

# **Polyurea Elastomer Technology: History, Chemistry & Basic Formulating Techniques**

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## ***Abstract:***

The *polyurea* elastomer coating / lining technology has shown some very significant inroads since the introduction of the technology back in the late 1980's. Initially, the *polyurea* technology had set itself in a different class of coating / lining systems as compared to conventional urethane coating / lining systems. This has been primarily due to the unique characteristics of the technology, both in processing and performance. However; over the years there has been a melding of the various technologies, and many have now classified or implied that *polyureas* are the same as urethane and/or urethane/urea systems. There is now a new class of *polyurea* systems that have different processing characteristics and some feel that these are not *polyurea* systems at all. "They can't be" people say since you don't need the high-pressure plural component processing equipment for application. This has led to some reluctance on the part of engineers and specifiers to confidently specify *polyurea* systems for projects. As a result, there has been some major confusion as to what classifies a system as a *polyurea* and, what is not. This paper will take a look at the *polyurea* technology, formulation basics; and, compare that to what a polyurethane and polyurethane/polyurea system is, along with some performance issues.

## **INTRODUCTION:**

Two-component polyurea elastomeric coating / lining systems are the newest technology to the protective coating / lining industry. Polyurea systems have sometimes been characterized as modified two-component polyurethane systems. While they both may have some characteristics in common, polyurea systems are actually a unique technology in itself.<sup>1</sup>

Two-component polyurea systems are typically known for a very rapid dry time (typically less than 30 seconds), achieved without the use of a catalyst as in the two-component polyurethane systems. This rapid dry time is very consistent / uniform over a very broad ambient temperature range. While the fast reaction / rapid dry time is virtually unaffected by ambient moisture, the presence of moisture on a substrate must be

considered when achieving adhesion to that substrate. This is all made possible by a unique chemistry of raw materials used to develop the two-component polyurea systems.

Two-component fast set polyurea systems typically do not contain any solvent or Volatile Organic Compounds (VOC). They are normally processed by specialized plural component equipment, which develops high pressure and high temperature for spray application. The two components are mixed inside the impingement mix spray gun, as there typically is not any pre-mixing or hot potting.

Since the introduction of the two-component polyurea technology, a wide variety of applications are seen. These include coating / lining applications over concrete, geotextile membranes, various metals for corrosion and decorative areas as well as some plastics. For all of these, the rapid dry time of the technology means that the area of application can be returned to service rather quickly.

Polyurea systems with a slower / modified reactivity and set time are also finding use in joint sealant / filler system applications. Here the material is combined in low pressure, low temperature via “folding” in a static mix tube and applied as a bead of material.

In 2000, the Polyurea Development Association prepared and published a definition of polyurea systems. That is identified as follows:

“A *polyurea* coating / elastomer is that derived from the reaction product of an isocyanate component and a resin blend component. The isocyanate can be aromatic or aliphatic in nature. It can be monomer, polymer, or any variant reaction of isocyanates, quasi-prepolymer or a prepolymer. The prepolymer, or quasi-prepolymer, can be made of an amine-terminated polymer resin, or a hydroxyl-terminated polymer resin.

The resin blend must be made up of amine-terminated polymer resins, and/or amine-terminated chain extenders. The amine-terminated polymer resins will not have any intentional hydroxyl moieties. Any hydroxyls are the result of incomplete conversion to the amine-terminated polymer resins. The resin blend may also contain additives, or non-primary components. These additives may contain hydroxyls, such as pre-dispersed pigments in a polyol carrier. Normally, the resin blend will not contain a catalyst(s).”

Well, that is a mouthful and what does it all mean? This paper will attempt to present a basic overview of the technology and is not meant to be a complete chemistry / technology lesson on polyureas, hybrids and polyurethane systems.

## **A BRIEF HISTORY of POLYUREA DEVELOPMENT:**

The first actual reference to polyurea came in 1948 when some researchers were evaluating thermal properties / melting points of various polymer systems.<sup>2</sup> They were comparing polyesters, linear polyethylene, polyurethanes, polyamides and polyureas; and, found that the polyureas had far superior thermal properties and an extremely high

melting point. Keep in mind that these polymers were manufactured in a laboratory environment and were not very conducive to coating / lining applications. Figure 1 is a graphical depiction of the melting points of various polymers for comparison.

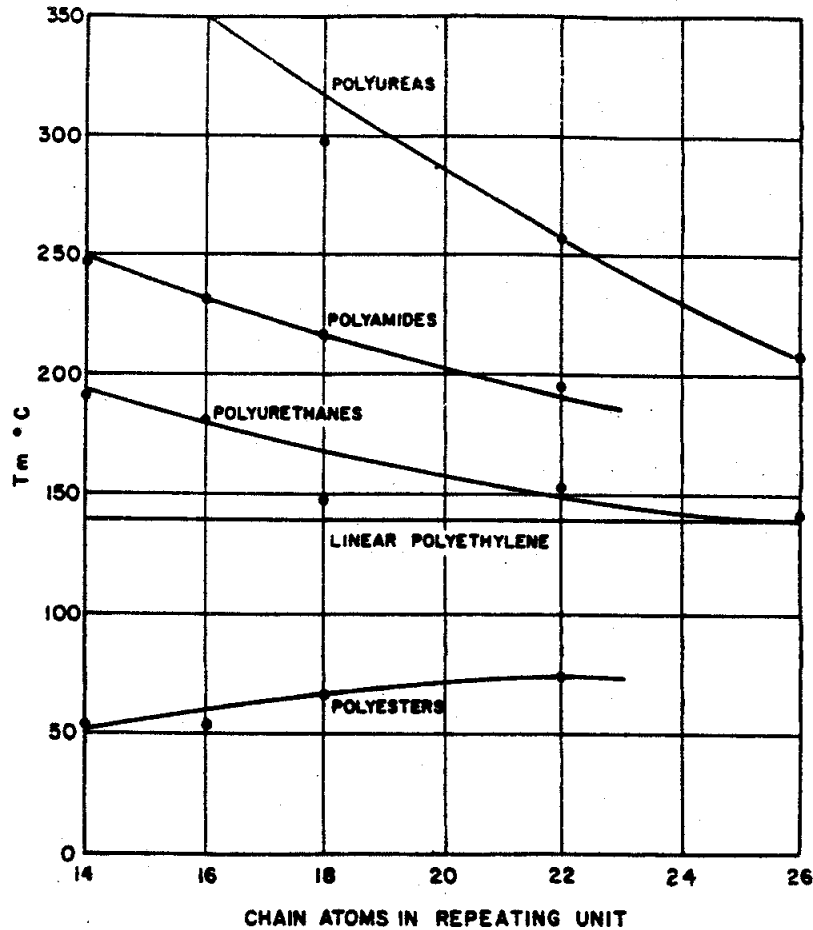


Figure 1: Trend of Crystalline Melting Points in Homologous Polymer Chains

The two-component polyurea elastomeric coating / lining technology is a derivation of the polyurea Reaction Injection Molding (RIM) technology developed in the early 1980's.<sup>3</sup> Polyurea RIM was used to produce a variety of automotive exterior body panel and fascia (bumper covers) parts. The most noted use was in the Pontiac Fiero, which employed the space frame concept. Other parts included fascia for the Camaro, Firebird / TransAm, Corvette, Pontiac Bonneville and GrandAm, and rear quarter panels / fenders for the dually trucks, like Ford, Dodge and GM.

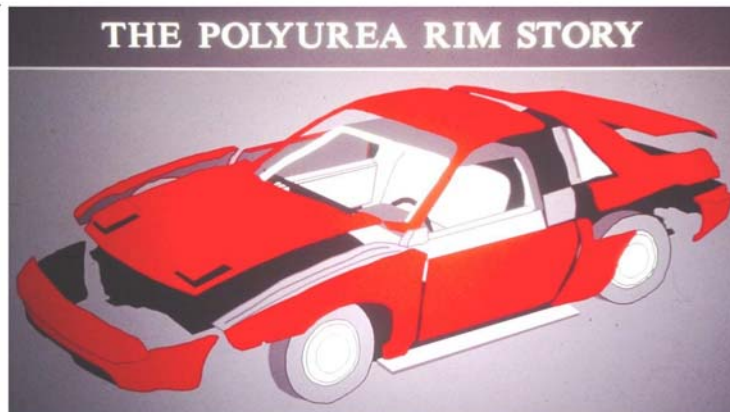


Figure 2: Polyurea RIM

The advantages or unique characteristics of polyurea over polyurethane and polyurethane/polyurea hybrid system in RIM applications included rapid molding / cure time which was typically 2 – 3 second set or gel times with a dry time of less than 10 seconds. Also realized was reduced part scrap rate and most importantly, the ability to paint the parts using the online Electrophoretic Paint Deposition (ELPO) process. This process involved heating the parts to almost 400°F (205°C), a temperature that was very detrimental to a polyurethane and most hybrid systems. Polyurea systems are noted for their high thermal stability.

The two-component fast set polyurea coating / lining technology was first introduced to the industry in 1988, following the development in 1986.<sup>4,5</sup> This technology evolved from the need to develop a more stable, durable and 100% solids polymer system for coating rigid, spray applied polyurethane foam used in roofing and other insulation applications. Some of the first plural component spray applied polyurea formulations had get times of 1 – 2 secs, with tack free of < 10 secs. The actual first commercial application of the polyurea elastomeric coating / lining technology was as a roofing system in 1989.

However, this was not the first actual work with the spray applied two-component polyurea technology. Earlier work in the 1970's utilized modified polyamines and high levels of plasticizers and solvents to achieve a sprayable system for coating work.<sup>6</sup> While this proved successful in laboratory applications, poor field performance was noted and this technology never gained acceptance.

A unique, solvented polyurea / epoxy / urethane hybrid type system was also utilized in the 1970's for production of a composite traction system.<sup>7</sup> Other uses included temporary shelters, roofing and blast protection. This was not a true *polyurea* system though.

In 1998, the National Association of Corrosion Engineers (NACE) issued a Technical Report on polyurea systems in an attempt to give an initial description / comparison of polyureas to polyurethanes.<sup>8</sup> This document gives a very general view of the technology, with limited basic details as to the chemistry involved.

## POLYUREA CHEMISTRY / FORMULATION:

Since we have been focusing our efforts on defining the technology, we need to identify what part of the technology / reaction we are looking to that classifies whether a *polyurea* or not. The consensus seems to be that we are looking at a 2-part processed system, whether it was spray, caulk, pour or RIM processed. Therefore, the identifying reaction would be the reaction that takes place between the 2-part system, i.e. the reaction of the polyisocyanate component and the resin blend component. This would be the polymerization / curing part. This is a thermoset reaction.

The main distinguishing characteristic with the polyurea technology over polyurethanes is that amine terminated (-NH<sub>2</sub>) resins are used rather than hydroxyl terminated (-OH) resins, commonly referred to as polyols. The reaction of the amine terminated resins with the isocyanate component results in the formation of a urea linkage. Since this is a polymer and these units repeat, the term polyurea then applies. A simple illustration of the “polyurea” reaction is given below (Figure 3), compared to polyurethane in Figure 4:

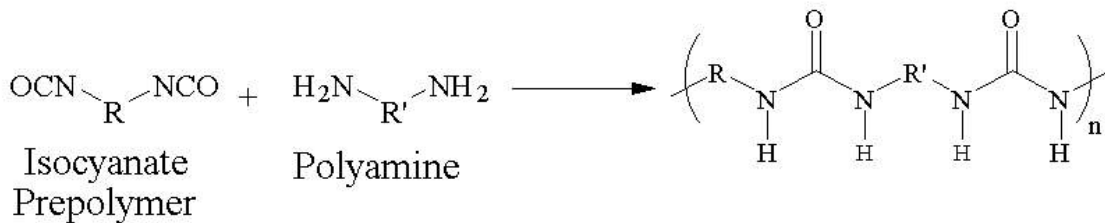


Figure 3: Polyurea Formation Reaction

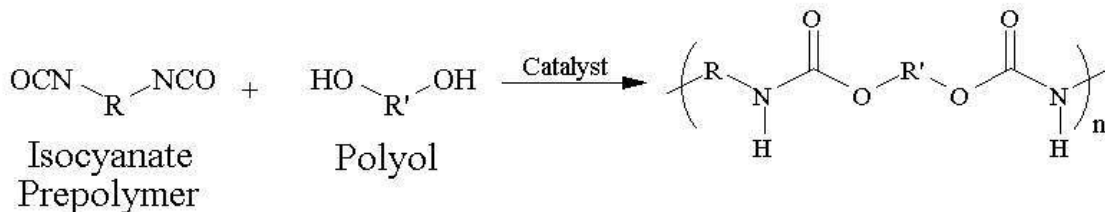


Figure 4: Polyurethane Formation Reaction

It should be noted that “polyurea” is a description of a technology and it in itself is not a coating / lining system. There are a variety of formulation possibilities to achieve desired performance, as well as various additives that may be used. This is made possible by the selection of various raw materials in the formulation, much like that for polyurethane chemistry. The selection of proper raw materials for the system can be a very complex procedure.

Based on reactive equivalents between the polyisocyanate component and the resin blend component for the 2-part systems, the following Table I can be established:

Table I  
*Formulation Basics vs Technology Type*

<u>Resin Part</u>	<u>Chain Extender</u>	<u>System Type</u>
<b>Polyetheramine</b>	<b>Amine Terminated</b>	<b>Polyurea</b>
Polyether Polyol	Amine Terminated	Polyurea/Polyurethane
Polyetheramine	Glycol	Polyurethane/Polyurea
Polyether Polyol	Glycol	Polyurethane

To understand Table I and the derived system type, one must assume for the above chart that we are processing a 2-part system, where the volume ratio is 1:1, or very close to that. The isocyanate content of the polyisocyanate component would be 8 to 16%.

To illustrate the reactive equivalents in a system and a distinction of whether a polyurea/polyurethane or polyurethane/polyurea, the following example is shown in Table II. The isocyanate portion of the system is based on an isocyanate quasi-prepolymer with a total isocyanate (NCO) content of 15.5% (equivalent weight of 271; reactive milli-equivalents or MEQ’s is 369). The resin was formulated to achieve an INDEX, ratio of isocyanate equivalents to reactive hydrogen equivalents, of 1.05

Table II  
*Formulation Basics / Reactive Equivalent Contribution*

<u>Resin type</u>	<u>pbw</u>	<u>equivalent weight</u>	<u>Reactive MEQ’s</u>
PEA, Di	65	1041	57.6
PEA, Tri	10	1889	5.3
Chain Extender	25	89	281
<b>Total</b>	<b>100</b>		<b>344</b>

\* based on a 1:1 by volume, 1.05 INDEX, 15.5% NCO content isocyanate

From Table II, one can see that for the resin blend portion of the 2-part fast set polyurea elastomer systems, the chain extender contributes the most part of the reactive hydrogen equivalents with the isocyanate reactive equivalents. In this case, over 80%. The chain extender is really the determining factor on what makes a polyurea. There are no polyols, or hydroxyl terminated materials, used as the main reactive resin in the resin blend portion of a two-component polyurea elastomer system. If so, then these would be classified as a polyurea/polyurethane hybrid system.

One might then also point to the reaction of moisture with the polyisocyanate component. When moisture enters into the reaction mechanism, the moisture would react with the isocyanate to form a carbamate. This will very quickly dissociate into an amine-terminated molecule, which would then very rapidly react with an isocyanate specie / moiety to form a urea linkage. Hence forth, a single component moisture cured urethane system could be considered a polyurea system, but not a two-part system. The moisture reaction is the curing mechanism to reaction.

There is also some interest and work in the 2-part systems where part of one component is blocked, both parts are mixed and reaction / curing occurs when another factor is introduced. This other factor may be heat, as is the case of blocking the isocyanate component (using oximes and phenols). The other would be moisture, as in the case of blocked amine resin blends (formation of aldimines).

### ***Aromatic Based Polyurea:***

Aromatic based two-component polyurea systems have been the workhorse of the two-component polyurea technology. Aromatic refers to the nature of the chemical backbone of the polymer system. The two-component systems are comprised of an isocyanate part and a resin blend component. The isocyanate component is typically an isocyanate quasi-prepolymer, prepared from methylene diisocyanate (MDI) (Figure 5).

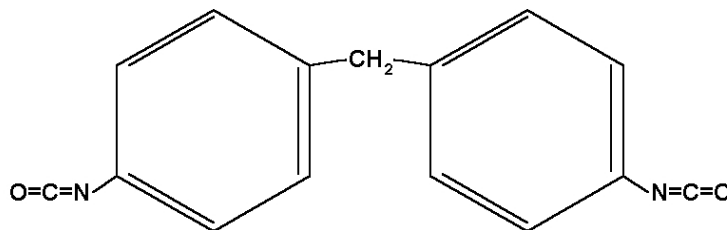


Figure 5: Methylene Diisocyanate Structure

The quasi-prepolymer is based on the MDI and a polyether polyol. By changing the type / structure of the MDI and the polyol, a wide variety of elastomer physical properties,

performance and reactivities can be achieved. Reactive diluents may also be employed to lower the viscosity of the isocyanate component.

The MDI is partially polymerized with a polyol in order to reduce the overall isocyanate content and allow for application processing at a 1:1 volume ratio with the resin blend component. It should be noted that toluene diisocyanate (TDI) has typically not been used in two-component, fast set spray polyurea elastomer systems. There are some results that do show some unique viability in certain applications and some recent use has been noted.

The resin blend portion of an aromatic based polyurea system is the more complex portion of the system. The resin blend utilizes soft-block and hard-block segments for the reactive constituents. The soft-block segments are the high molecular weight resins, referred to as polyetheramines or amine terminated polyethers. These polyetheramines are either di-functional or tri-functional with blends of the two providing for certain elastomer physical properties and performance. Figure 6 is an illustration of the diamine and Figure 7 is an illustration of the triamine.

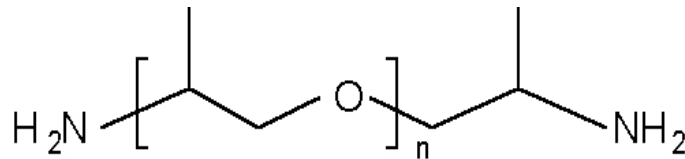


Figure 6: Polyoxypropylene Diamine Structure  
Polyether Diamine

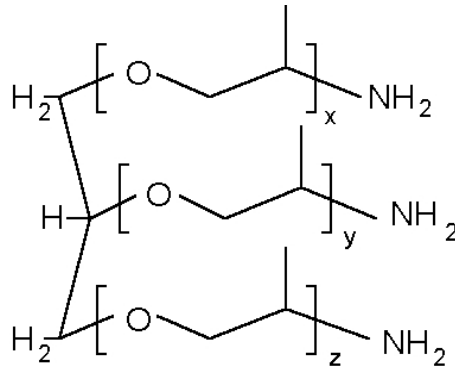


Figure 7: Polyoxypropylene Triamine Structure  
Polyether Triamine

The polyoxypropylene diamine is typically in the 2000 molecular weight range while the polyoxypropylene triamine is in the 5000 molecular weight range. These resins provide the flexibility in the resulting polyurea polymer system. They also provide for that initial



reaction or set in the polymer system when the isocyanate and resin blend components are mixed.

There are other high molecular weight amine terminated resins that are making recent inroads in polyurea applications. These are based on aromatic or linear hydrocarbon chains, as well as silicone resin backbones. This paper is designed merely to touch on / hi-light the overall polyurea technology and concept and cannot address all specific types.

The other portion of the resin blend component is the hard-block, or more commonly called the chain extender. A chain extender is the low molecular weight amine terminated resin that completes the polymer chain and extends / controls the overall system dry time. The most common chain extender used in two-component polyurea elastomer systems is diethyltoluene diamine (DETDA). It is available as an 80,20 isomer of the 2,4 -diamine to 2,6 -diamine. Figure 8 is an illustration of DETDA.

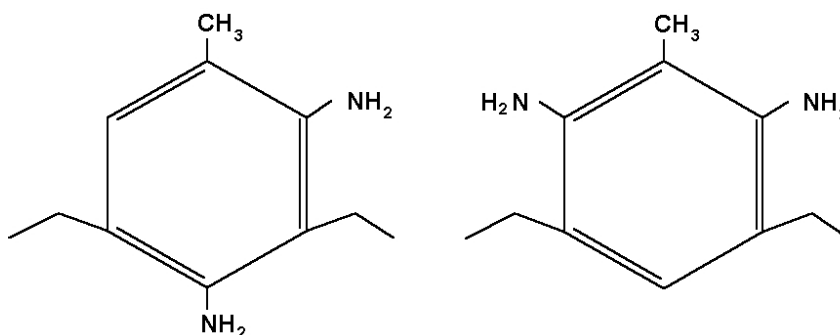


Figure 8: DETDA; 80,20 Isomer Structure

To assist in controlling the dry time of the two-component polyurea systems, a co-chain extender will be used with the DETDA. This co-chain extender is also an amine terminated material, but is generally a secondary / hindered amine. Figure 9 is an illustration of a common hindered amine chain extender based on methylene dianiline.

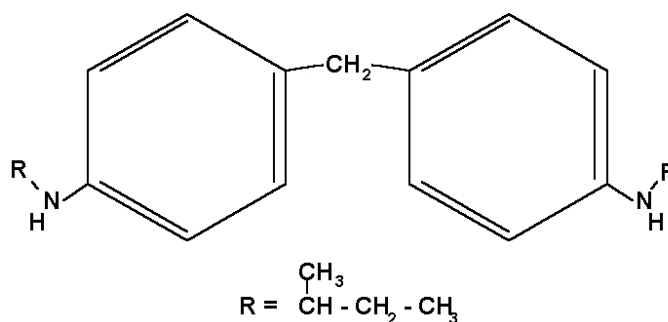


Figure 9: N,N'- Dialkyl Methylene Dianiline

For non-polyurea type systems, low molecular weight glycol type chain extenders are used. They are hydroxyl terminated and the reaction with the isocyanate portion yields the urethane linkage. Figure 10 gives the general structure of ethylene glycol and 1,4-butylene glycol, two commonly used hydroxyl-terminated chain extenders for reference.

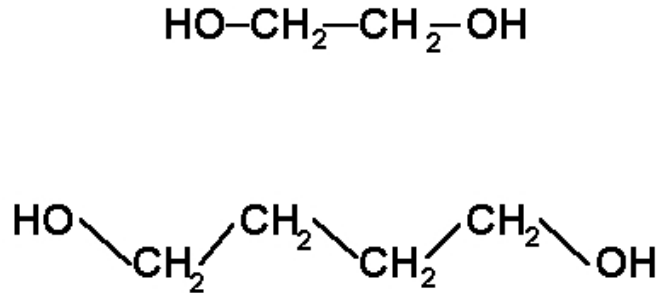


Figure 10: Ethylene Glycol and 1,4-butylene Glycol

To get a better understanding of the effect of the secondary or hindered amine co-chain extender, Table III illustrates the effect on the two-component polyurea dry time as these chain extenders are adjusted. It should be noted that the isocyanate component remained the same composition, and the overall systems were adjusted to achieve the 1:1 volume ratio processing.

Table III  
*Effect of Secondary / Hindered Amines on Dry Time*

Resin	pbw					
Polyether Diamine, 2000 mw	40	40	39	39	38	38
Polyether Triamine, 5000 mw	27	27	26	26	25	25
DETDA	30	25	17	9	4	0
Secondary Amine, Figure 9	3	8	18	26	33	37
Gel time, secs	2	2.5	3.5	5.0	12	23
Dry time, secs	2.5	3.0	4.0	10	70	130

These are not the only two types of chain extenders that may or are currently used; there are others that can provide the same effect. Many of these are solids at room temperature and may be hard to blend into the resin blend portion by the manufacturer of the system. Table IV shows the relative reaction rates of an isocyanate component with various

amine terminated materials. The secondary or hindered diamines extend the reactivity of the rapid dry two-component aromatic polyurea elastomer technology to allow for improved processing and better substrate wetout / adhesion.

Table IV  
*Relative Reaction Rates of Isocyanate with Active Hydrogen Compounds*

Active Hydrogen Compounds in Order of Decreasing Reactivity with an Isocyanate

Active Hydrogen Compound	Typical Structure	Relative Reaction Rate Uncatalyzed at 25°C
Primary Aliphatic Amine	$R - NH_2$	100,000
Secondary Aliphatic Amine	$R_2 - NH$	20,000 - 50,000
Primary Aromatic Amine	$Ar - NH_2$	200 - 300
Primary Hydroxyl	$R - CH_2 - OH$	100
Water	$H - O - H$	100
Secondary Aromatic Amine	$Ar - \overset{R'}{\underset{ }{N}}H$	100
Carboxylic Acid	$R - \overset{O}{\parallel}C - OH$	40
Secondary Hydroxyl	$R - \overset{R'}{\underset{ }{C}}H - OH$	30
Ureas	$R - NH - \overset{O}{\parallel}C - NH - R'$	15
Tertiary Hydroxyl	$R - \overset{R'}{\underset{R''}{\underset{ }{C}}} - OH$	0.5
Urethanes	$R - NH - \overset{O}{\parallel}C - O - R'$	0.3
Amide	$R - \overset{O}{\parallel}C - NH_2$	0.1

In most cases, pigment dispersions are used to pigment the elastomer systems. These dispersions are solid pigments in a carrier media such as a polyetheramine or polyether or polyester polyol. Use here would be in typical additive type amounts and would have no bearing on the classification of the system. The resin blend portion may also contain various additives such as adhesion promoters, UV stabilizers and antioxidants. This would also apply to the aliphatic-based systems described later.

The main limitation of the aromatic two-component polyurea system is overall color stability of the resulting polymer. While pigmentation will help, all aromatic based two-

component polyurea elastomer systems will fade or change color when exposed to ultraviolet light. It should be noted that this is only a surface effect on the polymer.

### ***Aliphatic Based Polyurea:***

Following the introduction of the aromatic based two-component polyurea elastomer systems; the fast dry aliphatic-based materials were developed.<sup>9,10</sup> For these systems, you also have an isocyanate component and a resin blend portion. The isocyanate is also a quasi-prepolymer, like with the aromatic based two-component polyurea systems. However, the isocyanate used is a light stable monomer and the “polyol” may actually be the polyoxypropylene diamine. The common isocyanate used is isophorone diisocyanate (IPDI) (Figure 11).

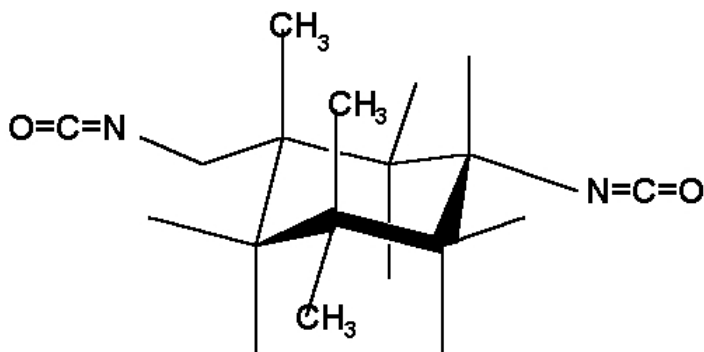


Figure 11: Isophorone Diisocyanate Structure

The resin blend of the aliphatic-based two-component polyurea systems is very similar to the aromatic based system. Blends of the high molecular weight polyoxypropylene amines (Figures 6 and 7) are used to develop flexibility and initial set in the polymer system.

The chain extender portion of the two-component fast dry aliphatic polyurea elastomer system is different than the aromatic based system. Here, the chain extender may actually be a “soft” hard-block or a conventional “hard” hard-block. For the “soft” hard-block segment, chain extenders of a low molecular weight (typically less than 400) are used based on the polyoxypropylene amines as shown in Figures 6 and 7. These provide for an aliphatic polyurea elastomer that has a limited thermal resistance, typically less than 176°F (80°C).

The more common form of chain extender for the two-component fast dry aliphatic polyurea technology is the cycloaliphatic diamines. The most common of those would be isophorone diamine (IPDA) (Figure 12).

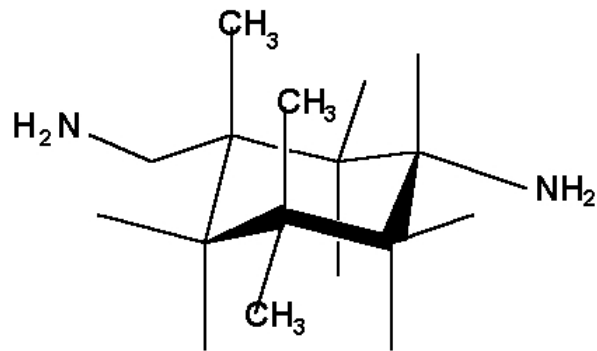


Figure 12: Isophorone Diamine Structure

There are other cycloaliphatic diamines that may be used as well, these include various isomers of cyclohexane diamine, hydrogenated versions of methylene dianiline's, or tetramethyl xylene diamine.

There will also be a co-chain extender used with the IPDA to control overall polyurea elastomer system dry time, very similar to that with the aromatic based two-component polyurea elastomers. These co-chain extenders will either be secondary or hindered aliphatic amines. They are typically derivatives of IPDA, hydrogenated methylene dianiline (HMDA) or other cycloaliphatic diamines.<sup>11-15</sup> These to provide for extending the dry time of the rapid dry two-component aliphatic polyurea systems and to aid in processing and improved substrate wetout.

The fast dry two-component aliphatic polyurea systems will utilize some of the same additives found in the aromatic based systems.

### ***Polyaspartic Ester Based Polyurea:***

In the early 1990's a new technology of two-component aliphatic polyurea was introduced to the industry.<sup>16, 17</sup> This technology was introduced primarily for thin film applications where high gloss and excellent color stability are important. The polyaspartic ester polyurea technology is considered a slow dry technology, with dry times of up to 120 minutes.

This technology primarily uses isocyanate components based on either trimers or dimers of hexamethylene diisocyanate. Rather than the somewhat complex reactive resin selections as with the rapid dry two-component polyurea systems, the resin choice for the slow dry polyaspartic esters is somewhat simpler than conventional two-component fast set polyurea systems. The resin blend is composed primarily of the polyaspartic ester amine resins (Figure 13).

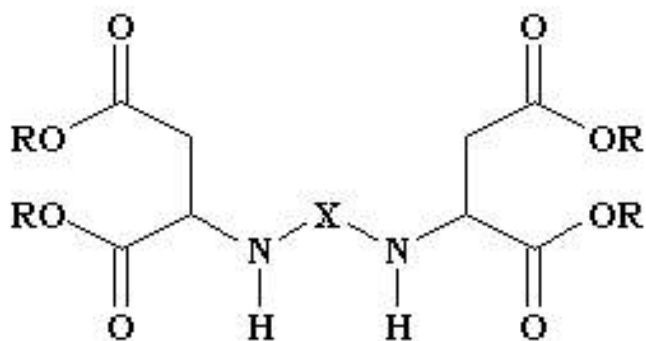


Figure 13: Polyaspartic Ester Amine Resin

The polyaspartic ester amine resins are relatively low in viscosity and molecular weight. The primary backbone structure (X from Figure 13) is cycloaliphatic, but can be a linear diamine. This technology can be easily applied by brush, roller or by pre-mixing and application through airless spray techniques. Solvents may be used in small amounts to assist in mix viscosity control and application.

The polyaspartic ester amine resins may also be used as co-chain extenders in the rapid dry, two-component aromatic and aliphatic polyurea elastomer systems. These will have an effect of extending out the dry time of the systems and allow for improved wetout of the substrate.

## PERFORMANCE ISSUES:

In general, the basic fast set polyurea spray technology is comparable to physical properties of polyurethane/polyurea hybrids and polyurethane systems. In other words, these technologies of coatings / lining systems can be formulated to achieve a variety of elastomer physical properties.

The truly big advantage of the polyurea technology is the speed of reaction and the ability to put the structure or facility back into service very quickly. One has to be very careful here though because polyurea systems may set and give an initial cure very quickly that will allow this “return to service” very quickly, but not develop ultimate elastomer physical properties for 24 hours or more. This all depends on the exact polyurea system formulation.

The polyurea systems do tend to have better flexibility at lower temperatures than to the corresponding polyurethane/polyurea hybrid or polyurethane system. The technology also performs very well with regard to thermal shock resistance.

## ***Moisture and Temperature Sensitivity:***

One of the major advantages of the polyurea technology is the relative insensitivity to moisture during processing / application. As the amine – isocyanate reaction tends to be preferential over the hydroxyl – isocyanate reaction, foaming of polyurea systems is almost impossible. However, it can occur, especially if a catalyst is present. For polyurethane/polyurea hybrids and polyurethane systems, catalysts are used to control the reaction. If moisture is present, they may exhibit some foaming which leads to lower density, porosity and poor performance.

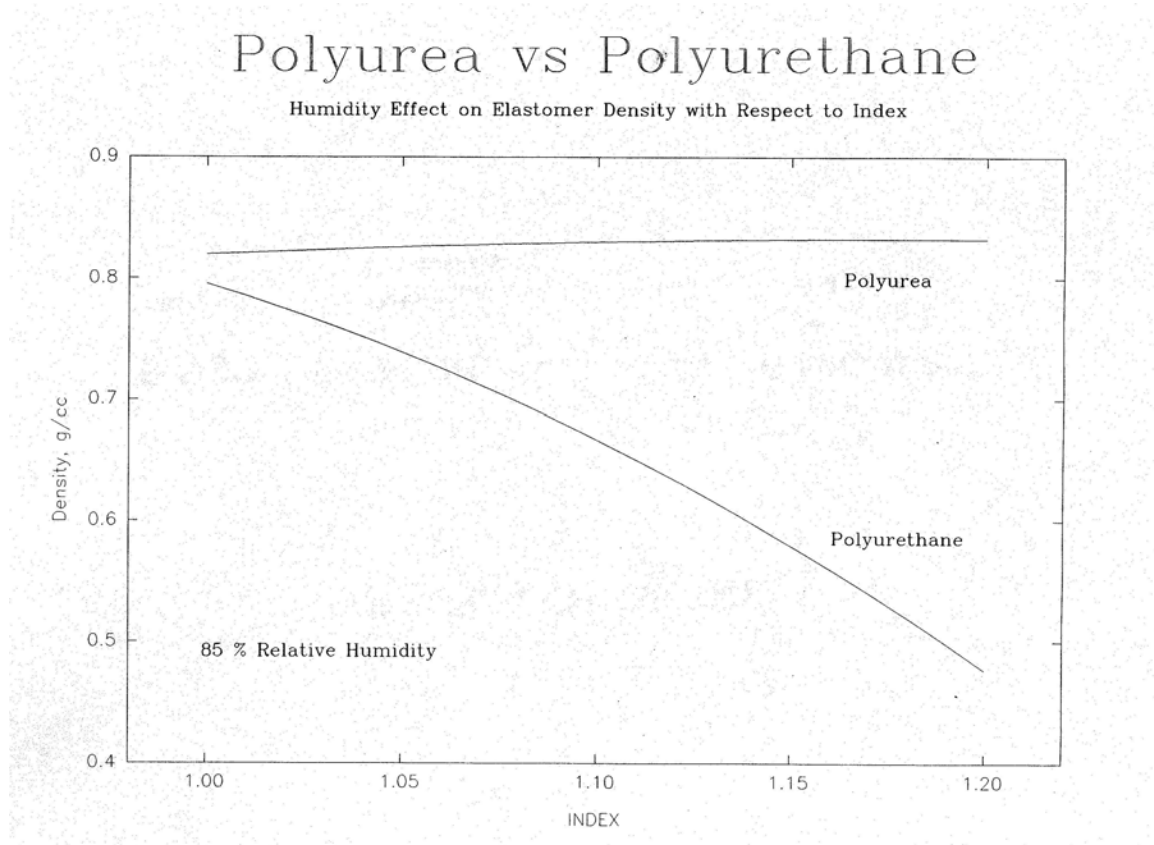


Figure 14: Effect of Moisture on Elastomer Density

Figure 14 illustrates the effect of moisture / humidity during processing of both a fast set spray polyurea and spray polyurethane systems. As the INDEX increases, ratio of isocyanate equivalents to reactive hydrogen equivalents, the density of a polyurea system remains constant while the polyurethane system shows a decrease in elastomer density. The non-polyurea system foamed due to the catalyzed reaction of isocyanate with the moisture in the air. This reduction of density / foaming would result in overall performance issues for the polyurethane system. Similar results have also been shown with a polyurethane/ polyurea hybrid technology.

While polyurea systems may show insensitivity to moisture, that does not mean they can be applied over a wet substrate. The polyurea will react over the water, but the applied system will not bond to the substrate in that area.

The ambient temperature and substrate temperature may have little affect on the reaction and cure of a polyurea system as compared to the others. But, the real important issue is substrate temperature and dew point. Industry standard coating practices must also be followed with polyurea systems and application in that the substrate temperature must be 5° above dew point and rising. If not, moisture will condense on that substrate and cause adhesion issues with the polyurea technology, as with other coating / lining systems.

### ***Chemical Resistance:***

Polyurea systems in general exhibit similar chemical resistance properties as that of comparable formulated polyurethane / polyurea hybrids and polyurethanes. This is due primarily to the fact that all have the polyether backbone in the elastomer. The urea linkage found in the polyurea as well as the hybrid system is more resistant to hydrolysis than the urethane linkage. Polyurea systems do tend to have better resistance to alkali, high pH, than the hybrids or polyurethane systems. Aromatic polyurea systems are subject to chemical oxidation.

There are some newer technologies of polyurea systems that are showing significantly higher chemical resistance with respect to highly acidic environments. Keep in mind that chemical resistance / performance can be directly related to processing conditions of the polyurea systems. Those that do not achieve complete mix and contain porosity will have lower chemical resistance performance than those processed at the optimum conditions. This would include proper processing temperatures and pressures as well as the proper mix configuration in the spray gun.

These newer technologies of polyurea systems have different polymer backbones in the chain. These can be ester, epoxy, silicone or a combination of proprietary modifications to the polymer chain.<sup>18</sup>

### ***Thermal Analysis of Two-Component Rapid Dry Polyureas:***

One very interesting note about the rapid dry two-component aromatic and aliphatic polyurea elastomer systems is the resultant thermal properties of the polymer films. Two-Component polyurea elastomer systems are amorphous in nature, not crystalline like polyurethane systems. This amorphous nature is similar to that of epoxy type systems except that two-component polyurea system do not have a true glass transition temperature. Instead, 2 distinct  $T_g$ 's can be noted, one corresponding to the melting point of the soft-block in the polymer and the other corresponding to the melting point of the hard-block in the polymer (Figure 15).



From Dynamic Mechanical Spectroscopy evaluations of typical two-component polyurea elastomer systems, a low temperature  $T_g$  is noted at about  $-50^\circ$  to  $-60^\circ\text{C}$  with a high temperature  $T_g$  of about  $230^\circ$  to  $260^\circ\text{C}$  for the aromatic based systems. The two-component aliphatic polyurea systems have a low temperature  $T_g$  about the same as the two-component aromatic polyurea but have a high temperature  $T_g$  of about  $110^\circ$  to  $120^\circ\text{C}$ .<sup>10</sup> The response curve between these two points remains relatively flat. This would be the performance range, temperature wise, for a polyurea elastomer system. In lay terms, the polyurea elastomer systems would tend to show some significant stiffening at temperatures less than  $-50^\circ\text{C}$  with some polymer softening, or possible decomposition, at the upper temperatures  $T_g$ 's.

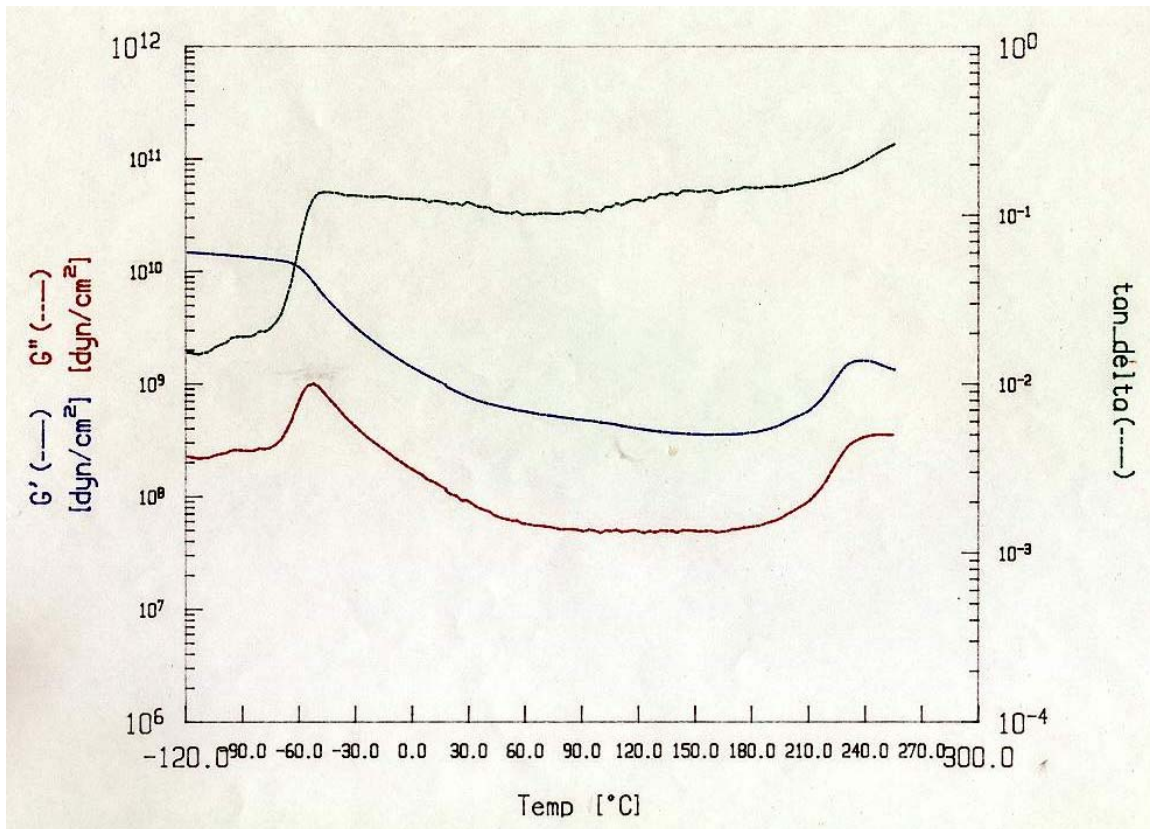


Figure 15: Dynamic Mechanical Spectroscopy of Aromatic Polyurea Spray

### *Shrinkage During Cure:*

Since formation of the elastomeric polyureas are based on a thermoset reaction, some linear shrinkage during cure will occur. This is not thermal expansion / contraction due to temperature changes. The total amount of shrinkage will depend on the reactive constituents of the isocyanate and resin blend components, even though the elastomeric system may have elongation values greater than 200%. These linear shrinkage forces

may be strong enough to curl the corners or edges of the applied work and could lead to disbondment or destruction of the substrate. The elastomeric polyurea systems used should be designed for the particular coating / lining application work.

Shrinkage values for some polyurea spray elastomer system may actually exceed 5% linearly. For some specific application areas, the polyurethane / polyurea hybrid systems are better suited due to the lower shrinkage values exhibited in these systems.

### ***Weatherability Properties:***

The Aromatic polyurea systems have good resistance to ultraviolet light from an overall performance standpoint. Even with the use of UV Stabilizers / Antioxidants, they will however become discolored and fade over time when used in light colors for exterior exposure environments.

Aliphatic polyurea systems have excellent resistance to degradation by ultraviolet light and are used for a variety of exterior and interior atmospheric services. By modifying the aromatic based systems with inclusion of aliphatic isocyanates or chain extenders, some color stability enhancement may be noted. However, these still have aromatic specie in the polymer backbone and are not color stable.

### **CONCLUSION:**

Two-component polyurea elastomeric coating / lining systems may be somewhat of a newcomer to the industry, but it has shown a good deal of versatility and application use. The rapid dry time characteristics provides for an extremely good cost and time-effective solution to a variety of coating / lining applications over conventional technologies. With the extreme efforts for industrial rehabilitation and increasing need to comply with environmental, economic and time constraints, the speed and durability of the two-component polyurea technology hold great promise.

As the use of this technology grows, so does the confusion as to what is a polyurea and what is not. Hopefully this text will have given the reader a better understanding of what a polyurea systems is as compared to similar technologies of polyurethane/ polyurea hybrids and polyurethane systems.

The two-component polyurea technology must be treated as other coating type systems with regard to proper and complete surface preparation. The uniqueness of the technology is not a cause to limit or even eliminate proper, industry accepted surface preparation guidelines. The substrates must be clean, dry and free of contaminants.

Continuous development of new raw materials for formulation work will move this technology to a higher level of industrial coating / lining work while preserving the uniqueness of the polyurea technology.

## References:

- <sup>1</sup> Primeaux II, D. J., Evolution of Polyurea “Spray”. In *Building on the Future, PDA Annual Meeting*, New Orleans, Louisiana, November 30 – December 1, 2000.
- <sup>2</sup> Hill, R.; Walker, E.E. Trend of Crystalline Melting Points in Homologous Series of Aliphatic Polymers. *Journal of Polymer Science*, Volume 3, 1948, pp 609.
- <sup>3</sup> Grigsby, R.A.; Dominguez, R.J.G.D. Polyurea RIM – A Versatile High Performance Material. In *The Magic of Polyurethane, Proceedings of the SPI 29<sup>th</sup> Annual Technical / Marketing Conference*, Reno, Nevada, October 1985, pp 248 – 253.
- <sup>4</sup> Primeaux II, D.J.; Grigsby, R.A.; Rice, M. Polyurea RIM in Exterior Body Panel Applications. In *SAE International Congress and Exposition*, Detroit, Michigan. February – March 1988, pp 7 – 14.
- <sup>5</sup> Primeaux II, D.J. Spray Polyurea – Versatile High Performance Elastomer for the Polyurethane Industry. In *Polyurethanes 89, Proceedings of the SPI – 32<sup>nd</sup> Annual Technical / Marketing Conference*, San Francisco, California, October 1989, pp 126 – 130.
- <sup>6</sup> Rowton, R.L. Cyanoethylated Polyoxypropylenepolyamines: Polymer Formers of Unique Reactivity. *Journal of Elastomers and Plastics*, Volume 9, October 1977, pp 365 – 375.
- <sup>7</sup> Grubs, Paul, Earliest & Largest Applications of Polyurea. In *Polyurea: The Future is NOW!*, PDA 2<sup>nd</sup> Annual Meeting, Orlando, Florida, November 28 – 30, 2001.
- <sup>8</sup> NACE 6A198. *Introduction to Thick-Film Polyurethanes, Polyureas, and Blends*; NACE: Houston, 1998.
- <sup>9</sup> Primeaux II, D.J. 100% Solids Aliphatic Spray Polyurea Elastomer Systems. In *Polyurethanes World Congress 1991, Proceedings of the SPI/ISOPA*, Acropolis®, Nice, France, September 1991, pp 474 – 477.
- <sup>10</sup> Primeaux II, D.J. 100% Solids Aliphatic Spray Polyurea Elastomer Systems. *Journal of Elastomers and Plastics*, Volume 24, October 1992, pp 323 – 336.
- <sup>11</sup> Primeaux II, D.J. U.S. Patent 5,162,388 (1992).
- <sup>12</sup> House, D.W. et.al. U.S. Patent 5,312,886 (1994).
- <sup>13</sup> Primeaux II, D.J. U.S. Patent 5,504,181 (1996).
- <sup>14</sup> Primeaux II, D.J. et.al. U.S. Patent 5,616,677 (1997).
- <sup>15</sup> Primeaux II, D.J. et.al. U.S. Patent 6,013,755 (2000).
- <sup>16</sup> Wicks, D.A.; Yeske, P.E. Control of the Reaction Between Polyaspartic Esters and Aliphatic Polyisocyanates. In *Water-Borne & Higher-Solids and Powder Coatings Symposium*, New Orleans, Louisiana, February 1993, pp 1 – 8.
- <sup>17</sup> Luthra, S.; Wayt, T.D.; Yeske, P.E. Applications of Polyaspartic Esters in Polyurea Coatings. In *21<sup>st</sup> Higher Solids and Waterborne Coatings Symposium*, New Orleans, Louisiana, February 1998, pp 398 – 419.
- <sup>18</sup> US Patent 6,797,789, Visuron Technologies, Inc., Bay City, MI. (2004)

## **Bibliography:**

Sections of this text also appear in *The Inspection of Coatings and Linings 2<sup>nd</sup> Edition, Chapter 5.3*, Dudley J. Primeaux II author, and the soon to be released new edition of *Generic Coating Types*, Two-Component Polyurea Coatings / Linings chapter, Dudley J. Primeaux II author. Both texts are published by the SSPC: The Society for Protective Coatings.

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Deo Vindice, Resurgam!

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Dudley J. Primeaux II is President and owner of Primeaux Associates LLC, a private consulting business. Mr. Primeaux specializes in the polyurea industry; including equipment, application, training, and expert witness while working through a variety of companies throughout the world.

Mr. Primeaux received a Master of Science Degree in Organic Chemistry from Lamar University in Beaumont, Texas in 1984. He was employed by Texaco Chemical Company - Austin Research Labs and Huntsman Corporation where he was involved in the development, and first demonstrated the 100 % solids polyurea spray elastomer technology.

Mr. Primeaux was also Managing Partner / Chief Chemist with EnviroChem Technologies where he was responsible for all formulation development for the *EnviroLastic*® polyurea product line and marketing of those systems and applications. He also trained and interacted with the Certified Contractor Network on products and application techniques. Application equipment setup, training and servicing also fell under his responsibilities. He is currently involved with all aspects of polyurea coating / lining training work through The Polyurea Training Group, and Technical support for The Hanson Group, LLC.

Mr. Primeaux is SSPC C-1 "Fundamentals of Protective Coatings for Industrial Structures" and C-2 "Specifying and Managing Protective Coatings Projects" Certified and in process of completion of his Protective Coatings Specialist certification. He also served as President of the Polyurea Development Association. He is named inventor of 25 US Patents and 6 European Patents on polyurethane and polyurea foam applications as well as polyurea spray elastomer systems/applications. He also has 35 technical publications on the polyurea elastomer technology.