

The Processing of Spray Polyurea Elastomer Systems

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ABSTRACT

A new, leading edge technology of two-component spray elastomer systems is on the horizon generating large market and application interest in the industry. These high performance elastomer systems are based on amine-terminated polyether resins, amine chain extenders and isocyanates. The fast, consistent reactivity of these polyurea elastomer systems is possible without the use of catalysts. These systems are finding acceptance not only in spray applications but also in pour techniques. Recent advances in spray equipment design have significantly contributed to the development of these 100% solids spray polyurea elastomer systems.

In order to process this exciting technology, high pressure, impingement mix spray equipment is required. The instant reaction of the amine-terminated polyether resins with the isocyanate gives rapid viscosity increases in the mixing system. Heating capability of the spray equipment is very important for lowering the mix viscosity to improve spray processing. High pressure is necessary to adequately mix these highly reactive systems. Non-impingement mix processing fails to give proper mixing of the two components. This fast viscosity build during processing leads to frequent plugging of these type mixing chambers. The impingement mix concept, employed in high performance RIM applications, wipes clean the mixing chamber after the gun is de-triggered. This self cleaning process eliminates the need for solvent or air flushing after processing is terminated. This same concept can also be employed to polyurea pour systems as well. Information will be presented in this paper on processing spray and pour polyurea elastomer systems using commercially available high pressure, impingement mix application equipment.

INTRODUCTION

The spray polyurea elastomer technology has been a subject of considerable discussion and research over recent years [1-5]. This work has led to the development of

solventless, plural component aromatic and aliphatic polyurea elastomer systems. This technology, based on amine-terminated polyether resins, JEFFAMINE® amines, offers many processing and performance advantages over polyurethane and polyurethane-urea systems. The processing advantages observed are due to the unique processing characteristics of the polyurea elastomer technology. This processing uniqueness of the polyurea elastomer technology makes it essential that high performance equipment and parameters be used. In order to insure good mixing and fat dispersion of the material, impingement mixing using high temperature, high pressure, two-component spray equipment is essential. This relatively low cost, commercially available equipment can be used to process a wide variety of both aromatic and aliphatic polyurea elastomer systems by either spray or pour techniques. By utilizing both a leading edge technology and high performance application equipment, polyurea elastomer systems can be employed for coating and non-coating applications.

CHEMISTRY

In order to understand the importance of the high pressure, impingement mix requirement, the chemistry of the polyurea elastomer technology must be addressed. Polyurea elastomers result from the reaction of amine terminated resins and chain extenders with isocyanates. A general depiction can be seen in Figure 1.

The polyurea elastomer systems, unlike polyurethane elastomer systems, require no catalysts for reactivity. For the polyurea elastomer technology, this amine/isocyanate reaction is very fast, consistent and predictable over a broad range of ambient temperatures. The key to this technology is in the amine terminated resins. These products are primary amine terminated polyethers, generally having polyoxypropylene backbones. They are commonly referred to as JEFFAMINE® amines.

The reaction of the primary amine terminated polyethers with the isocyanates is almost instantaneous. This

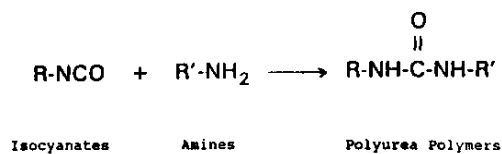


Figure 1. Polyurea chemistry.

is true for both the aromatic and aliphatic based isocyanates, unlike with hydroxyl terminated polyether resins. In conventional polyurethane and polyurethane-urea, catalysts are required to complete these reactions. This instant reaction yields significant viscosity builds in the elastomer system during mixing, commonly not seen with the polyurethane technology. This initial viscosity build in the mixing system explains why the use of conventional approaches to plural component processing do not apply.

As mentioned, the polyurea elastomer technology is a plural component technology based on an isocyanate and a resin blend. This is true for both the aromatic and aliphatic polyurea elastomer technology. General elastomer formulation information for these two systems can be found in Table 1.

EQUIPMENT

The major key in processing the polyurea elastomer technology is in the application equipment. For this study, commercially available high pressure, high temperature impingement mix spray equipment from GUSMER® Corporation was used. This paper discusses both aromatic and aliphatic polyurea elastomer technology, each using a similarly configured equipment setup.

For all of the polyurea elastomer spray and pour work, GUSMER H-2000 proportioners were used. These proportioners are both set so as to deliver isocyanate to resin

Table 1.

Isocyanate Portion	
Aromatic isocyanate quasi-prepolymers based on MDI and polyether polyols	
or	
Aliphatic isocyanate quasi-prepolymers based on m-TMXDI™ and polyether polyamines	
Resin Blend	
Blend of polyether polyamines	
Aromatic amine terminated chain extenders	
Pigments	
or	
Blend of polyether polyamines	
Aliphatic amine terminated chain extenders	
Pigments	
Processing	
INDEX	1.05 to 1.10
Iso/Res volume ratio	1.00

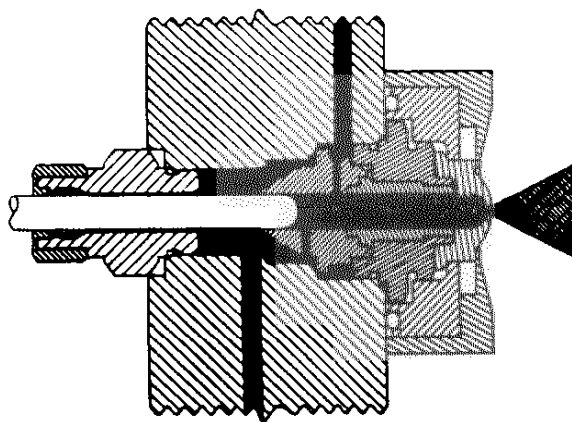


Figure 2. GX-7 spray gun—impingement mixing process (Courtesy of Gusmer, Lakewood, NJ).

volume ratio of 1:1. Variable ratio capability is possible; however, the 1:1 volume ratio tends to yield the best mix. These H-2000 proportioning units are capable of system pressures up to 2,200 psig (136 bars) with component temperatures up to 170°F (77°C). The dual electrically heated hoses used ranges in length from 35 to 85 ft (10.7 to 26 meters), including a 10 ft (3.1 meter) whip hose. Temperature on the hoses was maintained at the same temperature as the block heater on the proportioning unit.

For spray, and pour, a GUSMER GX-7 gun was used. The GX-7 spray gun incorporates easily changeable mixing modules and Pattern Control Disks (PCDs) utilizing the impingement mix concept. A diagram of the impingement mix system can be seen in Figure 2.

The equipment setup was modified to utilize small system delivery tanks as well as drum supplied material. Two-gallon (8.5 L) paint pots were installed and pressurized with either dry air or nitrogen. This allowed for small quantity preparation of as little as 10 lbs (4.5 kgs) for research and development applications. An illustration of this setup can be found in Figure 3.

Although material recirculation was not employed, this equipment can easily be fitted with loops to allow for recirculation before processing. By using this feature, material can be preheated before processing. For this study, a minimum of 25°C was maintained on the material supply containers to insure adequate supply to the proportioner by the 2:1 drum transfer pumps.

PRESSURE/TEMPERATURE STUDIES

It has already been stated that both high pressure and temperature are required to process the polyurea elastomer technology. These are both required at the same time during processing in order to properly atomize and mix the highly reactive primary amine based systems. For the pressure/temperature studies, only the aromatic system was used as given in Table 1. This system had an effective gel time of 2.5 secs. This same information can also be applied to the aliphatic polyurea elastomer technology.

Due to the fast, preferential reactivity of the primary amines with the isocyanates, high pressure (high velocity) impingement mix is very important. This process has been well demonstrated in the polyurea RIM technology where

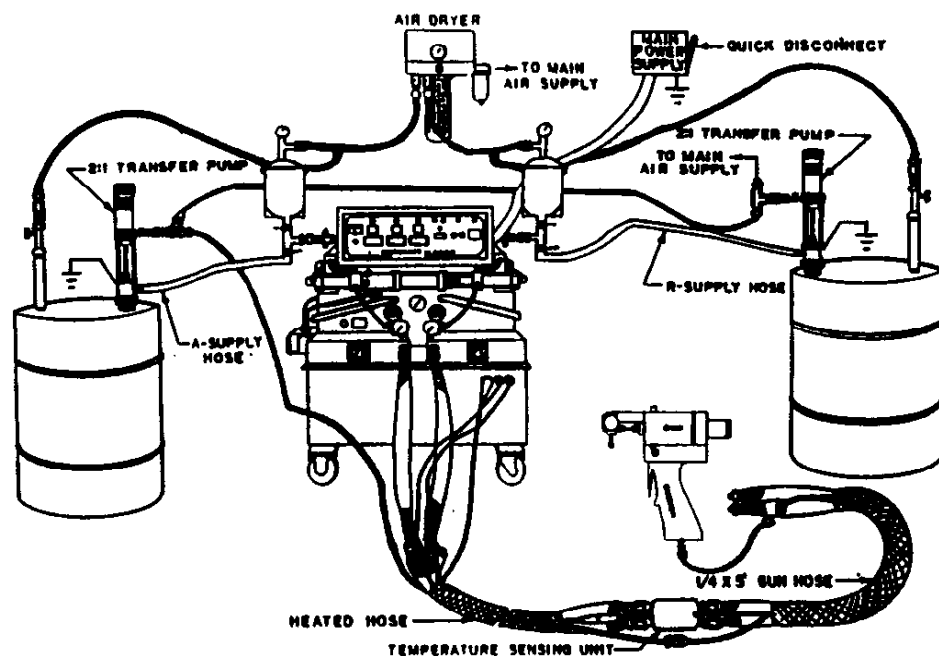


Figure 3. Spray equipment configuration.

impingement mix processing is also employed. In Table 2, the relationships of processing pressure to elastomer physical properties are given. For processing, component temperature was maintained at 160°F (71°C). A 3160-10-125 Module, with all ports drilled to 0.052", and a 16182-210-A PCD was used. Note that properties like tensile strength, elongation and tear strength significantly improve as processing pressure increases. The degree of atomization also improved as the processing pressure increased. Elastomer surface appearance went from a grainy, orange peel texture to a smooth surface as pressure increased.

In addition to high processing pressures, elevated processing temperatures are also required. In processing polyurethane elastomer systems, increasing the processing temperature typically increases the system reactivity. This is not necessarily the case in polyurea technology. By increasing the processing temperature, the mix viscosity of the system is lowered, giving improved mixing and flowability of the elastomer. This gives the impression that system reactivity in the polyurea elastomer technology is

slowed down by increases in processing temperature. Table 3 shows a comparison of the processing temperature to elastomer physical properties using the same formulation given in Table 1 and processed using the same spray gun mixing components as in the previous example. Notice the improvement in elastomer physical properties such as elongation, tear and impact strength. As the processing temperature increased, the atomization and flowability of the elastomer system also improved.

SYSTEM OUTPUT STUDIES

Now that the issue of high pressure, high temperature impingement mix has been addressed, elastomer system output can be evaluated. In order to change the system output of the spray polyurea elastomer system, changes must be made in the mixing chamber configuration of the standard GUSMER GX-7 spray gun. For this study, both aromatic and aliphatic spray polyurea elastomer systems

Table 2. Processing pressure vs. elastomer physical properties.

Mix pressure, bar ¹	61	68	75	95	122	136
Mix pressure, psi	900	1000	1100	1400	1800	2000
Tensile strength, mPa	7.9	9.9	12.1	12.6	14.6	12.9
Tensile strength, psi	1150	1430	1750	1830	2115	1870
Elongation, %	14.4	40.1	71.5	87.8	158	151
Tear strength, N/m ²	50.8	59.7	67.8	69.7	72.7	77.8
Tear strength, pli	290	340	390	400	415	445
Shore D hardness	45	45	50	56	54	58
Impact, notched, J/m	124	219	200	256	224	353
Impact, notched, in-lbs/in	27.8	49.3	45.1	57.5	50.4	79.5

¹Mix temperature of 71°C.
²X 1000.

Table 3. Processing temperature vs. elastomer physical properties.

Mix temperature °C ¹	38	49	54	60	66	71
Tensile strength, mPa	11.9	10.0	10.1	11.8	13.1	12.8
Tensile strength, psi	1720	1455	1470	1710	1900	1850
Elongation, %	16.3	41.8	67.7	76.4	126	150
Tear strength, N/m ²	48.3	49.2	60.9	65.0	66.1	68.1
Tear strength, pli	275	280	350	370	380	390
Shore D hardness	42	47	54	56	53	53
Impact, notched, J/m	218	223	284	237	284	372
Impact, notched, in-lbs/in	49.0	50.2	63.9	53.5	63.8	83.6

¹Mix pressure of 136 bars.

²X 1000.

were used. These two formulations are generalized in Table 1. These two systems will be referenced throughout the rest of this paper as simply the aromatic spray polyurea and the aliphatic spray polyurea system. These two formulations represent typical aromatic and aliphatic spray polyurea elastomer systems, and are given for purposes of discussion on the processing characteristics of the polyurea elastomer technology. The aromatic spray polyurea elastomer system had an effective gel time of 2.5 secs while the aliphatic spray polyurea elastomer system's was 3.0 secs.

As has been mentioned previously, the reaction of the primary amine terminated polyethers with isocyanates is very fast and preferential over hydroxyl terminated polyethers. This fast reactivity leads to significant viscosity builds of the material in the mixing chamber of the spray gun. It is then very important that the mixing polyurea elastomer system enter and exit the mixing chamber as quickly as possible. This is easily accomplished by adjusting the number and size of the mixing ports in the mixing module of the GUSMER GX-7 spray gun. Also important, is the Pattern Control Disk (PCD) which is used. Table 4 gives a comparison of the mixing chamber/PCD configurations to system output and elastomer physical properties

of the aromatic spray polyurea elastomer system. Also given is the relative size of the elastomer spray pattern. Note that in examples 1, 2, 5 and 6, the system output is simply adjusted by changing the PCD for the same configuration mixing module. Notice also that elastomer physical properties and processing remained relatively constant through the mixing chamber studies.

The same process can also be applied to the aliphatic spray polyurea elastomer technology. Given in Table 5 is the same relation given for the aromatic spray polyurea elastomer system. The aliphatic spray polyurea elastomer system was processed under similar conditions to the aromatic polyurea elastomer system discussed in Table 4. Physical property results are shown to be similar to the variable processing of the aromatic system.

By utilizing the GUSMER GX-7-400 series configuration, which has a total mixing chamber volume half that of the standard GX-7, spray outputs down to 2.0 kgs/min (4.4 lb/min) are easily obtained. The same concept of getting the mix material into and out of the mixing chamber as quickly as possible also applies here. Also, elastomer film thicknesses of less than half of that using the standard GX-7 configuration are easily obtained. Table 6 gives a comparison of the mixing chamber configuration to the

Table 4. Aromatic spray polyurea elastomer system output vs. elastomer physical properties.

	-1	-2	-3	-4	-5	-6
Mixing module ¹						
iso, ports	2	2	2	2	2	2
diameter, in	0.052	0.052	0.046	0.046	0.052	0.052
res, ports	2	2	2	2	2	2
diameter, in	0.052	0.052	0.043	0.043	0.052	0.052
Pattern control disk ²	212	213	213	203	202	209
Output, kg/min	4.1	5.4	5.4	8.4	10.4	12.0
Output, lb/min	9.0	12.0	12.0	18.5	23.0	26.5
Pattern, cm ³	30.5	40.6	40.6	50.8	55.9	50.8
Tensile strength, mPa	133	122	129	158	165	148
Tensile strength, psi	1915	1990	2375	2000	2280	2320
Elongation, %	133	122	129	158	165	148
Tear strength, N/m ²	80.7	79.5	75.8	73.4	80.2	89.8
Tear strength, pli	460	455	435	420	460	515
Shore D hardness	52	55	58	54	52	55
Impact, notched, J/m	125	200	165	292	339	208
Impact, notched, in-lbs/in	28.2	45.1	37.0	65.8	76.2	46.8

¹GX-7 Gun Module 16100-125-100 (3160-10-125 drilled).

²PCD 16182-size A.

³At 24 inches (61 cm) above substrate.

⁴X 1000.

Table 5. Aliphatic spray polyurea elastomer system output vs. elastomer physical properties.

	-1	-2	-3	-4
Mixing module ¹				
iso. ports	1	2	2	2
diameter, in	0.036	0.052	0.046	0.052
res. ports	1	2	2	2
diameter, in	0.031	0.052	0.043	0.052
Pattern control disk ²	212	212	210	203
Output, kg/min	4.1	4.8	9.1	11.4
Output, lb/min	9.0	10.5	20.0	25.0
Pattern, cm ³	30.5	30.5	45.7	40.6
Tensile strength, mPa	10.6	10.8	11.3	12.0
Tensile strength, psi	1535	1565	1640	1740
Elongation, %	347	398	351	361
Tear strength, N/m ²	42.2	42.6	47.8	47.5
Tear strength, pli	241	245	275	270
Shore D hardness	34	37	39	41

¹GX-7 Gun Module 16100-125-100 (3160-10-125 drilled)

²PCD 16182-size-A.

³At 24 inches (61 cm) above substrate.

⁴X 1000.

system output for both the aromatic and aliphatic spray polyurea elastomer systems discussed here. Note that examples 1 through 4 in Table 6 are for the aromatic spray polyurea elastomer system while examples 5 and 6 are for the aliphatic spray polyurea elastomer system. As with the standard mixing chamber configuration, the high temperature and pressure must be maintained for the smaller mixing chamber volume configuration.

REINFORCEMENT INCORPORATION

Polyurea elastomer systems can also be processed with reinforcement incorporation. This is done so as to improve flexural modulus, impact strength and thermal properties. Reinforcements are quite common in polyurea RIM for automotive exterior body panel applications. These reinforcement materials can either be incorporated into the polyurea elastomer system as it is being processed, or by incorporation into the plural component system before processing.

The first, incorporation into the polyurea elastomer system during processing, involves the use of a glass chopper and glass roving. For this work, a Venus R-84 roving cutter was fitted to the GUSMER GX-7 spray gun. A 15-blade rotor was used giving a chop length of 0.25 in. The chopped glass roving is then dispensed into the spray pattern of the polyurea elastomer systems, similar to polyester sprayup work. Table 7 gives a comparison of two aromatic polyurea elastomer systems, both with and without chopped glass roving. These aromatic systems are like that described in Table 1 with effective gel time of 2.0 to 2.8 sec. Approximately 6% by weight glass was incorporated into these polyurea elastomers. Note the improvement in elastomer flexural modulus, tear strength and thermal characteristics.

For the glass chop work, there are many possible chop lengths available for the roving cutters. However, the .25" to .5" chop length gives improved glass fiber "laydown" than the longer chop length, 1.25". This is due to the faster reactivity of the polyurea elastomer system and the inability to "roll out" the system after spraying.

As stated previously, reinforcing agents can also be incorporated into the components of the polyurea elastomer system before processing. Since most of these reinforcing agents tend to be extremely abrasive, a special mixing chamber had to be incorporated in the GUSMER GX-7 spray gun. A mixing module of tungsten carbide was prepared to replace the GUSMER module in the GX-7 spray gun, along with the coated valving rod [6]. For this study, sized wollastonite, G-RRIM™ WOLLASTOKUP® 10012, from NYCO was used. This material was dispersed in the resin components of aromatic polyurea spray elastomer systems and processed using the same 1:1 volume ratio high pressure, high temperature impingement mix technique with the tungsten carbide module. Table 8 gives a comparison of two aromatic polyurea elastomer systems, both with and without the sized wollastonite. Note the improvement in elastomer flexural modulus, tensile strength, tear strength and abrasion resistance with the incorporation of the reinforcing material.

POUR APPLICATIONS

Using this same impingement mix concept, low output pour applications can also be done. This is accomplished by using the same spray equipment setup with the pour con-

Table 6. Polyurea elastomer output studies GUSMER GX-7 400 series spray gun.

	Aromatic Polyurea				Aliphatic Polyurea	
	-1	-2	-3	-4	-5	-6
Mixing module ¹						
iso. ports	1	1	1	1	1	1
diameter, in	0.024	0.028	0.028	0.037	0.024	0.028
res. ports	1	1	1	1	1	1
diameter, in	0.020	0.024	0.024	0.033	0.018	0.024
Pattern control disk ²	212	212	213	210	212	212
Output, kg/min	2.3	2.7	2.9	5.7	2.0	2.9
Output, lb/min	5.0	6.0	6.5	12.5	4.5	6.5
Pattern, cm ³	20.3	25.4	22.9	40.6	20.3	30.5

¹GX-7 Gun Module 17100-(400 Style).

²PCD 16192-size.

³At 24 inches (61 cm) above substrate.

Table 7. Aromatic spray polyurea elastomers chopped glass roving reinforcement.

Chopped glass level, % ¹	0	5.7	0.0	6.0
Tensile strength, mPa	16.0	14.7	12.7	15.6
Tensile strength, psi	2325	2130	1835	2260
Elongation, %	150	17.5	165	160
Tear strength, N/m ²	65.1	87.6	67.9	81.4
Tear strength, pli	370	500	390	465
Shore D hardness	52	56	43	55
Flexural modulus				
25°C, mPa	262	390	220	305
25°C, psi	38,010	56,695	32,100	44,265
70°C, mPa	145	375	173	280
70°C, psi	20,810	54,030	25,060	40,885
-29°C, mPa	695	745	485	525
-29°C, psi	100,910	108,110	70,390	75,925

¹Using 0.25 inch chopped Fiberglas*

*X 1000.

figuration components in the GUSMER GX-7 spray gun. Typically, slower effective gel time systems process better, exhibiting a better mix of the polyurea elastomer system. The faster effective gel time systems can be processed successfully at the higher output ranges.

The pour configuration allows for high velocity streams to soft flows which allow applications such as crack and joint fill to potting. For these pour applications, high temperature processing must be maintained; however, lower processing pressures can be utilized on the slower reactive pour systems. Since system atomization is not required, the faster reactive systems can also be processed at the lower pressures in the pour applications.

To illustrate this concept, an aromatic polyurea elastomer, which had a slower effective gel time than the polyurea spray elastomer systems discussed earlier, was

used. Table 9 gives a comparison of the system output to mixing chamber configuration in the GUSMER GX-7 spray gun. The PCD utilized has a round tip to allow for a stream to exit the gun tip. Note that examples -1 thru -4 all use the same module with a different PCD. More forward velocity is produced with the smaller PCD (-46) than with the larger size (-125). In the pour application, processing pressure can also be much lower, as shown in Table 9. With the pour configuration, 1.3 cm (0.5 in) wide strips could easily be applied. As little as 1.2 gm shots could also be made with excellent mix of the material.

CONCLUSION

Processing the spray polyurea elastomer technology can be accomplished as easily as with the polyurethane tech-

Table 8. Aromatic spray polyurea elastomers containing sized wollastonite.

Filler level, % ¹	0	5.0	0.0	5.0
Mixing module ²				
iso, ports	3	3	3	3
diameter, in	0.043	0.043	0.043	0.043
res, ports	3	3	3	3
diameter, in	0.043	0.043	0.043	0.043
Pattern control disk ³	210	210	210	210
Tensile strength, mPa	15.3	16.0	14.3	15.6
Tensile strength, psi	2220	2325	2070	2260
Elongation, %	165	130	185	160
Tear strength, N/m ²	70.9	78.8	70.0	81.4
Tear strength, pli	405	450	400	465
Shore D hardness	50	56	52	55
Flexural modulus				
25°C, mPa	210	320	225	315
25°C, psi	30,275	46,615	32,600	45,450
70°C, mPa	150	245	176	245
70°C, psi	22,155	35,750	25,515	35,830
-29°C, mPa	545	655	450	720
-29°C, psi	79,200	94,835	65,110	104,200
Abrasion resistance, wt loss, mg (1000 gms, 1000 rev, H-18)	330	240	250	220

¹Filler level in elastomer: G BRIM[®] WOLLASTOKUP[®] 10012

²Mixing module made of tungsten carbide

³PCD 16182-size-A.

*X 1000.

Table 9. Aromatic polyurea pour applications.

	-1	-2	-3	-4	-5	-6
Mixing module ¹						
iso. ports	1	1	1	1	1	1
diameter, in	0.024	0.024	0.024	0.024	0.025	0.028
res. ports	1	1	1	1	1	1
diameter, in	0.020	0.020	0.020	0.020	0.023	0.024
Pattern control disk ²	46	55	90	125	125	125
Output, kg/min ³	0.8	1.1	1.1	1.1	1.4	1.8
Output, lb/min	1.7	2.5	2.5	2.5	3.0	4.0

¹GX 7 Gun Module 16100-125-100.

²PCD 16182 size A.

³At static pressure of 68 bar/mix pressure of 40 bar (1000 psi/600 psi).

nology. Understanding the truly fast reactivity of the polyurea elastomer technology is the real key to successfully processing this leading edge technology. By combining high pressure, high temperature impingement mix equipment and the polyurea elastomer technology properly, a variety of applications are made possible for the polyurea materials. The aromatic and aliphatic systems can easily be sprayed by making minor adjustments in this relatively simple spray equipment. These simple adjustments allow for system outputs from 2.0 to 12.0 kg/min (4.5 to 26.5 lb/min) with spray patterns from 20 to 45 cm (8.0 to 18.0 in). In addition to spray applications, changes in system formulation and spray gun configurations allow for pour dispensing of the polyurea materials.

The unique processing characteristics of the polyurea elastomer technology, coupled with this commercially available high performance equipment, yields an elastomer system suited for a variety of applications. While this paper has discussed the use of GUSMER spray equipment, other spray equipment could possibly be used. Like the GUSMER equipment, this equipment must be capable of high pressure, high temperature impingement mix.

ACKNOWLEDGEMENTS

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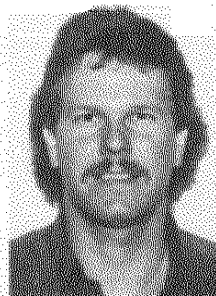
The author dedicates this paper to the memory of his father, Dudley J. Primeaux, Sr., whose thirty-eight plus years of devoted service to Texaco and his family devotion have been the inspiration for the author's work.

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BIOGRAPHIES

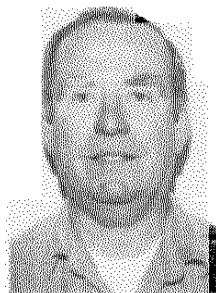
Dudley J. Primeaux II



Dudley received a 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. 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 a Project Chemist in this group. Dudley also holds numerous patents in polyurethane foam and spray polyurea elastomer developments.

Kenneth C. Anglin



Kenneth joined Jefferson Chemical Company (Texaco Chemical Company) in 1966, working in the polyurethane foam application area and foam physical testing lab. After working with the Process Development Group in the process demonstration unit starting polyol and amine catalyst synthesis projects, the majority of his career was spent in the applications development of flexible slab and molded

polyurethane foam and amine catalyst application. In 1988, Ken joined the Performance Polymers Group, as a Technician Specialist, and is involved in the applications development of the spray polyurea elastomer technology.