sequences. The polyurethane linkage is formed if the extender is a polyol, and the polyurea linkage is formed if the extender is an amine. The hard and soft blocks are usually immiscible and tend to associate in different regions or domains. The association of hard blocks from many different chains into rigid domains produces a network structure in the copolymer in Fig. 4.

The properties of the elastomer depend largely on secondary or hydrogen bonding of polar groups in the polymer chains⁸. Hydrogen bonding occurs readily between the NH-groups and the carbonyl groups of the polyurethane-polyurea linkages.

When polyester polyols are used in the coating formulation, hydrogen bonds can be formed between the NH-group of the polyurethane-polyurea linkage and the carbonyl oxygen atoms of the polyester chains. If polyether polyols are used, the ether oxygens of the polyether chains also tend to align by hydrogen-bonding with the NH-groups; however, these hydrogen bonds are much weaker.

The hard blocks and especially the stiff polyurea hard blocks have stronger secondary bonding, often agglomerating into hard block domains in the structures that have long flexible chains. The strength of these secondary and hydrogen bonds is not strong, resulting in the relatively poor chemical resistance of many elastomeric polyurethane coatings. Many aromatic moisture-cured and elastomeric polyurethane coatings available in the market use high molecular weight and long chain polyether polyols to achieve their elongation or flexibility, which further reduces the chemical resistance of the coatings.

Coatings chemists at Madison Chemical and research scientists at ICI Polyurethanes¹² both found that adhesion of 100% solids polyurethanes to a substrate can be significantly decreased as their molecular weight and the length of the soft block chains increases, affecting their ability to provide corrosion protection. This finding is consistent with the fact that many elastomeric polyurethane coatings available in the market require a primer to achieve their adhesion and protective properties.

100% solids elastomeric polyurea coatings. In general, the hard and soft block structure illustrated in Fig. 4 for elastomeric polyurethanes can also be applied to the 100% solids elastomeric polyurea coatings¹⁰. The diisocyanate component functions as the system's rigid "hard block," while the Jeffamine polyetheramine segments are "soft blocks." Specialty amines generally possess soft, flexible polyoxypropylene backbones that significantly contribute to the hydrophobic/waterproof nature of the respective polyurea coatings. The C-N bonding in the polyurea structure is stronger than the C-O bonding in a polyurethane elastomer, resulting in generally better thermal stability of the polyurea elastomer. As a result, 100% solids polyurea systems have higher heat resistance, heat distortion resistance and heat sag properties than comparable elastomeric polyurethanes. However, it is difficult to make the comparison between the elastomeric polyurea and rigid polyurethanes because of different polymeric structures.

100% solids rigid (or structural) polyurethane coatings. In a 100% solids rigid polyurethane system, both the isocyanate and polyol reactants are resins that contain multiple functional groups to form a highly crosslinked structure. In contrast to the secondary and hydrogen bonding of elastomeric polyurethanes, rigid polyurethanes have a high density of covalent cross-linking as shown in Fig. 5, which is significantly stronger than hydrogen and secondary bonding. This is achieved by the use of multifunctional polyols, amines and isocyanates, as well as by the better arrangement of the polymer's chain orders, NCO:OH index, and molecular weight of polyols or extenders.

Increasing the density of cross-linking also causes a significant increase in the glass transition temperature (T_g) of these rigid polyurethane coatings. This results in many changes in their physical properties: increased hardness, tensile strength and modulus, dielectric strength, cohesive strength, thermal resistance and chemical resistance; and decreased

elongation; coating tackiness, solubility and permeability.

The better arrangement of the polymer's chain orders, NCO:OH index and molecular weight of polyols or extenders can impact the coating's adhesion, reactivity, recoatability and curing properties. The end result of these changes is greatly improved polyurethane coating systems which not only have excellent chemical and corrosion resistance but also possess superior physical properties and resilience that could match the requirements of being a structural material by their own. Hence 100% solids rigid polyurethane coatings can also be described as "structural" polyurethane coatings.

Fig. 6 illustrates the structure-property relationships in 100% solids polyurethane and polyurea coatings, compared with other common polyurethane products. The question remains whether the development of a limited degree of crosslinking in 100% solids elastomeric polyurethane or polyurea coatings is desirable so that improved mechanical strength and chemical and corrosion resistance can also be achieved for the elastomers as in the case of rigid polyurethanes. Increased chemical crosslinking, however, can interfere with the formation of the domain network structure of the $[AB]_{n>2}$ as shown in Fig. 4. That is primarily responsible for the flexible, rubber-like and high elongation properties of the elastomeric polyurethanes¹³.

Earlier studies of Pigott and coworkers¹⁴ indicated the existence of a minimum in the tensile modulus of polyester-polyurethane elastomers as a function of cross-linking density. Only below the M_c (molecular weight per cross-link) corresponding to the minimum cross-link could properties improve. Beyond this point, improvements can only be made due to a better-segmented structure in the polymer.

These influences were confirmed in 100% solids elastomeric polyurethane coatings for corrosion protection through the work at Madison Chemical¹⁵. In the case of elastomeric polyurea coatings, it was found that

with increasing functionality of the polyurea system, the cross-link efficiency was lost and as a result, improvements on physical and chemical resistance properties were not obtained. It was then suggested that in a typical formulation with a gel time of two to four seconds, a functionality of 2.2 or below should be taken¹⁶.

Performance and Application Properties

The chemistry and structural differences between 100% solids elastomeric polyurethane, elastomeric polyurea and rigid/structural polyurethane coatings result in significantly different performance and application properties.

The key feature of the elastomeric polyurea coatings technology is that the amine/diisocyanate reaction is almost instantaneous (typical gel time three to 10 seconds), without the use of a catalyst as in the case of many elastomeric polyurethane coatings. This reaction is normally faster than the diisocyanate can react with moisture or water, which produces carbon dioxide bubbles. This feature gives an advantage to the application of the polyurea coatings in high-humidity climates or regions and is also helpful if a substrate is moist.

The polyurea coatings are not sensitive to moisture and humidity and do not normally produce coating defects associated with moisture such as bubbles, foaming and moisture-caused blisters. However, it is important to note that to achieve long-term corrosion protection, it is not recommended to apply any coating system over wet or moist substrate unless it is properly primed to ensure the proper substrate adhesion of the coating. While trapped moisture will not react with the coating as it sets, it will impair adhesion and lead to premature failure. It is also important to understand that a high tolerance of ambient moisture can be achieved with properly designed 100% solids elastomeric and rigid polyurethane coatings.

The lack of a catalyst for curing or the auto-catalytic nature of the 100% solids elastomeric polyurea coatings may give them improved performance

	100% solids elastomeric polyurethane coating	100% solids elastomeric polyurea coating	100% solids rigid polyurethane coating
Tensile strength, psi	1,000 – 2,000	1,100 – 4,000	3,500 – 7,000
Shore Hardness	A20 to D65	A20 to D65	D50 – D90
Elongation, %	50 – 1,500%	20 – 1,000%	3 – 50%
100% Modulus, psi	300 – 1,000	500 – 2,000	800 – 3,500
Tear strength, pli	350 – 700	250 – 600	200 – 500
Taber abrasion resistance (CS17, 1 Kg, 1000 cycles), after 3 hours of initial curing	60 – 200 mg weight loss	40 – 300 mg weight loss	40 – 80 mg weight loss 20 – 40 mg weight loss* * ceramic modified
Taber abrasion resistance (CS17, 1 Kg, 1000 cycles), fully cured	2 – 40 mg weight loss	6 – 70 mg weight loss	30 – 60 mg weight loss 10 – 30 mg weight loss* * ceramic modified
Impact resistance after 3 hours of initial curing, 40 mils (1 mm) DFT	60 – 150 in.lbs	5 – 35 in.lbs	25 – 120 in.lbs 40 – 150 in.lbs* * ceramic modified
Impact resistance, fully cured, 40 mils (1 mm) DFT	80 – 200 in.lbs	60 – 200 in.lbs	30 – 125 in.lbs 45 – 160 in.lbs* * ceramic modified
Water absorption (ASTM 570, immersed in water for 48 hours at 50°C/122°F)	5 – 15%	5 – 16%	1-2%
Chemical resistance (ASTM D716, 1,000 hours immersion)	20% NaOH 10% H2SO4 25% H2SO4 3% NaCl Gasoline Toluene	Pass Pass Fail Pass Fail Fail (significant swelling <24 hours)	Pass Pass Pass Pass Pass Pass
Cathodic disbondment (ATM G95, 3% NaCl, -1.5 volts, 30 days, 23°C)	10 mm to 35 mm disbonding radius	25 mm to 38 mm disbonding radius	3 mm to 15 mm disbonding radius
Adhesion to steel (SP10, 2 mil profile), psi	700 – 2,200	500 – 2,000	1,000 – 4,000
Adhesion to concrete, dry, no primer, psi	> 350 Concrete failure	>350 Concrete failure	>350 Concrete failure

Table 3: Performance characteristics of typical 100% solids elastomeric polyurethane, elastomeric polyurea, and rigid (or structural) polyurethane coatings.

when exposed to UV light or high temperatures because a catalyst in the system would promote polymer degradation under these conditions. Physical property retention in weathering applications of an aliphatic polyurea could be better than an aliphatic polyurethane if the polyurethane system is overly catalyzed. In typical aromatic elastomeric polyurea systems, however, it was found that the polyetheramine and other amine reactants have a tendency to yellow slightly more than the hydroxyl polyol-based polyurethanes.

There are several weak areas associated with the 100% solids elastomeric polyurea coatings and their extremely fast reactivity. These areas are important for corrosion protection,

thus demanding special attention from coating formulators, applicators and inspectors.

• *Application/equipment friendliness:* Because of high curing speed and very short mixing time, it is more difficult to achieve proper mixing and atomization of the polyurea technology compared with polyurethanes, which is essential for plural component systems in order to eliminate coating defects and produce the designed properties for a specific application. To overcome this problem, better formulating is required to reduce the viscosity of the individual components and the initial mix viscosity of the system for spray. This can be achieved by modifying the diisocyanate-rich component with non-

VOC reactive diluents, e.g., propylene carbonate⁹, or by developing new and lower viscosity isocyanate prepolymer, e.g. MDI-prepolymers with higher 2,4'-isomer content¹⁶.

The use of higher temperature, higher pressure and more elaborate impingement mix spray equipment is often needed to help the situation. In other words, optimum performance of both formulation and equipment operation configurations is always required for the polyurea, which is not easily obtained, especially in field applications where application and equipment conditions are difficult to control. For example, experiments have proven that polyurea films produced at 65°C, 70°C, and 80°C have different properties and that these improve with increasing temperature¹⁶. Handling and maintaining such high temperatures is not an easy task in field applications. Common defects associated with improper mixing of the polyurea system are uneven color, blisters, pinholes, uneven cured sections, poor initial film properties and most commonly a rough orange peel texture on the surface.

• *Surface wetting:* From the chemical structural point of view, the elastomeric polyureas do not have any additional adhesion characteristics compared with a polyurethane elastomer. However, surface wetting has been a long time problem linked to the development phase of the polyurea coatings with the use of extremely fast spray systems, due to having less time for the coatings to flow into the surface profile of a prepared but unprimed substrate. Newly developed system formulations help out the situation, and good experimental results of initial adhesion values were reported¹⁷⁻¹⁸, especially with aliphatic polyurea systems due to the relatively slower reactivity between aliphatic isocyanates-amines and aromatic isocyanate-amines. However, while the adhesion of the elastomeric polyurea may be adequate in non-critical applications, a primer is necessary for immersion applications or dynamic applications like abrasion resistance. Performance enhancements of aro-

	100% solids elastomeric polyurethane coating	100% solids elastomeric polyurea coating	100% solids rigid polyurethane coating
Application temperature	-20°C to 65°C (-13°F to 150°F)	-40°C to 50°C (-40°F to 122°F)	-40°C to 65°C (-40°F to 150°F)
Initial curing time	10 minutes to 2 hours @23°C/73°F	3-120 seconds @23°C/73°F	30 sec. to 45 minutes @23°C/73°F
Cure to handle time	1-12 hours @23°C/73°F	1-3 hours @23°C/73°F	1 minute to 1.5 hours @23°C/73°F
Recoat time	30 minutes to 24 hours @23°C/73°F	1 minute to 12 hours @23°C/73°F	5 minutes to 8 hours @23°C/73°F
Cure to dry service	3 to 36 hours @23°C/73°F	2-5 hours @23°C/73°F	10 minutes to 4.5 hours @23°C/73°F
Cure to immersion service	12 hours to 7 days @23°C/73°F	12 - 48 hours @23°C/73°F	45 minutes to 48 hours @23°C/73°F
Ultimate cure	7-10 days @23°C/73°F	7-10 days @23°C/73°F	5-7 days @23°C/73°F
Service temperature, dry	-30°C to 80°C (-34°F to 182°F)	-45°C to 150°C (-42°F to 302°F)	-40°C to 125°C (-40°F to 250°F)
Service temperature, wet	-30°C to 50°C (-34°F to 122°F)	-45°C to 150°C (-42°F to 302°F)	-40°C to 90°C (-40°F to 195°F)
Typical dry film thickness requirements for service on a steel substrate	30 to 60 mils (0.76 mm to 1.5 mm)	40 to 60 mils (1 mm to 1.5 mm)	15 to 30 mils (0.38 mm to 0.75 mm)
Typical dry film thickness requirements for service on a concrete substrate	60 to 150 mils (1.5 mm to 3.8 mm)	60 to 150 mils (1.5 mm to 3.8 mm)	40 to 80 mils (1 mm to 2 mm)
Application methods	Spray, cast, trowel, roller, brush, pour	Spray, pour	Spray, cast, trowel, roller, brush, pour
Spray gun type	Plural or single component, static mixer or whip hose mixing possible	Plural component direct impingement, no static mixer	Plural or single component, static mixer or whip hose mixing possible
Spray pump	Plural component	Plural component	Plural component
Humidity sensitivity	Sensitive to little sensitive	Insensitive	Sensitive to insensitive
Requirement for perfect equipment operating	Important	Very critical	Important
General surface finish	Smooth to glossy to smooth	Orange peeling look	Smooth to glossy

Table 4: Application characteristics of typical 100% solids elastomeric polyurethane, elastomeric polyurea and rigid (or structural) polyurethane coatings.

matic elastomeric polyurea spray coatings through the use of primers were recently studied by A. Perez and C. Shen¹⁹.

- *Film property development:* Although it has extremely fast reactivity in the absence of any catalyst, the current elastomeric polyurea coatings technology does not have fast film property development ability. In contrast to polyurethanes (particularly rigid polyurethanes), it takes the elastomeric polyurea coating significantly longer to reach its physical properties before it can be handled. This limits the application of the 100% solids elastomeric polyurea technology. An example of this limitation is external coat-

ings for pipes. Because of the pipe's weight, a coating needs to be sufficiently cured before the pipe is stored, transported, and installed. Other applications will be freight ship liners, train wagon liners and heavy-traffic industrial floors, where the need of quick cure time is crucial to put the product on transport or back into service.

The lack of fast film property development of 100% solids elastomeric polyurea is caused by the high internal stress build-up during the initial phase of curing due to high reactivity¹⁶. The stress has a negative influence on the development of physical properties of the coating such as

impact resistance, initial adhesion, abrasion resistance, etc., and the coating needs time to relax from such high initial stress build-up.

- *Minimum film thickness:* Because the development of physical properties is often very dependent on the temperature of the coating during the first few moments of cure, a film build of 40 mils (1 mm) or more in a single coat is typically required in order for 100% solids elastomeric polyurea coating to cure properly. Failing this, the physical properties may be severely compromised. So long as the film build is achieved or exceeded, the polyurea will develop sufficient exothermic heat to cure properly, regardless of ambient temperature.

In general, the chemical resistance of 100% solids elastomeric polyurethane and polyurea coatings is very similar to one another, but neither is comparable to the chemical resistance of 100% rigid/structural polyurethane coatings. Elastomeric polyurethane and polyurea coatings are resistant to diluted acids, alkali and salt solutions. When exposed to organic solvents and oils, the elastomeric polyurea systems tend to swell significantly more than the elastomeric polyurethanes⁴. To compensate for the difference in chemical resistance, application of 100% solids elastomeric polyurethane and polyurea coatings at a dry film thickness of less than 40 mils (1 mm) is not recommended. In contrast, most 100% solids rigid polyurethane coatings have been used as a primary lining material for aggressive chemicals such as toluene, crude oils, saturated NaOH solution and 25% H₂SO₄ at a dry film thickness of less than 20 mils (500 microns).

Table 3 and Table 4 compare the performance and application properties of typical 100% solids elastomeric polyurethane, elastomeric polyurea, and rigid (or structural) polyurethane coatings, which are currently available from the market. It is important to note that new product developments have been continuously achieved, and as a result, the above commentary can only be used as a

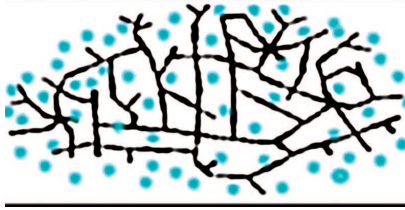


Figure 7: Ceramic modification on 100% solids rigid polyurethane coatings.

general comparison based on the current and commercialized systems. End users are encouraged to consult with coatings manufacturers and suppliers for actual product properties and application recommendations.

Coatings Selection Guideline and Application

When it comes to selection of a coatings system, it is important to understand that if optimum performance as well as cost/performance balance is needed, one product or one technology cannot always be used as a universal solution. It is also important to understand that there is no such thing as a "miracle" coating product or coating technology, because each chemistry or system will have its advantages and disadvantages. It would be a huge mistake for a coatings manufacturer, a specifying engineer, an applicator or an end user to limit himself to a single chemistry or specific coating type.

These considerations should also be applicable to 100% solids elastomeric polyurea, elastomeric polyurethane and rigid polyurethane. As discussed previously, there are differences and similarities among these three systems. In general, all three technologies fit the description of a system that is 100% solids, solventless, fast cure and curable at low/cold temperatures, pigment compatible, tough, reinforcing and exhibit excellent physical properties and formulation flexibility. However, each of the three has specific areas where their properties excel, and it is up to the end user, with the help of the coating manufacturer, to select and decide whether an elastomeric polyurea or elastomeric polyurethane, or a rigid polyurethane is the best choice for an application. A

manufacturer who offers all these technologies will be able to provide unbiased advice with regard to the relative merits for a particular end use.

The first important consideration in selecting a suitable polyurethane/polyurea coating for corrosion protection is to decide if aliphatic polyurethanes or aromatic polyurethanes should be used. Aliphatic polyurethanes/polyureas are more expensive but provide the best UV resistance and color stability among all types of industrial coatings. They are, therefore, often used for exterior applications and any other places where color stability is concerned. Aromatic polyurethanes/polyureas are less expensive and often used for interior or underground applications. Depending on their formulation design, aromatic polyurethanes/polyurea will exhibit a certain degree of yellowing after a few days/months of UV exposure. However, their UV resistance is generally better than that of common epoxies. Most 100% solids polyurethane/polyurea coatings available today are aromatic.

The second important consideration is whether an elastomeric polyurethane/polyurea or a rigid polyurethane coating should be used. The properties of 100% solids polyurethane/polyurea coatings vary from very soft, rubbery elastomers (like running shoe soles) to hard, ceramic-like systems. A good chemist can formulate the 100% solids polyurethane/polyurea to do almost anything. Chemical bonds in the more rigid systems are highly crosslinked to each other to create hard, dense systems that have very good chemical and moisture resistance. Rigid systems usually have excellent adhesion and are the best choice for the corrosion protection of metals, particularly for immersion service.

On the other hand, elastomers have a more linear structure with much less cross-linking that allows them to be very stretchy and elastic. These systems normally have great abrasion resistance, impact strength and flexibility but relatively poor adhesion and chemical resistance. Elastomers are well suited to protecting concrete

because of its tendency to crack, but they do work reasonably well on metallic substrates for non-immersion or dry services. The lower chemical and corrosion resistance of the elastomers may be compensated for to a certain extent if the systems are applied relatively thickly. As a result, 100% solids elastomeric polyurethane or elastomeric polyurea coatings are excellent choices for dry contact hopper car linings, truck bed liners, concrete secondary containment applications, concrete basins, concrete slurry holding fields, concrete waterproof applications, and architectural construction applications where the cost of a thick film system can be justified.

On the other hand, 100% solids rigid/structural polyurethane coatings will be the technology of choice for heavy-duty, sub-immersion and immersion services as a primary coating or lining material. These include pipe lining and coating, primary tank lining, underground structure corrosion protection, marine piling and infrastructure protection in harsh, industrial or marine environments. Applications requiring quick cure-to-handle time of the coating system and fast film property development would also demand the use of 100% solids rigid/structural polyurethane coatings. Some of these are freight ship liners, train wagon liners and heavy pipe lining/coatings.

While both 100% solids elastomeric polyurethane and 100% solids elastomeric polyurea are flexible and often used in similar applications, consideration can also be made to select the best system between the two based on their performance and application differences. For example, a 100% solids elastomeric polyurethane coating would be a better choice if a smooth gloss finish and good adhesion is needed during application in a hot summer, because a 100% solids polyurea coating would set too fast to have proper wetting into the substrate and would produce orange peel texture. On the other hand, a 100% solids elastomeric polyurea is better suited when applying the coating system to a heat sink substrate such as cold steel



Figure 8: The application of a highly abrasion resistant 100% solids rigid polyurethane lining on a 36" steel pipe for extremely high water flow rate.

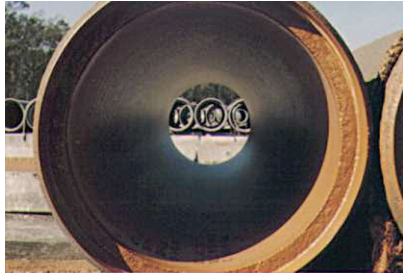


Figure 9: The application of a 100% solids elastomeric polyurethane system (both ceramic and anti-microbial modified), for a wastewater pipeline project involving the lining for 4,000' long, 72" diameter-size concrete pipes.

because of its autocatalytic nature.

When applying a system for a concrete secondary containment containing many organic solvents and oils, a 100% solids elastomeric polyurethane would perform better than a 100% solids elastomeric polyurea. Applications such as waterproofing membranes often require a low modulus and a high elongation elastomer; in this case, a 100% solids elastomeric polyurethane would be a better choice because they typically have lower modulus than elastomeric polyureas. Finally, if application under high humidity conditions and/or the quick completion of the work is required, a 100% solids elastomeric polyurea coating would be the product of choice.

The third consideration is the mixing ratio format of the selected polyurethane or polyurea coating system. The best 100% solids plural-component polyurethane coatings are the ones that are in a 1:1 mixing ratio. This is because isocyanates and polyols/ amines in a 100% solids polyurethane or polyurea system are reacted normally at around the ratio range of 1:1, which is the easiest way

to configure the set up from the application perspective²⁰. A 100% solids polyurethane or polyurea coatings system with a mixing ratio other than 1:1 will have a greater chance to cause mismetering problems (often called off-ratio) during its application. The greater the ratio differential is, the higher the possibility it will occur. This is particularly the case with many polyurea systems when their mixing time is very limited.

Finally, considerations should be made towards the cost of the coatings system selected. The cost premium of a "pure" elastomeric polyurea system over an elastomeric or rigid polyurethane correlates to the use of the polyetheramines, which are more expensive than most polyols. The raw material cost of a general aromatic polyurethane system is about double that of the polyols used. Therefore, if a company supplies a coating of low material price and still claims the coating system is a "polyurea," make sure it is not a polyurethane with zero percent or a few percent of polyetheramines. For the same reason, 100% solids elastomeric or rigid polyurethane coatings normally keep a better cost/performance balance than 100% solids elastomeric polyurea coatings.

Continuous R&D development on 100% solids polyurethane and polyurea coatings technology may have an impact on these general guidelines and alter recommendations over time. For example, recent developments in 100% solids polyurethane/polyurea coatings technology have resulted in several new innovations. One involves the modification of 100% solids polyurethane or polyurea coatings by using fine ceramic microspheres. The modification of 100% solids rigid polyurethanes in this manner could lead to the improvement of their abrasion and impact resistance to reach the same level of that possessed by an elastomeric polyurethane or polyurea system (Fig. 7 and Table 3).

While 100% solids rigid polyurethanes feature excellent abrasion resistance compared with common



Figure 10: The application of the 100% solids rigid aliphatic polyurethane on a galvanized steel communication tower.

corrosion resistant coatings such as epoxies and polyesters, applications involving extremely high flow rates and unusually abrasive instances demand more. Newly developed ceramic modified 100% solids rigid polyurethane coatings are engineered to meet the challenge of highly abrasive or high-flow applications, offering unbelievable durability and impact resistance, accompanied by high corrosion and chemical resistance. Another innovation involves the development of a 100% solids polyurethane/polyurea coating by incorporating a non-leachable anti-microbial additive. With the anti-microbial fortification, 100% solids polyurethane or polyurea coatings can offer long-term corrosion protection by modifying the environment while protecting the substrate from microbiologically influenced corrosion.

Perhaps one of the most exciting and newest developments is 100% solids, rigid, UV- and color-stable, aliphatic polyurethane coating technology, which has been developed over the past five years. Compared with 100% solids elastomeric aliphatic polyurethane and polyurea systems, this rigid aliphatic polyurethane technology provides much better adhesion over non-primed steel or galvanized surface (>1,500 psi), faster initial film property development and superior corrosion and chemical resistance.

Making the Right Choice

Both 100% solids polyurethane and polyurea coatings technology are

becoming the fastest growing technology of choice in a number of end industries. There are significant differences and similarities between the 100%

solids elastomeric polyurea, elastomeric polyurethane and rigid (or structural) polyurethane coatings systems in terms of chemistry, structure, physical and chemical properties and application characteristics. In general, all three technologies fit the description of a system that is 100% solids, solventless, fast cure and curable at low/cold temperatures, pigment compatible, tough and reinforcing, while offering excellent physical properties and formulation flexibility. However, each has specific areas where their properties excel. End users need to select and decide whether an elastomeric polyurea, elastomeric polyurethane or a rigid (or structural) polyurethane is the best choice based on the requirements of achieving optimum performance and the cost/performance balance. ●

References

1. M. Agosta, *Polyurethane Technology*, *Coatings World*, June 2002, p. 36
2. O. Bayer, H. Rinke, W. Siefken, L. Ortner and H. Schild, German Patent 728,981 (to I.G. Farbenindustrie), 1942
3. O. Bayer, *Angew. Chem.* A59, 1947, p. 257
4. Futura Coatings Inc., *The Truth and Myths of Polyurea*, 2001
5. ASTM, *Standard Terminology for Paint, Related Coatings, Materials, and Applications*, D16-00
6. NACE International, *Standard Recommended Practice for Lining Over Concrete for Immersion Service*, RP0892-92, 1992, p. 6
7. C.G. Munger, *Corrosion Prevention by Protective Coatings*, NACE International, 1986, p.112
8. G. Woods, *The ICI Polyurethanes Book*, 1990
9. D.J. Primeaux II, *Spray Polyurea-Versatile High Performance Elastomer for the Polyurethane Industry*, *Polyurethane '89*, The SPI 32nd Annual Technical/Marketing Conference, p.126-130
10. Huntsman, *Polyurea Spray*, 2001, p.2
11. J.L. Reddinger and K.M. Hillman, *Polyurea Spray Elastomers: An Overview of Current Technology*, *Polyurethane '2001*, September 30-October 3, Columbus, OH, 2001
12. Unpublished notes of group discussions between Madison Chemical and ICI Polyurethanes, 1993/5
13. R. E. Camargo, *Kinetics and Phase Segregation Studies on the RIM Polymerization of Urethane Elastomers*, Ph.D. Thesis, University of Minnesota, 1984, p. 66
14. K.A. Pigott, et al., *Development of Cast Urethane Elastomers for Ultimate Properties*, *J.Chem. and Eng. Data*, 5, 1960, p. 391
15. S. Guan, *Development of Advanced 100% Solids Elastomeric Polyurethane Coatings - Flexcel II and Flexcel II TX (Madison Chemical)*, unpublished, 1994-1998
16. Marc, Broekaert, *Polyurea Spray Coatings: The Technology and Latest Developments*, *Human Polyurethanes*, 2002
17. D.J. Primeaux II, *Polyurea Spray Technology in Commercial Applications*, *The Proceedings of The 60 Years of Polyurethanes*, edited by J. Kresta, E. Eldred, Technomic Publishing Co. Ltd., 1998, p. 228
18. D.J. Primeaux II, *Application of 100% Solids, Plural Component Aliphatic Polyurea Spray Elastomer Systems*, *The Proceedings of SSPC 2000*, Nashville, Tennessee, November 12-16, 2000, p. 95
19. A. Perez, Jr. and C. Shen, *Performance Enhancements of Aromatic Polyurea Spray Coatings by the Use of Conventional Primer Systems*, *Huntsman*, 2001
20. S. Guan, *The Selection, Application, and Inspection of 100% Solids Polyurethane Coatings for Corrosion Protection*, *The Proceedings of SSPC 2000 the Industrial Protective Coatings Conference*, November 12-16, 2000, Nashville, TN.

This paper was presented at The 2nd China International Corrosion Control Conference, held in Beijing, People's Republic of China, November 4-8, 2002.

Register Now!

2003 Coatings Science Short Course Series and On-line Offerings

Six courses to meet your needs:

- March 10-13, 2003** • Practical Emulsion Polymerization Technology
- Powder Coatings Science and Technology
- May 19-22, 2003** • Coatings Science for Coatings Technicians
- Introduction to Coatings Science
- June 9-12, 2003** • Coatings Science for Coatings Formulators
- Coatings Science for Coatings Chemists

These courses will be at the Shelby Freland Thames Polymer Science Research Center on USM's campus at Hattiesburg, Miss. Short courses are four (4) days, Monday through Thursday, 8 a.m. to 5 p.m. Please refer to course description on our web site for more details.

Dr. Shelby F. Thames, Series Director

For further information contact Debbie Witherby

The University of Southern Mississippi • School of Polymers and High Performance Materials
Box 10037 • Hattiesburg, MS 39406-0037

E-mail: Deborah.Witherby@usm.edu • Phone: (601)-266-5618 • Fax: (601)-266-5880

ON-LINE

April 3rd, 2:00 p.m. EST - 2-hour course on "Introduction to Polymer Science in Coatings" (chemistry background is not necessary) Lecture and Round Table Discussion by the Thames Research Group, \$295.00 (one fee per location and course, regardless of the number of participants)

WWW.COATINGS SCIENCE.COM