

Spray Polyurea Elastomers Offer Performance Advantages

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THE DEVELOPMENT OF two-component spray elastomer and coating systems has been an active field of research and interest for many years. Research into typical polyurethane systems has evolved to high-performance, 100-percent-solids polyurethane elastomers based on reaction injection molding (RIM) technology. Further evolution brought forth two-component spray elastomer systems incorporating high-molecular-weight polyols, amine chain extenders and amine catalysts. Refinements in spray application equipment made processing of these high-performance materials possible. Recent development of polyurea RIM has produced a new evolution in spray elastomer technology.

Polyoxyalkylene diamines and triamines have replaced the polyols; amine chain extenders are utilized; and catalysts have been eliminated. This leading edge technology gives rise to versatile high-performance elastomer systems herein referred to as spray polyurea elastomers.

Chemistry and Concept

Some of the first polymers used in two-component spray processing were polyurethanes. These systems consisted of polyether polyols, glycol chain extenders, catalysts and aromatic polyisocyanates. The need for higher-performance elastomer materials, coupled with new advances in RIM technology,¹ re-

placed the current technology with polyurethane/urea spray elastomer systems. These systems consist of polyether polyols, diamine chain extenders such as diethyltoluenediamine (DETDA), catalysts and aromatic polyisocyanates (See Figure 1). Showing improvements over polyurethane technology, these polyurethane/urea spray elastomer systems seemed to satisfy the needs of the industry. As RIM technology evolved to polyurea RIM materials, developed at the Austin Laboratories of Texaco Chemical Co.,²⁻¹⁰ so has the two-component spray elastomer technology.¹¹ Two-component, 100-percent-solids spray polyurea elastomer systems seem to be just on the horizon.

Polyureas are defined as polymers formed by the reaction of isocyanates with primary or secondary amine-terminated materials, wherein the linkages thus formed are urea groups (See Figure 2). These systems consist of the key ingredient, JEFFAMINE polyetheramines, diamine chain extenders such as DETDA and aromatic polyisocyanates. It is important to note that in spray polyurea elastomer systems, polyether polyols are replaced by polyether polyamines. Also, no catalysts are used in the spray polyurea elastomer technology. This evolution of the two-component spray elastomer technology is summarized in Table I.

The amine/isocyanate reaction in the spray polyurea elastomer systems is normally very fast, proceeding to completion within a few seconds without any catalysts. Typically, working times or system "gel times" are less than three seconds. This fast reaction is very consistent and predictable, unlike many fragile systems which depend on the life of a sensitive catalyst package for reactivity.

The key to the advantages of the spray polyurea elastomer technology is in the JEFFAMINE polyetheramines from Texaco Chemical Co. As mentioned previously, the products are amine-terminated polyethers, generally having polyoxypropylene backbones. Suitable JEFFAMINE amines for use in spray polyurea elastomer technology in-

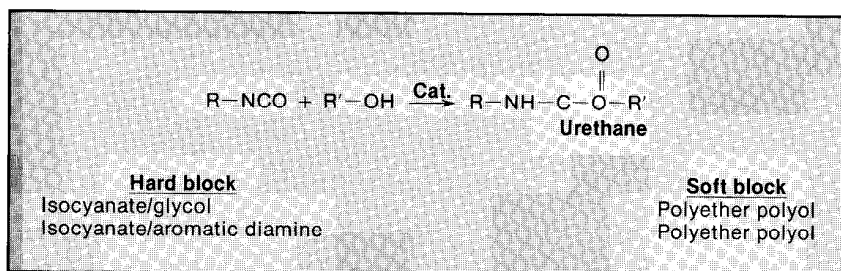


Figure 1. Polyurethane and polyurethane/urea.

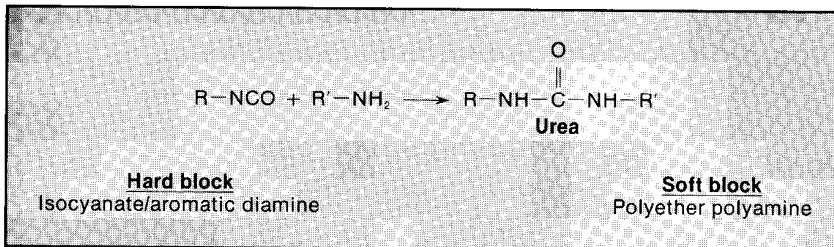


Figure 2. Polyurea.

Table I. Evolution of Two-Component Spray Elastomer Technology		
	Isocyanate	Polyether
Polyurethane	MDI Based	Glycols EO Capped Polyols Catalysts
Polyurethane/Urea	MDI Based	Aromatic Diamine EO Capped Polyols Catalysts
Polyurea	MDI Based	Aromatic Diamine Polyether Polyamine

clude, but are not limited to, those presented in Table II.

The isocyanate component of this emerging technology is a soft block quasi-prepolymer based on methylene diphenyl diisocyanate. In the quasi-prepolymer preparation, high-molecular-weight, high-performance polyether diols and/or triols are used. JEFFAMINE polyetheramines have also been used as the soft block constituent in the MDI quasi-prepolymer. However, high pressure mixing and caution should be exercised in their preparation. A variety of spray polyurea materials are possible, ranging from soft elastomers to hard polymers, by varying the soft block content in the quasi-prepolymer and the amine chain extender in the resin, maintaining an A-component to B-component volume ratio of 1:1.

Spray Equipment

In order to process this new technology, some consideration should be given to processing equipment. Due to the fast reaction rates, conventional static mix, solvent flush equipment cannot be used. In order to insure good fixing and fast dispersion of the material, impingement mixing by high-pressure, two-component spray equipment is required. This is very similar to the impingement mixing technique used in the RIM process. Use of relatively low-cost, commercially-available high-pressure proportioning units, coupled with either spray or pour guns available from Gusmer Corp., opens up many opportunities for polyurea elastomer materials outside of molded RIM parts. An illustration of the impingement mix system can be found in Figure 3.

Recently, newly-designed Gusmer variable ratio H-2000 spray equipment has been made available. This new feature allows for broader formulation flexibility in the polyurea elastomer technology. This equipment has also afforded the opportunity to study the effects of varying ratios on the processing and performance of a given spray polyurea elastomer system.

Technology

As previously discussed, spray polyurea elastomers result from the high pressure, impingement mixing of a soft block quasi-prepolymer based on MDI with a resin component made up of polyetheramines and amine chain extenders, to yield this highly reactive elastomer system. Elastomers with excellent physical properties result from these self-catalytic systems. A comparison of a typical spray polymer elastomer sys-

Table II. JEFFAMINE* Polyetheramine

	Functionality	Approximate molecular weight
JEFFAMINE T-5000	3	5000
JEFFAMINE D-4000	2	4000
JEFFAMINE T-3000	3	3000
JEFFAMINE D-2000	2	2000
JEFFAMINE T-403	3	400
JEFFAMINE D-230	2	230

*JEFFAMINE is a registered trademark of Texaco Chemical Co.

Table III. Spray Elastomers: Polyurethane vs. Polyurethane/Urea vs. Polyurea

	Polyurethane	Polyurethane/urea	Polyurea
Chain extender	Ethylene glycol	DETDA	DETDA
Gel time, sec	2.5	2.2	1.8
Tensile strength, psi	640	1700	2220
Elongation, %	200	200	190
Tear, pli	140	390	440
Impact, notched, ft-lbs/in	3.0	3.9	5.2
Abrasion resistance, wt loss mg (1000 gm, 1000 rev, H-18 wheels)	250	180	195
MVT, perms at 30 dry mils	0.077	0.034	0.023

tem to a polyurethane/urea and a polyurethane system can be found in Table III.

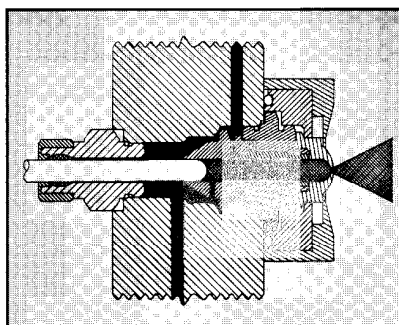
It should be noted that for both the polyurethane and the polyurethane/urea, catalysts are required to promote the reaction of the hydroxyl materials in the resin with the quasi-prepolymer of MDI. Catalysts consisted of a tertiary amine, TEXACATE TD-33A, and a tin catalyst, T-12. The green strength of the polyurea elastomer system was superior to those of the other two. In addition to these reported physical properties, it has been well known that polyurea materials have superior high temperature performance over polyurethane, polyurethane/urea and

polyamine polymers. Also, elastomers prepared from JEFFAMINE polyether amines would have better hydrolytic resistance compared to systems based on polyether polyols.

Due to the fast reaction rates and cure of the polyurea elastomer systems, sloped or vertical surfaces can be sprayed without forming runs or drips. Surfaces can be walked on within seconds after spraying and in the case of open-mold spray production, parts can be stacked without fear of sticking together. This fast, preferential reaction of the polyether amine and amine chain extender compared to hydroxyl materials yields spray polyurea elastomer systems which are relatively insensitive to water during processing. While processing of the system described in Table III, damp substrates were sprayed upon in order to evaluate adhesion and moisture effects on the resulting polymer. No elastomer foaming was noted in the polyurea elastomer system while slight and moderate elastomer foaming was noted in the polyurethane/urea and polyurethane systems respectively.

Processing was also performed during periods of high relative humidity, >85 percent. For the polyurethane system, 1,4-butanediol extender, elastomer foaming was noted when processed at

Figure 3. GX7 spray gun from Gusmer Corp.



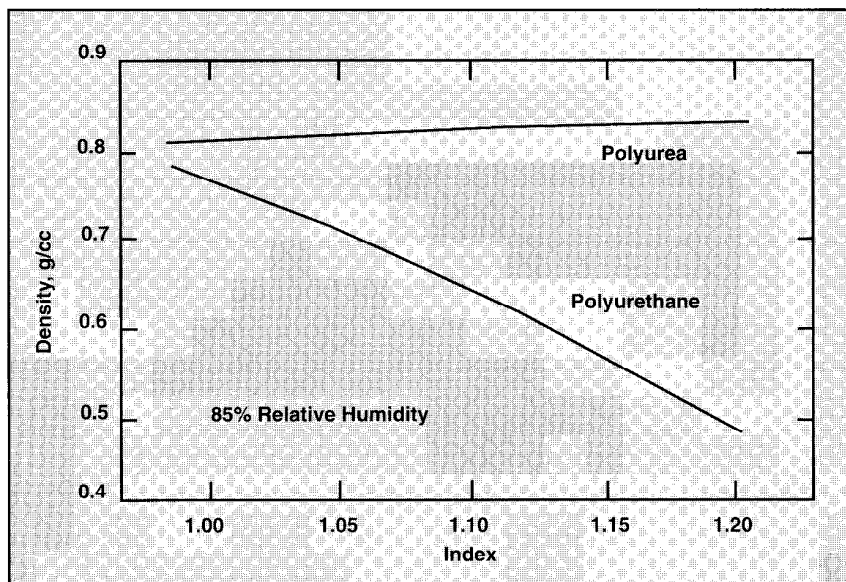
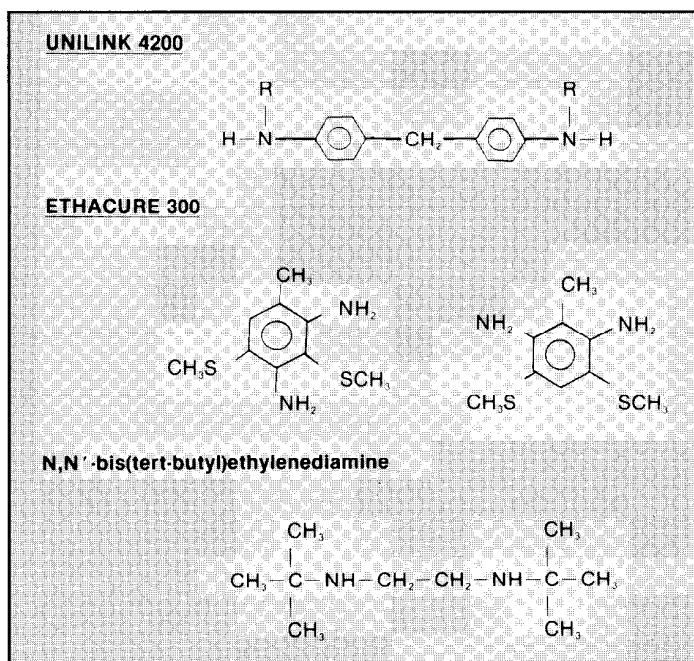


Figure 4. Polyurea vs. polyurethane: humidity effect on elastomer density with respect to index.

	Soft	Medium	Hard
Gel time, sec	2.5	2.0	1.8
Hard block content, %	29.2	38.3	47.4
Iso/Res vol. ratio	1.00	1.00	1.00
Elastomer Physical Properties			
Hardness, Shore D, 0 sec	24	43	55
Tensile strength, psi	880	1600	1890
Elongation, %	240	220	100
Tear, pli	230	360	456
Flexural modulus, psi			
25°C (77°F)	7200	20100	57170
70°C (158°F)	6860	19850	39490
-29°C (-20°F)	18450	56200	113160
Abrasion resistance, wt loss mg (1000 gm, 1000 rev, H-18 wheels)	770	450	400
MVT, perms at 30 dry mils	0.087	0.061	0.035
Water absorption, % wt gain (immersion for 24 hrs, 25°C)	8.35	3.13	2.74

Figure 5.



an index range of 1.00 to 1.20 using the variable ratio capability. No foaming was noted in the polyurea system processed under similar conditions. This can be illustrated in Figure 4.

As mentioned previously, soft elastomeric to hard polymer systems can be obtained suggesting wide formulation flexibility of the polyurea elastomer systems. Since these polyurea elastomer systems are 100 percent solids and processed at a 1:1 volume ratio, the range of elastomer systems hardness is affected by the composition of the soft block quasi-prepolymer isocyanate. The particular quasi-prepolymer utilized determines the content of the amine chain extender in the resin. The MDI content in the quasi-prepolymer and the chain extender level determine the elastomer's hard block content. The soft block content arises from the polyether polyol or polyether amine in the quasi-prepolymer plus the polyether amine content of the resin. Table IV gives the physical properties of selected spray polyurea elastomer systems over a range of material hardnesses. Note that the effective gel times of the soft polyurea elastomer systems are slower than those of the hardener polyurea spray elastomers. This is due to the lower ratio of the amine chain extender to the polyether amines in the resin component. Also note the change in polymer hard block content.

Slower Spray Polyurea Elastomers

It has also been demonstrated that less reactive spray polyurea elastomer systems can be prepared and still yield excellent physical properties. Incorporation of modified amine chain extenders in the spray polyurea elastomer systems slows down the effective gel times and allows for a wider application window. Examples of these modified amine materials are UNILINK 4200 from UOP Corp., N,N'-bis(tertiarybutyl)ethylenediamine from Virginia Chemicals and ETHACURE 300 from Ethyl Corp.^{14,15} These materials are depicted in Figure 5. Spray systems were developed on the basic formulation with an isocyanate quasi-prepolymer of ISONATE 143L and THANOL SF-5505 at a 60:40 weight ratio. For the resin side, a blend of JEFFAMINE T-5000 and DETDA was used at a 66:44 weight ratio. Examples of each of these amine chain extenders in this spray polyurea elastomer system are given in Table V. The vitrification of the spray polyurea elastomer system is slowed by the first two materials while the reaction between the

chain extender and isocyanate as well as the vitrification is affected by the ETHACURE 300.¹⁶ Note in Table V that the secondary aliphatic amine chain extender, N,N'-DTBEDA, has adverse effects on the heat stability of the polyurea elastomer as indicated by poor heat sag values in comparison to the other aromatic amine chain extenders.

The incorporation of increasing amounts of modified amine chain extenders relative to the DETDA content yields slower systems that can be processed either by spray or pour techniques. Complete replacement of the DETDA with these modified amine chain extenders gives systems with extremely slow gel times compared to the

all-DETDAs extended spray polyurea elastomer systems. An example of a spray polyurea elastomer system utilizing UNILINK 420 as the chain extender can be found in Table VI. Note that while this system is much slower than the other spray polyurea elastomers discussed (Tables III, IV and V) elastomer physical properties are very good. This has also been demonstrated with the other discussed amine chain extenders giving similar results.

Added reinforcement can also be incorporated into the spray polyurea elastomer technology by two methods. It has been demonstrated that WOLLASTOKUP 10012, aminosilane-treated wollastonite from NYCO, can be incorporated in the resin side of the polyurea elastomer systems with no adverse effects on system processing.¹⁷ Flake or milled glass as well as other reinforcing fillers can be incorporated. Internal mixing components made of carbide were instilled to eliminate deterioration of the spray equipment. An example of this application is illustrated in Table VII. Note that while elastomer elongation was lowered, improvements were noted in elastomer stiffness and heat sag characteristics. Note also the improvement in elastomer abrasion resistance. Use of sized calcium metasilicate improves the adhesion of the polymer material by forming a chemical bond to the filler material. This system had a gel time of 1.8 sec.

Another method of providing reinforcement is by use of a glass chopper and externally adding chopped glass roving into the spray pattern of the polyurea elastomer systems.¹⁸ Due to the fast reactivity of the polyurea elastomer technology, there is no time to roll the glass into the polymer material, as is done with polyester type systems. However, sufficient wet-out of the chopped glass roving is obtained to yield improvements in key physical properties. Table VIII depicts a spray polyurea elastomer system with a gel time of 2.5 secs incorporating the FIBERGLASS roving from Owens/Corning. Chopped glass roving has been successfully incorporated into a variety of spray polyurea elastomer systems at lengths of 0.25 to 1.25 ins. The shorter chop, 0.25 to 0.625 ins., seems to laydown better than the longer chop lengths. Glass incorporation content is also higher with the shorter chop lengths.

The technique of incorporating filler material in the spray polyurea elastomer system could be useful in the production of small automotive parts and other applications of spraying into open

Table V. Slower Spray Polyurea Elastomers Based on DETDA

	None	Unilink 4200	N,N'-DTBEDA	Ethacure 300
DETDAs replacement, %	0	25	28	25
Iso/Res. vol. ratio	1.00	1.00	1.00	1.00
Gel time, sec	1.5	2.2	2.5	2.5
Elastomer Physical Properties				
Tensile strength, psi	1920	1850	1750	1870
Elongation, %	120	120	140	130
Tear, pli	405	425	385	425
Hardness, Shore D, 0 sec	50	48	41	53
Flexural modulus, psi				
25°C (77°F)	42900	42230	41540	43690
70°C (158°F)	36820	29640	33480	33860
-29°C (-20°F)	83240	95640	73990	84850
Heat sag, mm				
150 mm - 250°F/60 min	1.9	3.1	15.1	4.0

Table VI. Spray Polyurea Elastomer — UNILINK 4200 Extended

Iso/Res. vol. ratio	1.00
Gel time, sec	45
Surface tack free, sec	90
Elastomer Physical Properties	
Tensile strength, psi	1715
Elongation, %	150
Tear, pli	450
Hardness, Shore D, 0 sec	56
Flexural modulus, psi	
25°C	45620
70°C	13100
-29°C	103080
Abrasion resistance, wt loss mg (1000 gm, 1000 rev, H-18 wheels)	170
MVT, perms at 30 dry mils	0.014
Water absorption, % wt gain	1.74

Table VII. Spray Polyurea Elastomers Incorporating Sized Mineral Particles

	Neat	Wollastokup 10012
Iso/Res vol ratio	1.00	1.00
Iso/Res wt. ratio	1.13	1.07
Filler in Polymer, %	0	4.6
Elastomer Physical Properties		
Tensile, psi	2520	2060
Elongation, %	125	30
Tear, pli	505	515
Hardness, Shore D, 0 sec	62	57
Flexural modulus, psi		
25°C	48120	70705
70°C	42170	42940
-29°C	110970	115090
Impact, notched, ft.lbs/in	9.15	3.43
Abrasion resistance, wt loss mg (1000 gm, 1000 rev, H-18 wheels)	550	280
Heat sag, mm		
150 mm - 250°F/60 min	15.0	4.0
150 mm - 311°F/60 min	*	18.5

* Complete sag

molds. The fast reactive rates, cure and superior physical properties could yield high productivity with minimal equipment investment. Reactive dyes from Milliken, pigments from Sun Chemical Corp. and PDI and other filler type materials can easily be incorporated into

this spray polyurea elastomer technology.

UV Stability

Since no catalysts are present, excellent retention of elastomer physical properties can be noted with the aro-

matic polyurea systems. While surface yellowing and discoloration can be noted, chalking and cracking are not present. For UV-testing, a QUV Weatherometer was used fitted with UVB-313 bulbs. Testing was performed using a continuous light source, no cycling, with a cabinet temperature of 50°C. Table IX gives selected physical property results both before and after 3,871 hours of exposure.

Aliphatic Systems

A more recent advancement in the spray polyurea elastomer technology is the development of 100-percent-solids, aliphatic polyurea elastomer systems. Aromatic MDI's have been replaced by meta-tetramethylxylene diisocyanates, m-TMXDI from American Cyanamid, in the quasi-prepolymer preparation. Also, the high-molecular-weight polyols normally used have been replaced by JEFFAMINE polyether amines to give polyurea quasi-prepolymers. Resins are based on JEFFAMINE polyether amines and JEFFAMINE amine chain extenders.¹⁹ System processing is like the aromatic polyurea elastomer systems and gel times from 1.5 to 15 secs are possible. Good weatherable spray polyurea elastomer systems could find broad applications in coating areas. Examples of some selected aliphatic spray polyurea elastomer systems can be found in Table X.

It is interesting to note that the low temperature properties of the aliphatic spray polyurea elastomer systems are also very good. Green strengths of these systems are superior to those of the aromatic spray polyurea elastomer systems. This is due to the relative softness of the hard block materials, m-TMXDI and the amine chain extenders. Note that the chain extenders used, a combination of JEFFAMINE T-403 and JEFFAMINE D-230, are very compatible with the soft block portion of the resin and isocyanate quasi-prepolymer. This is unlike the aromatic amine chain extender used in the aromatic spray polyurea elastomer system. This all indicates that possibly phase separation of the hard and soft blocks in the polymer is not occurring as with the aromatic systems. A variety of dyes, pigments and reinforcements can be incorporated in the aliphatic spray polyurea elastomer systems also.

UV Stability

As stated previously, the aliphatic spray polyurea elastomer systems would be excellent candidate systems for outdoor applications. As with the aromatic

Table VIII. Spray Polyurea Elastomers Containing Chopped Glass Roving*

Glass content, % ¹	0	5.7
Tensile strength, psi	1844	2131
Elongation, %	185	17.5
Tear, pli	375	500
Hardness, Shore D, 0 sec	52	56
Flexural modulus, psi		
25°C	38010	56695
70°C	20810	54028
-29°C	100910	95410
Heat sag, mm		
150 mm - 250°F/60 min	20	1.5
150 mm - 311°F/60 min	2	17

¹0.25 in chopped glass roving

*Complete sag

*Glass incorporated into elastomer using Venus R-84 Glass Chopper

Table IX. Aromatic Spray Polyurea - QUV Weatherometer Testing

	Initial	After 3871 hours ¹
Tensile strength, psi	1973	1953
Elongation, %	137	110
Tear strength, pli	435	481
Hardness, Shore D, 0 sec	59	63

¹Continuous using UVB-313 bulbs

Table X. Aliphatic Spray Polyurea Elastomers

Gel time, sec	3.0	3.0	3.0
Iso/Res volume ratio	1.00	1.00	1.00
Index	1.05	1.07	1.10
Elastomer Physical Properties			
Tensile strength, psi	970	1295	1245
Elongation, %	425	420	480
Tear strength, pli	210	250	210
Hardness, Shore D, 0 sec	39	36	38
MVT, perms at 30 dry mills	0.05	0.06	0.06
Abrasion resistance, wt loss mg (1000 gm, 1000 rev, H-18 wheels)	320	470	460
Low Temperature Properties (-20°F)			
Tensile strength, psi	1330	1665	1560
Elongation, %	310	350	350
Tear strength, pli	595	600	605

Table XI. Aliphatic Spray Polyurea - QUV Weatherometer Testing

Ti-Pure R-900, %	10.0	20.0
Iso/Res volume ratio	1.0	1.0
Elastomer Physical Properties		
Tensile strength, psi	657	1288
Elongation, %	398	338
Tear strength, pli	108	302
Hardness, Shore D, 0 sec	22	46
100% Modulus, psi	210	781
300% Modulus, psi	480	1165
Light Stability		
QUV Weatherometer, 5280 hours		
UVB-313 bulbs, visible changes	little	none

polyurea elastomer systems, aliphatic systems have been subjected to similar QUV Weatherometer testing. In this case, the systems were evaluated which contained loadings of titanium dioxide. Little to no color change was noted in these samples after 5,280 hours of continuous exposure at 50°C. Elastomer physical property results can be found in Table XI.

Conclusion

Spray polyurea elastomers have potential for limitless degrees of application and versatility. The advantages of both the aromatic and aliphatic spray polyurea elastomers will widely revolutionize the spray industry. These advantages have been summarized in Table XII. Spray processing of polyurea also shows the advantages associated with polyurea RIM and adds to the creative-

ness of polyurea technology. The exceptional properties, processing characteristics, toughness and processing freedom afforded by spray polyurea high performance elastomers are very appealing to consumers. The amorphous, non-crystalline nature of polyurea elastomers, as compared to polyurethanes, allows for a broad processing window.^{20,21} Formulations producing anything from soft elastomers to stiff, hard elastoplastics to aliphatic systems have been developed.

Acknowledgments

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Table XII. Advantages of Spray Polyurea Elastomers

- Fast Reactivity and Cure
- Relative Water Insensitivity
- Two-Component, 100% Solids (1:1 Volume Ratio)
- Excellent Physical Properties
- High Thermal Stability (up to 350°F)
- Wide Formulation Flexibility
- Reinforcement Incorporation Capability
- Easily Pigmented
- Ease of Application (spray or pour techniques)