

# Cast Polyurea Elastomers: Application, Processing and Performance

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Because of the handling performance and excellent physical properties and due to environmental reasons polyurea has found an increasing market interest in the last few years. Wherever solventless, catalyst free, 100% solid two component systems with fast cure are reactivity were needed and where ambient conditions should not affect the reactivity and the performance of the finished elastomer, the polyurea system could prove its application and property advantages. A lot of excellent results have been reported about polyurea RIM and polyurea spray in the past.

It is known that polyurea can also show its performance and its advantages in poured systems. For this application longer gel times and a special dosage unit and mixing head is needed.

The paper gives a short overview about the development of polyurea in spray and RIM applications. It reports on influence of different hindered primary amines on reactivity, handling performance, gel time and physical properties, i.e. hardness, tensile strength, tear resistance, flexural modulus and elongation of polyurea systems. In addition this paper introduces this new dosage unit with an L-shaped mixing head and reports on the influence of the processing conditions on the handling and on the above mentioned physical properties.

These new results, based on commercially available raw materials and machinery, open new application fields for the

environmental-friendly, 100% solid and catalyst free polyurea system. Some of these new possibilities will be discussed.

Two component elastomer systems have been known and used for decades. For example, the reaction of an alcohol with an isocyanate was discovered in 1849. In 1937 the reaction was expanded by Bayer coworkers to form polymers. During the fifties and the sixties urethane chemistry became one of the most important parts of organic chemistry. Urethane chemistry is described as the reaction of an isocyanate with a polyol, together with a catalyst. The reaction of an isocyanate with a primary amine also has been known for a long time. This reaction is much faster and needs no catalyst. (Figure 1).

It was not possible in the early days to use the isocyanate/amine reaction because of its high reactivity. This technology could only be used after the development of reliable two component high pressure technology. In the meantime industry started to use urethane systems in the elastomer area. Due to environmental, processing and performance reasons the next step was a combined urethane/urea technology. In this technology a catalyst was required. The last step to 100% urea systems was done approximately 15 years ago and eliminated the need for a catalyst as the aliphatic diamines Jeffamine\* polyetheramines were used. These products are di- or trifunctional primary polyetheramines with molecular weights between 230 through 5000. (Figure 2).

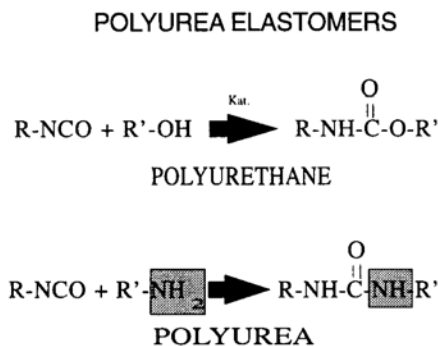


Figure 1

## Polyurea-Elastomers

Evolution of Two Component  
Polyurea Technology

	Isocyanate	Polyether
Polyurethane	MDI Based	Glycols EO Capped Polyols Catalysts
Polyurethane/Polyurea	MDI Based	Aromatic Diamine EO Capped Polyols Catalysts
Polyurea	MDI Based	Aromatic Diamines Aliphatic Diamines Polyether Polyamines
	TMXDI Based	Aliphatic Diamines Polyether Polyamines

Figure 2

### POLYUREA ELASTOMERS

Comparison of Performance Data  
Polyurethane-Polyurethane/Polyurea-Polyurea

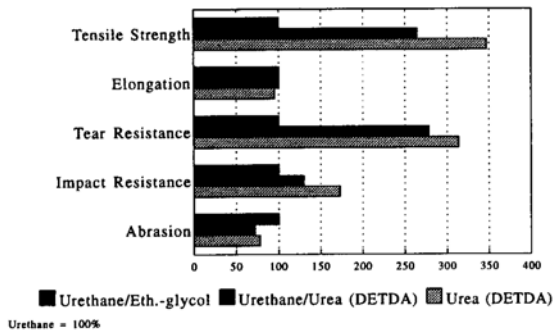


Figure 3

### POLYUREA ELASTOMERS

Advantages at a glance

- \* Two Component Systems
- \* Fast but Adjustable Reactivity and Cure
- \* 100% Solid / Solventfree
- \* Without Tin- or Amine Catalysts
- \* Excellent Physical Properties
- \* High Thermostability
- \* Aromatic and Aliphatic Systems
- \* Wide Formulation Flexibility
- \* Reinforcement Incorporation Capability
- \* Easily Pigmented
- \* Recyclable

Figure 4

### POLYUREA ELASTOMERS

Various Technologies

- \* POLYUREA SPRAY
- \* POLYUREA RIM
- \* POLYUREA CAST and Poured ELASTOMERS

Figure 5

### POLYUREA ELASTOMERS

Gusmer GX7 Spray Gun  
Impingement Mixing Process

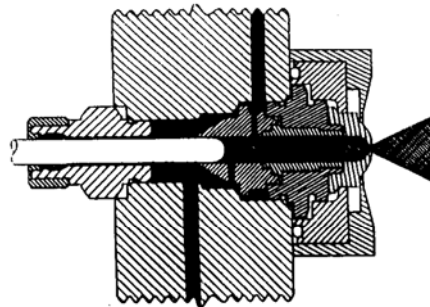


Figure 6

The development from 100% urethane systems to 100% urea systems was a logical step due to the higher performance of the urea technology. Improved abrasion resistance, faster gel time, increased tear resistance and higher thermostability supported this development. Especially the thermostability up to 180°C, and with short exposure times even more that 250°C should be mentioned as one of the reasons polyurea RIM has found such a big market in the automotive industry, where online painting and green strength is very important for some applications. (Figure 3).

Besides these performance advantages concerning physical data, there are a lot of other advantages concerning processing, environment, recyclability etc. The urea systems are basically fast systems. By using isocyanate quasi-prepolymers and the adequate chain extenders, you can adjust the gel and cure time. The systems are two component systems, which are mixed under high pressure. The systems are catalyst free, solvent free and 100% solid. Moisture during the application does not significantly influence the performance of the finished polymer. The prepolymer and the chain extender have medium viscosities (500 - 1500 Mpa) at ambient temperatures and are easy to use with the commercially available drum pumps. An important argument for the polyurea technology is the fact that used/recycled material can be dissolved up to 15% in the chain

extender component. Because of the good solvency behaviour of the Jeffamine\* Polyetheramines, it is a solution and not a dispersion.

The finished urea polymer made with the recycled material shows similar physical properties to the virgin material (Figure 4).

The first step was the introduction of the Polyurea RIM technology. Some years later this technology was expanded to spray applications. It should be mentioned here that three years ago the application of the urea reaction was also made possible in the foam area. Now as a logical consequence the third column in the elastomeric application is the use in cast or poured urea elastomers. (Figure 5).

As already mentioned the application of polyurea was not possible before developing the right machinery. Needed for this technology is a two component, high pressure unit with the appropriate mixing unit. (Figure 6).

The working pressure should be in the range of 70 - 250 bar. The temperature of the components in the mixing head should be around 60°-80°C to guarantee a viscosity that supports a satisfactory mixing within milliseconds. The output of this machinery is in the range of 600 g/min through 14 kg/min. This equipment has been commercially available for some years for

### POLYUREA ELASTOMERS

Spray  
Areas of Application

- \* Surface Coating of Concrete
- \* Protective and Abrasive Resistant Coating of Metals
- \* Road Striping
- \* Inmold Spray

Figure 7

### POLYUREA ELASTOMERS

Polyurea RIM Penetration in North America  
mt x1000

	1990	1991	1992	1993(EST)
Total Market	59,0	57,0	57,0	58,0
Polyurea RIM	0,8	3,5	5,9	7,3
% Polyurea	1,4	6,1	10,4	12,6

Figure 8

### POLYUREA ELASTOMERS

Polyurea RIM Application Worldwide  
Fascia

Model Year	Model	Application	Weight (KG)
1993	GM Pontiac F-Car (Firebird/Trans AM)	Front	5,5
1993	GM Pontiac H-Car (Bonneville Sedan)	Front and Rear	11,8
1993	GM Oldsmobile H-Car (Delta 88 Sedan)	Front and Rear	11,8
1993	GM Cadillac E-Car (Eldorado Sedan)	Front and Rear	11,8
1993	GM Cadillac K-Car (Seville Sedan)	Front and Rear	12,2
1993	GM F-Car (Pontiac and Chevrolet)	Front	8,2

Figure 9

### POLYUREA ELASTOMERS

Polyurea RIM Application Worldwide  
Side Body Moldings

Model Year	Model	Weight (KG)
1993	GM Pontiac Grand AM SE (2-Door Model)	9,1
1993	GM Pontiac Grand Prix	3,6
1993	GM Oldsmobile Cutless Supreme	5,0
1993	GM Oldsmobile Achieva	5,0

Figure 10

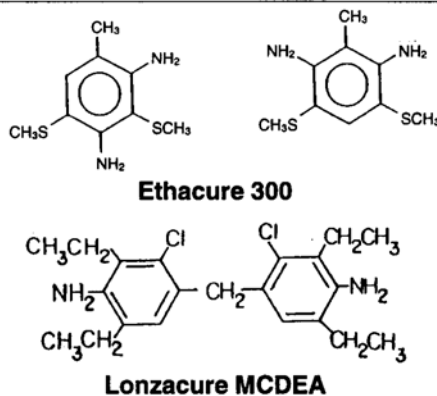
### POLYUREA ELASTOMERS

Polyurea RIM Application Worldwide  
Exterior Body Panels

Model Year	Model	Application	Weight (KG)	Location
1993	GM APV Minivan (Chevrolet, Pontiac, Oldsmobile)	Front Fenders	5,0	North America
1993	GM Chevrolet (Corvette)	Rocker Panels	3,0	North America
1993	Jeep Wrangler (Renegade)	Front and Rear Fenders, Side Step	15,0	North America
1993	GM F-Car (Chevrolet, Pontiac)	Front Fenders	10,0	North America
1993	Mazda Autozam AZ-1 (Seville Sedan)	Front Fenders	2,0	Japan
1993	Alfa 133 Spider	Front Fenders	2,0	Europe

Figure 11

# POLYUREA ELASTOMERS



Ethacure is a Trademark of Ethyl Corp., USA  
Lonzacure is a Trademark of Lonza, Switzerland

Figure 12

# POLYUREA ELASTOMERS

Influence of Ethacure 300 on Gel Time

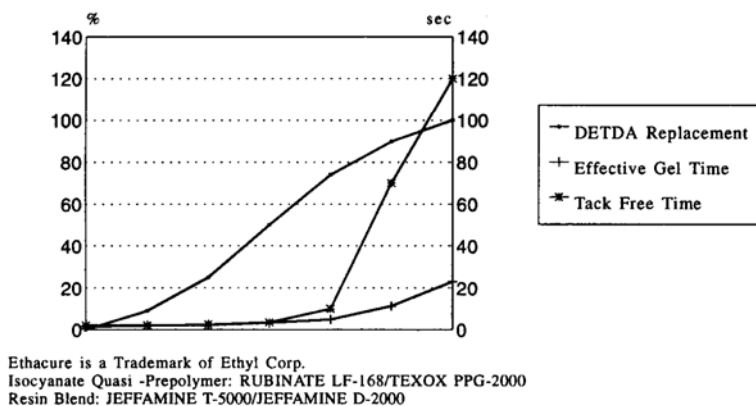


Figure 13

spray applications from US and European manufactures. Due to this many commercially used applications have been developed.

Here only the main applications are mentioned. Under these titles you can find many detailed uses of polyurea spray technology. Polyurea spray for example is used in sewer manholes, in concrete basins for tankfarms, for abrasive resistant coatings in the mining industry, etc. Parts of the runway markings at the Austin, Texas airport have been sprayed with polyurea material. (Figure 7).

In the RIM area you find even a more stormy development. In the US, polyurea RIM presently has a market share of 13% in automotive exterior RIM parts. (Figure 8).

In Europe we have also experienced a strong increase in the use of Texrim\* polyetheramine for this application. In future we anticipate further increases for this application in Europe since you can produce light, dimensionally stable parts with good paintability and recyclability.

Worldwide there is a great interest in polyurea RIM fascia, side body and exterior body panels applications. (Figures 9-11).

In this application the quantities used in the parts are in the area of between 2 through 12.2kg. These size parts are only possible if you can develop slower systems with working times of 20-50 secs. This is possible with special sterically hindered amines like Ethyl Ethacure 300 or Lonzacure MCDEA. (Figure 12).

The incorporation of increasing amounts of modified chain extenders, i.e. Ethacure 300, relative to the DETDA content, yields slower systems. Complete replacement of the DETDA with these modified chain extenders gives systems with extremely slow gel times. An example of the replacement of DETDA with Ethacure 300 is given in Figure 13. You can prolong the effective gel time from 1.5 seconds to 23 seconds. The tack free time is of course much more influenced.

With the Lonzacure MCDEA you can find the same effect. The gel time can also be influenced by the type of isocyanate

# POLYUREA ELASTOMERS

Isotherm PSM 80

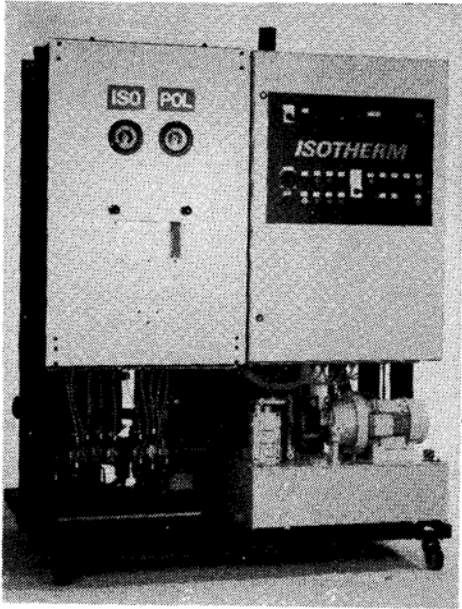


Figure 14

# POLYUREA ELASTOMERS

Isotherm PSM 80 / Function Chart

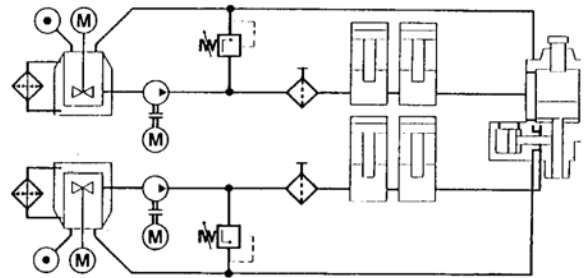


Figure 15

# POLYUREA ELASTOMERS

Isotherm L-shaped Mixing Head

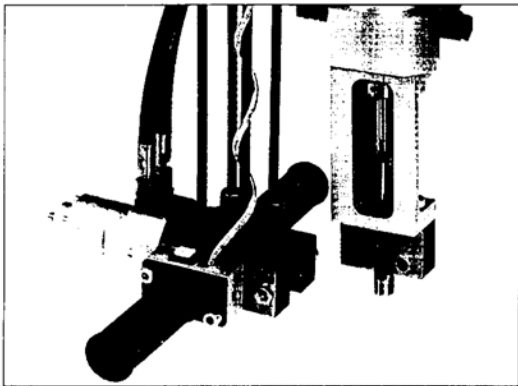
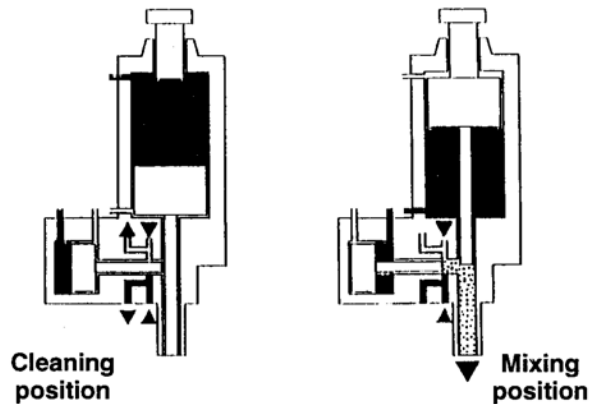


Figure 17 →

← Figure 16

# POLYUREA ELASTOMERS

Isotherm L-shaped Mixing Head  
Impingement Cast Mixing Process



# POLYUREA ELASTOMERS

## Aromatic Polyurea Elastomer Systems

	A	B
Isocyanate Component:		
Polyurea Spray Aromatic Quasi Prepolymer	100	100
NCO, %	16,5	16,5
RESIN Blend:		
JEFFAMINE Polyetheramine	65,1	64,5
Ethacure 300	34,9	-
Lonzacure MCDEA	-	35,5
Processing:		
Index	1,05	1,05
Iso/Res Vol. Ratio	1,00	0,50

Ethacure is a Tradename of Ethyl Corp.  
Lonzacure is a Tradename of Lonza

Figure 18

# POLYUREA ELASTOMERS

## Machinery Conditions

	Iso Side	Resin Side
System A:		
Pressure, bar	130	140
Temperature, °C	60	60
Iso Resin Ratio	1	1
System B:		
Pressure, bar	130	150
Temperature, °C	55	75
Iso Resin Ratio	1	2

Figure 19

# POLYUREA ELASTOMERS

## Properties of Cast Polyurea Systems

	A	B	Method
Working Time, sec	22	18	
Gel Time, sec	40	30	
Shore A	97	95	DIN 53505
Shore D	63	48	ASTM D-2240
Density, g/ml	1,14	1,14	DIN 53479
Tensile Strength, N/mm <sup>2</sup>	22,7	9,1	ASTM D-638
Elongation, %	505	345	ASTM D-638
Tear Resistance, N/mm <sup>2</sup>	107,7	64,8	ASTM D-624
Rebound Elasticity, %	53,0	46,1	DIN 53512
100% Modulus, MPa	12,5	7,2	
300% Modulus, MPa	18,1	8,9	ASTM D-638
Flexural Modulus, MPa	277,3	198,9	ASTM D-790

Figure 20

## POLYUREA ELASTOMERS

Roller System A

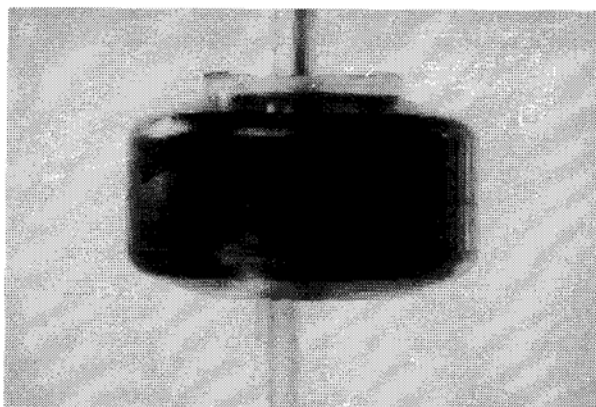


Figure 21

## POLYUREA ELASTOMERS

Roller System B

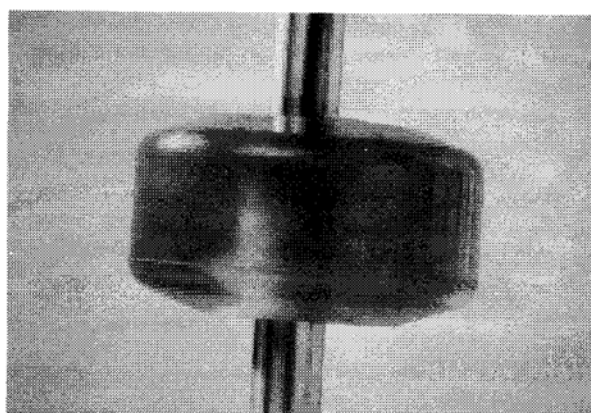


Figure 22

## POLYUREA ELASTOMERS

Advantages of Cast Polyurea Elastomers  
at a Glance

- \* Two Component Systems
- \* Fast but Adjustable Reactivity and Cure
- \* Easily Processed
- \* 100% Solid / Solventfree/Without Preflow
- \* Free of Metal- and Amine Catalysts
- \* Excellent Physical Properties
- \* Wide Formulation Flexibility
- \* Reinforcement Incorporation Capability
- \* Easily Pigmented
- \* Recyclable

Figure 23

quasi-prepolymer, by the ratio DETDA/polyetheramine and by the type of polyetheramine. As a result there are a lot of ways to prolong the working time and influence the properties of the elastomer.

The mixing and dosage unit plays, as already mentioned, an important role in this technology. All tests with poured polyurea were carried out on an Isotherm PSM 80. (Figure 14).

This two component high pressure unit was developed especially for high pressure small dosage of 10 - 300 g/seconds. The filters are motor driven. The dosage pump and hoses of the component are completely heated (water or oil) and the control of the temperature is guaranteed for the whole system. The mixing ratio is adjustable between 4:1 and 1:4. The components are recirculated during the processing time. (Figure 15).

The application is carried out with an L-shaped mixing head. (Figure 16).

It is a mechanically self cleaning mixing head and it works solvent free and without any preflow. The shot size is 3 - 300 grams. (Figure 17).

We investigated two polyurea systems. The isocyanate component was a polyurea aromatic quasi-prepolymer. The resin blend contained Jeffamine\* D-2000, Jeffamine\* D-4000 and Jeffamine\* T-5000. To adjust the gel times sterically hindered primary amines were used. System A was poured at a mixing ratio of 1:1, system B at a ratio of 2:1. (Figure 18).

The machinery conditions were as shown in Figure 19.

The systems were poured on heated (80°C) steel plates into a frame of 20 x 20 cm size. We received clear, transparent plates with the following properties. (Figure 20).

The physical properties are very good. They are in the same range that we already know from the polyurea spray and from polyurea RIM.

We also prepared some rollers as shown in **Figures 21 and 22**.

These rollers are currently being tested in a commercial application.

The results show that the polyurea technology is also applicable to cast or poured systems. The high performance and good properties of the urea systems are now also available for cast elastomer applications. This is a further step forward to broaden the use of Jeffamine\* polyetheramines in the chemistry. Especially if you see the challenges for the future to prepare low volatile, solvent free, 100% solid, catalyst free, recyclable elastomers. These demands can now be fulfilled in polyurea spray and polyurea RIM as well as in polyurea cast or poured systems. (**Figure 23**).

## BIOGRAPHIES

### **Dr. Karl-Franz Torges**

Dr. Torges received his Ph.D in Chemistry in 1985 from the Technical University of Clausthal-Zellerfeld, Germany. Afterwards he worked for the Henkel/Dehydag division as a Technical Sales Representative in Eastern Europe.

He joined Texaco Chemical Deutschland GmbH in 1989 as a Technical Sales Manager for the speciality chemical business. In 1991, in addition, he took over the responsibility as a Marketing Coordinator. Currently he is General Manager of Texaco Chemical Deutschland GmbH and he is also responsible for the marketing of the Texacat\* urethane catalysts in Europe.

### **Dudley J. Primeaux**

Dudley Primeaux received an M.S. Degree in Organic Chemistry from Lamar University in Beaumont, Texas, in 1984. He joined Texaco USA that same year in the Environmental and Customer Service Section. In 1985, he transferred to Texaco Chemical Co. - Austin Research Labs, Research Department, where he was involved in polyurethane foam development. Following the sale of Texaco Chemical Company's urethane polyol business to ARCO Chemical Company in 1987, Dudley joined the Performance Polymers Group where he has been involved in RIM and spray polyurea elastomer development and applications development of amine catalysts in polyurethane foams. Currently, he is Project Chemist in this group working with the polyurea spray elastomer technology. Dudley also holds numerous patents in polyurethane and polyurea foam as well as spray polyurea elastomer developments.