

100% Solids Aliphatic Spray Polyurea Elastomer Systems

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ABSTRACT

Regulations are continually being passed which limit the volatile organic content of elastomer coating systems. Because of this, high solids, two-component spray elastomers and coatings are attaining increases in market interest and sales volume. As this interest grows, the research and development effort focuses on newer and better polymer materials. The development of 100% solids aromatic polyurethane elastomer systems has shown promise with respect to the VOC issues. Recently, a further refined 100% solids spray elastomer system, based on polyurea RIM technology, has also been demonstrated. These systems, like polyurea RIM materials, are based on aromatic isocyanates, aromatic amine chain extenders and amine-terminated polyether resins. In order to take full advantage of the leading edge polyurea elastomer technology, 100% solids aliphatic polyurea elastomer systems have been developed. Amine-terminated polyether resins along with aliphatic isocyanates are incorporated into this next generation of spray elastomer materials.

Aliphatic spray polyurea elastomer systems, like the aromatic polyurea elastomer systems, require no catalysts and are extremely fast in reactivity and cure. Due to this fast reactivity and cure, these systems are virtually unaffected by moisture during processing. Application of the aliphatic polyurea systems is also possible in a variety of temperature ranges with little effect on the reaction profile and cure. Any VOC standards or regulations are easily complied with due to the 100% solids characteristic. Excellent elastomer physical properties are also noted at varied temperature ranges. Obviously, spray elastomer systems based on this aliphatic polyurea technology are good candidates for both coating and noncoating-type applications. Recent advances in the aliphatic spray polyurea elastomer technology will be discussed in this paper.

INTRODUCTION

In coating applications, elastomer systems with good mechanical properties are required so as to insure ex-

tended serviceability of the product. In addition to the good mechanical properties, the coatings must be stable to their exposed environments. Not only is the performance of the elastomer system important, but the material should be able to be easily applied in a variety of conditions and give comparable performance. It would also be of major importance that the elastomer system not release anything into the environment. Recent advances in two-component spray elastomer technology have yielded a new development which addresses these concerns [1,2]. This new, leading edge technology incorporates polyoxyalkylene diamines and triamines rather than high performance polyols and catalysts. Both aromatic and aliphatic isocyanates can be used to prepare this new technology, spray polyurea elastomer systems.

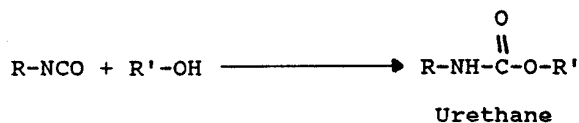
CHEMISTRY AND CONCEPT

Polyurethanes were some of the first polymers to be used in two-component spray elastomer applications. For the polyurethane elastomer systems, high performance polyether polyols, glycol type chain extenders and catalysts are used. For the polyurea elastomer systems, polyoxyalkylene amines and amine terminated chain extenders are used. One of the key advantages of the spray polyurea elastomer technology is that no catalyst is required. A representation of the polyurethane and polyurea technology can be seen in Figure 1.

The primary amine/isocyanate reaction in the spray polyurea elastomer system is normally very fast, proceeding to completion within a few seconds without any catalysts. This is even the case for the aliphatic isocyanates which usually require high catalyst levels with the polyurethane elastomer technology. The fast reaction of the polyurea elastomer technology is very consistent and predictable, unlike polyurethane systems which depend on the life of a sensitive catalyst package for reactivity.

The key advantages of the spray polyurea elastomer technology as in the JEFFAMINE® polyetheramines from Texaco Chemical Co. These products are amine terminated polyethers, generally having polyoxypropylene backbones.

POLYURETHANE



POLYUREA

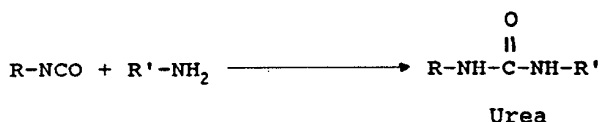


Figure 1.

These materials find use in the aliphatic spray polyurea elastomer technology as both the soft-block and chain extender portion of the system [3]. A listing of the commonly used JEFFAMINE® polyetheramines can be found in Table 1.

The isocyanate component of this emerging technology is a soft-block quasi-prepolymer based on aliphatic isocyanates. In the quasi-prepolymer preparation, the polyoxyalkylene amines are used as the soft block portion rather than slower reacting polyols. No catalysts or heating is required in the preparation of these polyurea isocyanate quasi-prepolymers. After preparation, these isocyanate quasi-prepolymers are ready for use and stable for extended periods of times. Table 2 gives a comparison of the isocyanate content of three selected polyurea isocyanate quasi-prepolymers. M-Tetramethylxylene diisocyanate (m-TMXDI®) from American Cyanamid was used in the isocyanate quasi-prepolymer preparations. It should be noted that by using a polyurea isocyanate quasi-prepolymer with the amine based resin system, 100% polyurea elastomer systems are produced.

A wide variety of aliphatic spray polyurea elastomer material are possible, ranging from soft elastomer to hard polymers. This is accomplished by varying the soft block content in the isocyanate quasi-prepolymer and the amine chain extender in the resin blend. Formulation work is easily done so as to maintain an isocyanate component to resin component volume ratio of 1 to 1. These systems can also be formulated to give excellent reaction injection molding (RIM) systems. However, RIM applications will not be discussed in this presentation.

Table 1. JEFFAMINE® polyetheramines.

| | Functionality | Approximate Molecular Weight |
|------------------|---------------|------------------------------|
| JEFFAMINE T-5000 | 3 | 5000 |
| JEFFAMINE T-3000 | 3 | 3000 |
| JEFFAMINE D-4000 | 2 | 4000 |
| JEFFAMINE D-2000 | 2 | 2000 |
| JEFFAMINE T-403 | 3 | 400 |
| JEFFAMINE D-230 | 2 | 230 |

Table 2. Aliphatic isocyanate quasi-prepolymers.

| | Isocyanate Content, meq/q | | |
|--------|---------------------------|--------------------------|-----------------------|
| | Calculated | Preparation ¹ | 6 Months ² |
| Soft | 2.60 | 2.52 | 2.50 |
| Medium | 3.94 | 3.69 | 3.67 |
| Hard | 4.86 | 4.83 | 4.80 |

¹One hour after preparation.

²Storage over dry nitrogen pad.

SPRAY EQUIPMENT

In order to process this exciting new technology, heralded as "An Entrepreneur's Dream" in an editorial in *Plastic Trends* [4], some consideration must be given to the processing equipment. Due to the fast reaction rates, conventional static mix, solvent flush equipment cannot be used. In order to insure good mixing 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 the aliphatic polyurea elastomer technology. An illustration of the impingement mix system can be found in Figure 2.

Using this spray equipment, elastomer output ranges from 2.0 to 11.8 kgs/min are easily obtained. Spray coverage ranges from 20 to 61 cm, in either fan or round spray patterns. Processing of the aliphatic systems in this equipment must be done at high temperature and pressure. Typically, these systems are processed at 60°C to 71°C with system pressures from 68 bars to 136 bars.

TECHNOLOGY

As previously discussed, spray polyurea elastomers result from the high pressure impingement mixing of a soft block isocyanate quasi-prepolymer, based on aliphatic isocyanates, with a resin component made up of poly-

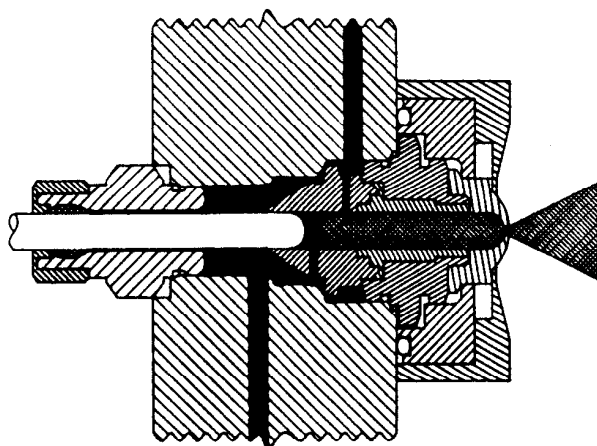


Figure 2. GX7 spray gun impingement mixing process (courtesy of Gusmer, Lakewood, NJ, U.S.A.).

etheramines and amine chain extenders. These highly reactive polyurea elastomer systems again require no catalysts. Due to the fast reaction rates and cure of the polyurea elastomer systems, sloped or verticle surfaces can be sprayed without forming runs or drips. Surfaces can be walked on within seconds after spraying. This fast, preferential reaction of the polyetheramines compared to hydroxyl materials yields spray polyurea elastomer systems which are relatively insensitive to moisture during processing. While processing an aliphatic spray polyurea elastomer system, 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 system while moderate elastomer foaming was noted in a comparable polyurethane system.

Processing was also performed during periods of relatively high humidity, >85%. For the polyurethane system, elastomer foaming was noted when processed at an index range of 1.00 to 1.20 using the variable ratio capability. No elastomer foaming was noted in the polyurea system processed under similar conditions. This can be illustrated in Figure 3.

Processing of the spray polyurea elastomer systems can also be done under low ambient temperature. Systems have been applied to substrates with temperatures of less than -28°C giving the same reactivity and cure as when sprayed on substrates at room temperature and also elevated temperatures. For processing at low ambient temperatures, the supply material to the spray unit must be heated to insure good supply to the spray equipment.

As mentioned previously, soft elastomeric to hard polymer systems can be obtained, suggesting wide formulation flexibility of the polyurea elastomer systems. Since these aliphatic polyurea elastomer systems are 100% solids and processed at a 1:1 volume ratio, the range of elastomer system's 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 blend. The aliphatic isocyanate content in the quasi-prepolymer and the chain extender level determine the elastomer's hard block content. The soft block content arises from the polyetheramine in the quasi-prepolymer plus the high molecular weight polyetheramine content of the resin. Table 3 gives the physical properties of selected aliphatic spray polyurea elastomer systems over a range of material hardness. Note that the effective gel times of the soft polyurea elastomer systems are slower than those of the harder

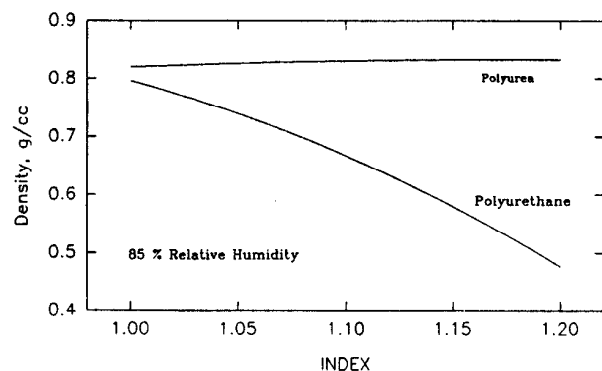


Figure 3. Polyurea vs. polyurethane—humidity effect on elastomer density with respect to index.

Table 3. Aliphatic spray polyureas.

| INDEX | 1.00 | 1.00 | 1.05 | 1.05 |
|---------------------------|------|------|------|------|
| Iso/Res volume ratio | 1.00 | 1.00 | 1.00 | 1.00 |
| Iso/Res weight ratio | 1.05 | 1.07 | 1.10 | 1.10 |
| Hard Block, % | 38.8 | 48.7 | 58.3 | 65.5 |
| Effective "gel" time, sec | 5.0 | 3.0 | 2.0 | 1.5 |
| Tensile strength, MPa | 3.76 | 7.52 | 6.59 | 11.4 |
| Elongation, % | 319 | 319 | 327 | 111 |
| Tear strength, N/m' | 19.4 | 45.5 | 46.7 | 58.5 |
| Shore D hardness | 26 | 37 | 46 | 51 |
| 100% modulus, MPa | 1.65 | 3.61 | 4.78 | 9.47 |

¹ × 1000.

polyurea spray elastomers. This is due to the lower ratio of the polyetheramine chain extender to the high molecular weight polyetheramines in the resin component. Also note the change in the polymer hard block content.

Water Absorption

The fast reactivity of the aliphatic spray polyurea elastomer systems leads to excellent moisture insensitivity during processing as discussed earlier. The aliphatic spray polyurea elastomers also have excellent moisture insensitivity as illustrated by water absorption in the polymer. This is due mainly to the polypropylene glycol backbone of the JEFFAMINE® amines. This can best be illustrated in the form of water absorption/freeze-thaw cycle testing on the aliphatic spray polyurea elastomer systems. It should be noted that these systems all used the polyetheramine chain extenders and high pressure, high temperature impingement mixing. Results can be found in Table 4.

Low Temperature Properties

In addition to the excellent range of room temperature physical properties, aliphatic spray polyurea elastomer systems also have excellent low temperature physical properties. Two selected aliphatic spray systems, with one system being pigmented, were tested at 25°C and -20°C . These systems were based on isocyanate quasi-prepolymers of m-TMXDI® and JEFFAMINE® amines with resin blends using the low molecular weight polyetheramines as chain extenders. This data is presented in Table 5.

Table 4. Water absorption/freeze-thaw cycles (spray polyurea elastomers).

| | Immersion ¹ | | Freeze/Thaw ² | |
|--|------------------------|------|--------------------------|------|
| | wt, % | t, % | wt, % | t, % |
| Aliphatic, ³ unpigmented | 3.77 | 1.40 | 4.76 | 3.20 |
| Aliphatic, ³ pigmented ⁴ | 3.14 | 1.19 | 3.62 | 2.60 |
| Aliphatic, solid | 0.38 | <1.0 | 0.54 | <1.0 |

¹Immersion at 25°C .

²9 freeze/thaw cycles.

³Sprayed samples, microcellular.

⁴Titanium dioxide pigment, 10% weight.

Table 5. Low temperature properties (aliphatic spray polyurea).

| | Pigmented ¹ | | Unpigmented | |
|---------------------------------|------------------------|-------|-------------|-------|
| | 25°C | -20°C | 20°C | -20°C |
| Tensile strength, MPa | 8.93 | 11.5 | 8.58 | 10.8 |
| Elongation, % | 420 | 350 | 480 | 350 |
| Tear strength, N/m ² | 43.8 | 105 | 36.8 | 106 |
| Shore D hardness | 36 | — | 38 | — |

¹2% titanium dioxide, by weight.

² × 1000.

It is interesting to note that these low temperature physical properties are quite good. Elastomer green strengths are also much better than in the polyurethane systems and even the aromatic polyurea systems. This is due to the relative softness of the hard block materials, m-TMXDI[®] and the polyetheramine chain extenders. Note that the chain extenders used, JEFFAMINE[®] T-403 and D-230, are very compatible with the soft block portion of the resin and isocyanate quasi-prepolymer. This is unlike the aromatic amine chain extenders used in the aromatic spray polyurea elastomer systems, indicating that possibly phase separation of the hard and soft blocks in the polymer is not occurring as with the aromatic systems [1,2].

In an independent study, samples of steel, concrete and asphalt were coated with an aliphatic spray polyurea elastomer. These samples were then sprayed for 30 seconds with a stream of liquid nitrogen (-196°C) at a distance of 30.5 cm from the surface with no damage occurring. When the distance was shortened to 10.2 cm, slight crazing of the elastomer was noted on the concrete and steel samples. No damage occurred on the asphalt sample. When the concrete coated sample was dropped from a distance of 1.8 meters, the concrete shattered but the aliphatic polyurea elastomer coating was undamaged and held the broken concrete pieces together [5].

UV Stability

Since no catalysts are present, excellent retention of elastomer physical properties is seen with the aromatic 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 6 gives selected physical property results both before and after 3871 hours of exposure.

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

Table 6. Aromatic spray polyurea (QUV weatherometer testing).

| | Initial | After 3871 hours ¹ |
|-----------------------------|---------|-------------------------------|
| Tensile strength, MPa | 13.6 | 13.5 |
| Elongation, % | 137 | 110 |
| Tear strength, N/m (× 1000) | 76.2 | 84.2 |
| Shore D hardness | 59 | 63 |

¹Continuous using UVB-313 bulbs.

Table 7. Aliphatic spray polyurea (QUV weatherometer testing).

| | | |
|-----------------------------|--------|------|
| Ti-Pure [®] R-900 | 10.0 | 20.0 |
| Tensile strength, MPa | 4.53 | 8.89 |
| Elongation, % | 398 | 338 |
| Tear strength, N/m (× 1000) | 18.9 | 52.9 |
| Shore D hardness | 22 | 46 |
| 100% modulus, MPa | 1.45 | 5.38 |
| 300% modulus, MPa | 3.31 | 8.03 |
| 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, two systems were evaluated which contained loadings of titanium dioxide. Little to no visual color change was noted in these samples after 5280 hours of continuous exposure at 50°C. Elastomer physical property results can be found in Table 7.

Cycloaliphatic Amine Chain Extenders

Aliphatic spray polyurea elastomer systems have also been demonstrated which incorporate cycloaliphatic diamine chain extenders. Two examples which have shown excellent results are 1,4-diaminocyclohexane (1,4-DCH) and isophorone diamine (IPDA) [6]. These diamine chain extenders give similar processing to the polyoxyalkylene amine extended aliphatic polyurea elastomer systems. Elastomer physical properties are also very good. A comparison of the cycloaliphatic diamine chain extended systems to the JEFFAMINE[®] amine extended systems can be found in Table 8.

Note that the hard block content decreased as the cycloaliphatic diamine chain extenders were incorporated. This is due to the fact that the same isocyanate quasi-prepolymer was used in each example and the equivalent weights are lower for the cycloaliphatic diamines. The

Table 8. Cycloaliphatic diamine chain extenders (aliphatic spray polyurea elastomers).

| | JEFFAMINE [®] | | |
|---------------------------|------------------------|----------------------|-------------------|
| | Amines ¹ | 1,4-DCH ² | IPDA ³ |
| INDEX | 1.05 | 1.05 | 1.05 |
| Iso/Res volume ratio | 1.00 | 1.00 | 1.00 |
| Iso/Res weight ratio | 1.07 | 1.06 | 1.06 |
| Hard block, % | 48.7 | 33.7 | 37.9 |
| Effective "gel" time, sec | 2.0 | 1.5 | 1.5 |
| Tensile strength, MPa | 6.56 | 6.90 | 6.45 |
| Elongation, % | 391 | 664 | 357 |
| Tear strength, N/m | 38.2 | 43.9 | 53.6 |
| Shore D hardness | 40 | 31 | 44 |
| 100% modulus, MPa | 2.90 | 2.86 | 5.26 |
| 300% modulus, MPa | 4.91 | 4.12 | 6.14 |

¹Blend of JEFFAMINE[®] T-403 and JEFFAMINE D-230.

²1,4-Diaminocyclohexane.

³Isophorone diamine.

Table 9. Advantages of aliphatic spray polyurea elastomers.

- Fast, consistent reactivity and cure
- Two-component, 100% solids
- Relative water insensitivity
- Excellent physical properties
- Wide formulation flexibility
- Easily pigmented
- Easily processed

volume ratio was also being maintained at 1:1, isocyanate to resin.

CONCLUSION

As one can observe, the aliphatic spray polyurea elastomers have potential for limitless degrees of application and versatility. The advantages of the aliphatic spray polyurea elastomers will widely revolutionize the spray industry. The two-component, 100% solids aliphatic formulations address many VOC issues. The fast, consistent reactivity yields many advantages in processing over conventional catalyzed polyurethane elastomer systems. Although not discussed here, reinforcements can also be incorporated into the aliphatic polyurea elastomer systems as easily as with the aromatic spray polyurea elastomer technology. These advantages have been summarized in Table 9.

The exceptional properties, processing characteristics, toughness and processing freedom afforded by the aliphatic spray polyurea high performance elastomers are very appealing to consumers. The amorphous, non-crystalline nature of the polyurea elastomers, as compared to polyurethanes, allows for broader processing and performance latitudes. Formulations producing anything from soft elastomers to stiff, hard elasto-plastic aliphatic systems have been developed. The aliphatic spray polyurea elastomer technology is truly a leading edge technology and an applicator's dream material.

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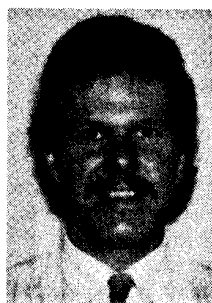
samples and operating the spray equipment. The GUSMER® Corp. has also played a key role in equipment development and assistance in the polyurea elastomer technology research. Special thanks go to Mrs. Starla Taylor for typing this text. I also wish to thank Texaco Chemical Co. for their support in this project.

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BIOGRAPHY

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Dudley J. Primeaux II 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. where he was involved in polyurethane foam development. He joined the Performance Polymers Group where he has been involved in RIM and spray polyurea elastomer development and application development of amine catalysts in polyurethane foams. He currently holds patents in polyurethane foam and spray polyurea elastomer developments.