100% Solids Aliphatic Spray Polyurea Elastomer Systems

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ABSTRACT: Regulations are continually being passed that limit the volatile organic content (VOC) of elastomer coating systems. Because of this restriction, 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

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the aliphatic spray polyurea elastomer technology will be discussed in this paper.

INTRODUCTION

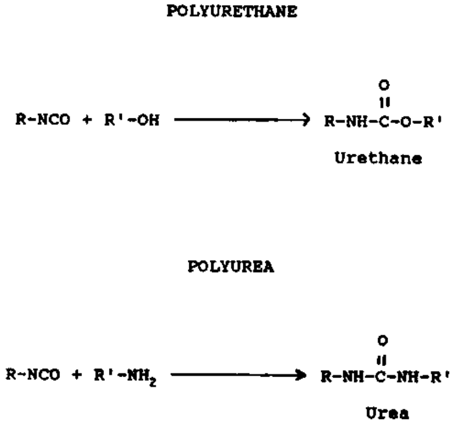
IN COATING APPLICATIONS, elastomer systems with good mechanical properties are required to insure extended serviceability of the product. In addition to the good mechanical properties, the coatings must be stable in their exposed environments. Not only is the performance of the elastomer system important, but the material should be capable of easy application 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 that 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 among 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 that depend on the life of a sensitive catalyst package for reactivity.

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



$$R\text{-}NCO + R'\text{-}OH \longrightarrow R\text{-}NH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R'$$

$$R\text{-}NCO + R'\text{-}NH_2 \longrightarrow R\text{-}NH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}R'$$

FIGURE 1. Polyurethane and polyurea technology.

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 are 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

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/g		
	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

[1] One hour after preparation.
[2] Storage over dry nitrogen pad.

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 is possible, ranging from soft elastomer to hard polymers. This range 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 to maintain an isocyanate component to resin component volume ratio of 1:1. These systems can also be formulated to give excellent reaction injection molding (RIM) systems. However, RIM applications will not be discussed in this presentation.

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 kg/min can be obtained. Spray coverage ranges from 20 to 61 cm in length, 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 to 71 °C with system pressures from 68 to 136 bars.

ELASTOMER PHYSICAL PROPERTY TESTING

Physical property testing for the spray polyurea elastomer samples was done in accord with standards of the American Society for Testing and Materials (ASTM). The ASTM test methods and their physical property test description are given below:

ASTM D-570	Water absorption
ASTM D-624	Tear strength
ASTM D-638	Tensile strength, elongation and 100% and 300% modulus
ASTM D-2240	Shore Hardness (A and D)
ASTM G-53	QUV Weatherometer testing

For Dynamic Mechanical Spectrometry (DMS) testing, Rheometrics RDS-2EH equipment was used. Testing was performed at 1 Hz.

TECHNOLOGY

As previously discussed, spray polyurea elastomers result from the high pressure impingement mixing of a soft block isocyanate quasiprepolymer, based on aliphatic isocyanates, with a resin component made up of polyetheramines and amine chain extenders. These highly reactive polyurea elastomer systems require no catalysts. 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. This fast, preferential reaction of the polyetheramines compared to hydroxyl materials yields spray polyurea elastomer systems that are relatively insensitive

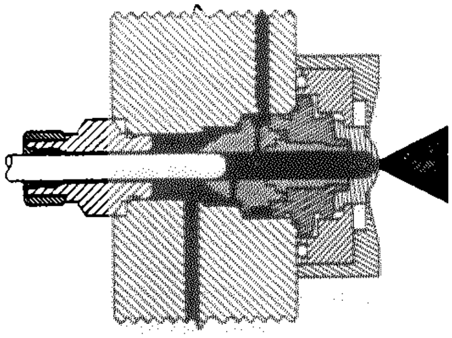


FIGURE 2. GX7 spray gun–impingement mixing process.

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 whereas moderate elastomer foaming was noted in a comparable polyurethane system.

Processing was also performed during periods of relatively high humidity– >85%. Elastomer foaming was noted for the polyurethane system 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 contrast is 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 below −28°C giving the same reactivity and cure as when sprayed on substrates at room temperature and at 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 the 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 polyurea spray elastomers, which 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

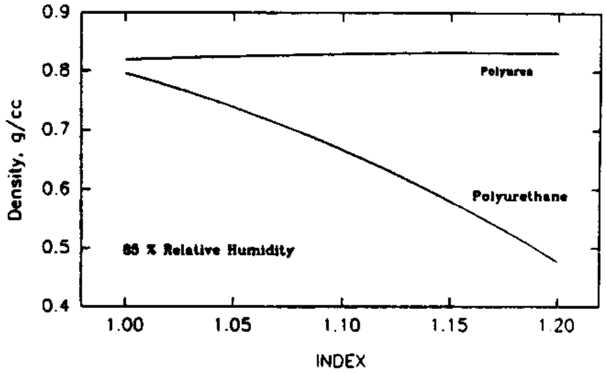


FIGURE 3. Polyurea vs. polyurethane–humidity effect on elastomer density with respect to index.

moisture insensitivity as illustrated by water absorption in the polymer. This insensitivity is due mainly to the polypropylene glycol backbone of the JEFFAMINE® amines, which 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

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[1]	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] x 1000

Table 4. Water absorption/freeze-thaw cycles for 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

[1] Immersion at 25°C.
[2] Nine freeze/thaw cycles.
[3] Sprayed samples, microcellular.
[4] Titanium dioxide pigment, 10% weight.

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.

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 strength 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 extender 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].

Table 5. Low temperature properties for 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	—

[1] Two percent titanium dioxide, by weight.
[2] × 1000

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 coated concrete 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 fitted with UVB-313 bulbs was used. Testing was performed using a continuous light source, no cycling, and 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 candidates for outdoor applications. As with the aromatic spray 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 that 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 decrease is due to the fact that the same isocyanate quasi-prepolymer was used in each exam-

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 (x 1000)	76.2	84.2
Shore D Hardness	59	63

[1] Continuous using UVB-313 bulbs.

Table 7. Aliphatic spray polyurea QUV Weatherometer testing.

Ti-Pure® R-900, wt%	10.0	20.0
Tensile strength, MPa	4.53	8.89
Elongation, %	398	338
Tear strength, N/m (x 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

Table 8. Cycloaliphatic diamine chain extenders for 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

[1] Blend of JEFFAMINE® T-403 and JEFFAMINE® D 230.
[2] 1,4-Diaminocyclohexane.
[3] Isophorone diamine.

ple and the equivalent weights are lower for the cycloaliphatic diamines. The volume ratio was also being maintained at 1:1, isocyanate to resin.

Use of these cycloaliphatic diamine chain extenders also gave polyurea elastomer systems with improved thermal properties over the polyoxyalkylene amine chain extenders. To demonstrate this concept, dynamic mechanical spectrometry (DMS) was used on comparative aliphatic spray polyurea elastomer systems. In Figure 4, note the relatively sharp tan δ at approximately $-50°C$ (T_g) for the aliphatic spray polyurea elastomer system using the polyoxyalkylene amine chain extenders (JEFFAMINE® T-403 and JEFFAMINE® D-230). The same sharp tan δ at $-50°C$ is also evident for the systems using 1,4-diaminocyclohexane and isophorone diamine, Figures 5 and 6 respectively.

The major difference is in the high temperature tan δ for these systems. In Figure 4, this high temperature tan δ for the polyoxyalkylene amine extended aliphatic polyurea elastomer is very broad with a peak at approximately 75°C. For the cycloaliphatic diamine chain extended systems, this tan δ is now peaked at approximately 115°C (Figures 5 and 6). This tan δ corresponds to the melting point of the hard block segment in the elastomer systems. This higher tan δ for the cycloaliphatic diamine extended aliphatic spray polyurea elastomer systems indicates higher thermal stability for these systems over the polyoxyalkylene amine extended systems. For comparison, an aliphatic spray polyurethane elastomer system is shown in Figure 7.

CONCLUSION

The two-component, 100% solids aliphatic spray polyurea elastomer technology addresses many VOC issues. The fast, consistent reactivity yields many advantages in processing over conventional catalyzed polyurethane elastomer systems. The use of polyurea isocyanate quasi-prepolymers coupled with the amine terminated resin blends yield elastomer systems which are truly all polyurea. The consistent reactivity of the amine terminated resins with the isocyanate and chemical backbone of the resin materials allow for relative water insensitivity during processing as well as elastomer performance. 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

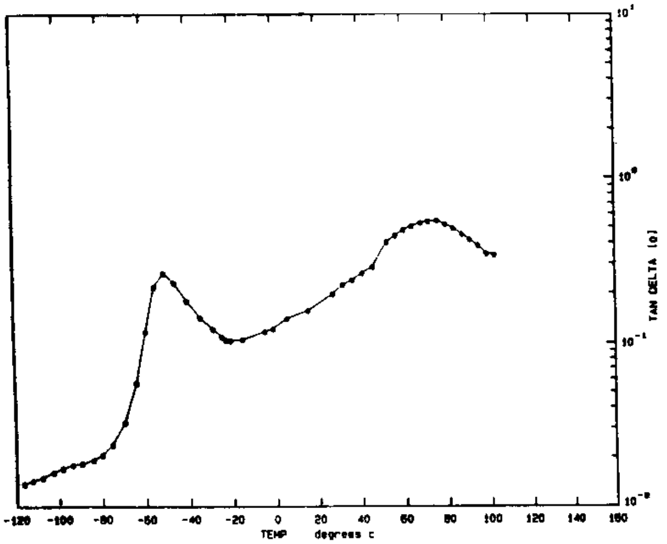


FIGURE 4. Aliphatic spray polyurea – JEFFAMINE* T-403/D-230 extended.

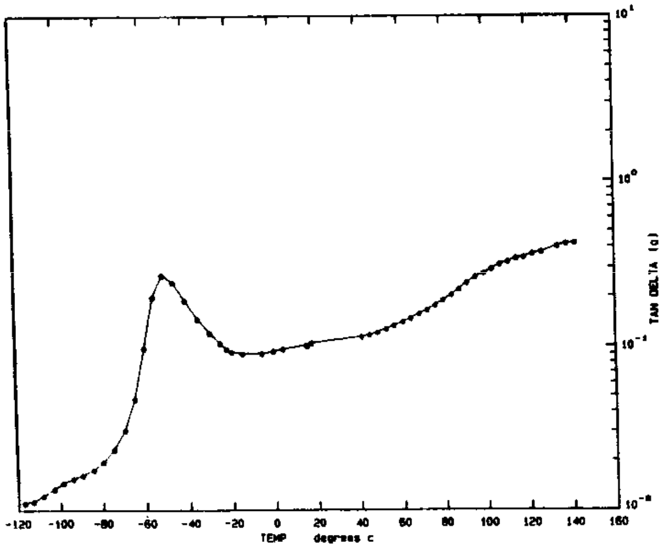


FIGURE 5. Aliphatic spray polyurea – 1,4-diaminocyclohexane extended.

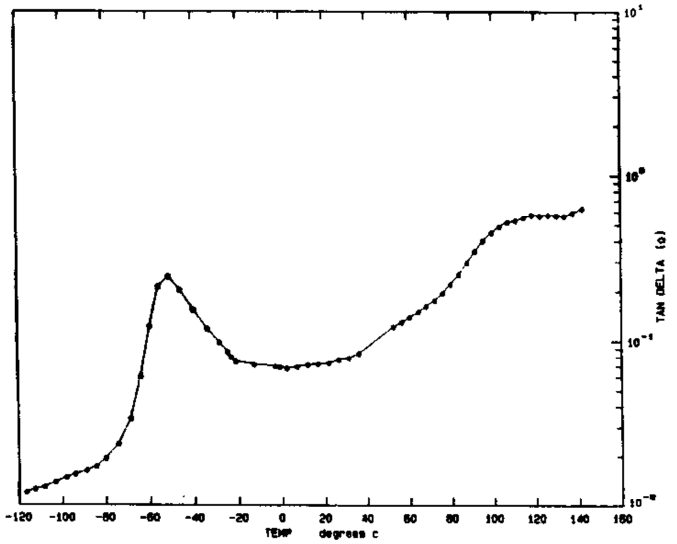


FIGURE 6. Aliphatic spray polyurea – isophorone diamine extended.

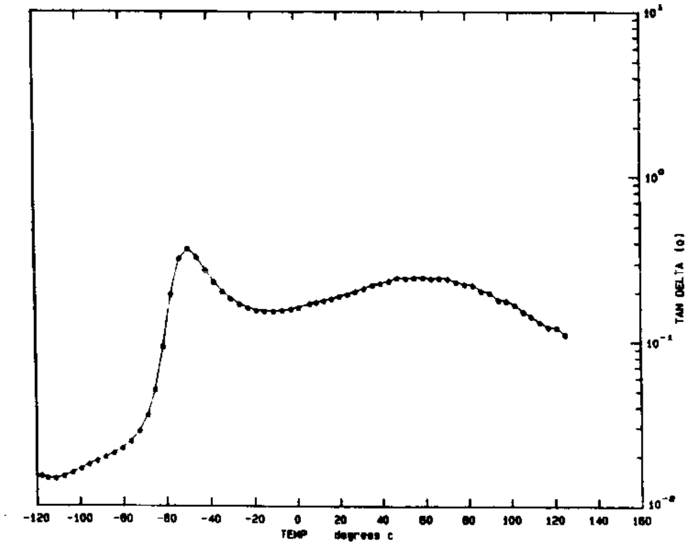


FIGURE 7. Aliphatic spray polyurethane.

aliphatic spray polyurea elastomer technology is truly a leading edge technology and an applicator's dream material.

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