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# PREPARATION OF URETHANE ADHESIVES

PDO 6989274, Final Report

B. G. Parker, Project Leader

Project Team:
J. W. McFarland

Published September 1976









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Bendix Kansas City Division

# NOTICE



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Final Report

Technical Communications Bendix Kansas City Division

PREPARATION OF URETHANE ADHESIVES

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Prepared by B. G. Parker, D/814, under PDO 6989274

The scale-up and production of two urethane prepolymers were investigated. The prepolymers can be used as adhesives which have potential use as a replacement for the Adiprene L-100/MOCA system (E. I. du Pont de Nemours & Company). One prepolymer is based on the reaction of a polytetramethylene ether glycol (PTMEG) with 4,4'-methylenebis(phenylisocyanate) (MDI) and in the other the PTMEG is reacted with 4,4'-methylenebis(cyclohexylisocyanate) ($H_{12}$MDI). The scale-up from the laboratory batches to pilot plant production is described. Several properties of the prepolymers and cured adhesives are presented.

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## SUMMARY

Both the Union Carbide Corporation and the Lawrence Livermore Laboratory (LLL) are continuing work on urethane adhesives to replace the Adiprene L-100/MOCA system (E. I. du Pont de Nemours & Company). Several alternate adhesives are in the final stages of development. Two prepolymers, Halthane 73 and Halthane 87, used in these adhesive systems, were scaled-up from laboratory synthesis to pilot plant production. Several physical properties of the prepolymers were determined. Physical properties of the prepolymers prepared in the laboratory are very similar to prepolymers prepared in the pilot plant.

The shear storage modulus of the cured adhesives was measured at various temperatures. The Halthane 73 adhesives have glass transition temperatures of -30° to -50°C with almost constant shear modulus from -10° to 120°C. Halthane 87 adhesive has a lower glass transition temperature of -60° to -70°C, but does not have as constant a shear modulus at higher temperatures as the Halthane 73 adhesive. Nineteen liter quantities of Halthane prepolymers required for additional test programs were prepared in the pilot plant and shipped to LLL.

## DISCUSSION

### SCOPE AND PURPOSE

Several adhesives are currently in the final stages of development. To support this effort Bendix Kansas City must develop processes to supply these adhesives.

### PRIOR WORK

The Halthane 73 and 87 urethane adhesives were synthesized at LLL for use in current projects. The adhesives were developed for replacement of the LW-520/MDA system, which has too high a viscosity and too short of a potlife, and the Adiprene L-315/polyol formulation, which does not have sufficient thermal stability for present applications.

### ACTIVITY

#### Preparation of Halthane 73 Prepolymer

Halthane 73 prepolymers are prepared by reacting 3.5 moles of 4,4'-methylenebis(phenylisocyanate) (MDI) with 1.0 mole of polytetramethylene ether glycol (PTMEG), of mixed molecular weight fractions. The mixed PTMEG was prepared by blending 86.5 percent by weight Polymeg 1000 (Quaker Oats Company) with 13.5 percent by weight Polymeg 2000 at 60°C.

MDI is a solid at room temperature and must be melted at 70° to 80°C. The MDI is then filtered to remove any moisture reaction products. The mixed PTMEG is melted at 60°C and purged with dry nitrogen for 16 hours then added to the reactor at a rate to maintain a reaction temperature of 50° to 60°C with stirring and purging with dry nitrogen. The reaction mixture is not allowed to exceed 70°C to prevent allophanate formation which would result in increased viscosity of the prepolymer.

Following addition of the PTMEG, the reaction temperature is maintained at 60° $\pm$ 5.0°C for 1 hour. The prepolymer is then degassed by pulling a vacuum on the reactor, and discharged into clean, predried containers, overlaid with dry nitrogen, and sealed.

#### Preparation of Halthane 87 Prepolymer

Halthane 87 is prepared by reacting 2.20 moles of 4,4'-methylenebis(cyclohexylisocyanate) ($H_{12}MDI$) Hylene-W (du Pont) with 1.0 mole of Polymeg 2000. $H_{12}MDI$ is a liquid at room temperature and can be filtered, without heating, to remove any moisture reaction products. The PTMEG is melted at 60°C and purged with dry nitrogen for 16 hours then added to the $H_{12}MDI$, while purging with dry nitrogen and stirring, at a rate to maintain a reaction temperature of 50° to 60°C. The reaction of $H_{12}MDI$ and PTMEG is not as exothermic as the Halthane 73 prepolymer and heat is required to maintain the reaction at 50° to 60°C. The reaction temperature is not allowed to exceed 70°C to prevent allophanate formation. After addition of the PTMEG, the reaction is maintained at a temperature of 60° ± 5.0°C for 3 or more hours. A vacuum is pulled on the reactor and then the prepolymer is discharged into predried containers, overlaid with dry nitrogen, and sealed.

## Scale-Up Procedures

The Halthanes were initially prepared in a 1-liter resin reactor to determine the amount of exotherm that might be encountered on larger runs. Halthane 73 proved to be moderately exothermic and Halthane 87 had little noticeable exotherm. The reactions were then scaled to a 4-liter resin reactor. Halthane 87 still had a very small exotherm and the exotherm of the Halthane 73 was controlled by the rate of addition of the mixed PTMEG.

With all of the laboratory scale preparations, the MDI and $H_{12}MDI$ were vacuum filtered directly into the resin reactor. The amount of MDI and $H_{12}MDI$ in the reactor was determined by reweighing the reactor after these additions. When scaling the reaction to 27 kg batches in the pilot plant, it was not possible to filter the isocyanates directly into the reactor and accurately determine the amount of isocyanate that would be transferred into the reactor; therefore, the isocyanates were filtered by pressurizing with dry nitrogen through filters and then collecting them. The filtered isocyanates were then weighed and transferred to the reactor. In laboratory preparations of the prepolymers, the PTMEG was added to the reactor with a pressure equalizing addition funnel. This allowed dry nitrogen to fill the space above the funnel and keep atmospheric moisture from entering the reactor.

In the pilot plant preparations, the PTMEG was poured into the reactor while being purged with dry nitrogen. This keeps most atmospheric moisture from entering the reactor; however, it is not as efficient in excluding moisture as the closed system used in the laboratory. Modification of the pilot plant reactors is being investigated so that both the isocyanate and polyol can be added to the reactor at a controlled rate with total exclusion of atmospheric moisture.

The prepolymers prepared in the pilot plant were also filtered when discharging and placed in metal cans. The cans were overlaid with dry nitrogen and sealed.

## Properties of the Prepolymers

Tables 1 and 2 list some physical properties of the Halthane prepolymers prepared in the laboratory and pilot plant. Percent free MDI or free Hylene-W was determined by gel permeation chromatography. Percent NCO was determined according to ASTM D1638 and the viscosity was measured using a Brookfield HBF viscometer. As seen in Table 2, Lots 5, 6, and 7 of the Halthane 87 prepolymers did not react completely until after 10 or more days at room temperature. This is further shown in Table 3. After 10 days at room temperature the viscosity and percent NCO level off. This indicates incomplete reaction of the Hylene-W and Polymeg 2000 during initial preparation. The reaction does not go to completion until after standing an additional 10 days at room temperature. The reaction time for Lots 6 and 7 was increased by 50 percent to 4.5 hours at 60° $\pm$ 5°C. This did not have any significant effect in driving the reaction to completion. No production problems are anticipated with the Halthane 87 preparation as long as the prepolymer is allowed to react for an additional 10 days at room temperature before testing is done.

The amine equivalents of the prepolymers were measured over several months to determine their shelf-life stability. Table 4 shows that there is a very small increase in the amine equivalent of both the Halthane 73 and Halthane 87 prepolymers over 3 to 4 months at room temperature. The small change in amine equivalents is probably due to reaction of the prepolymer with moisture in the air when the containers are opened to remove samples. This small change in amine equivalents indicates good shelf-life stability for both Halthane prepolymers.

## Properties of Cured Adhesives

There are two curing systems used with the Halthane 73 based adhesive. Halthane 73-14 is cured with a mixture of 1,4-butanediol in Polymeg 1000, while Halthane 73-18 also contains N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine (Quadrol, Wyandotte Chemicals Company) as shown in Table 5. The addition of the Quadrol helps to provide for a shorter cure time and better high temperature properties.

The NCO to polyol ratio for the Halthane 73 formulations was initially chosen at 1:0.9 because of better adhesion properties found with a slight excess of NCO. The ratio has since been changed to 1:0.95. Halthane 87 is cured with an eutectic diamine mixture (Tonox 60/40, Uniroyal Chemicals) using a 1:1 ratio of NCO to amine (Table 5).

The pot lifes of the two 73 systems and the 87 system are shown in Figure 1. The viscosity of a 350 gram sample of each adhesive was monitored with time using a Brookfield HBF viscometer. The exotherm of the adhesive was also monitored by measuring the temperature with time as is shown in Figure 2.

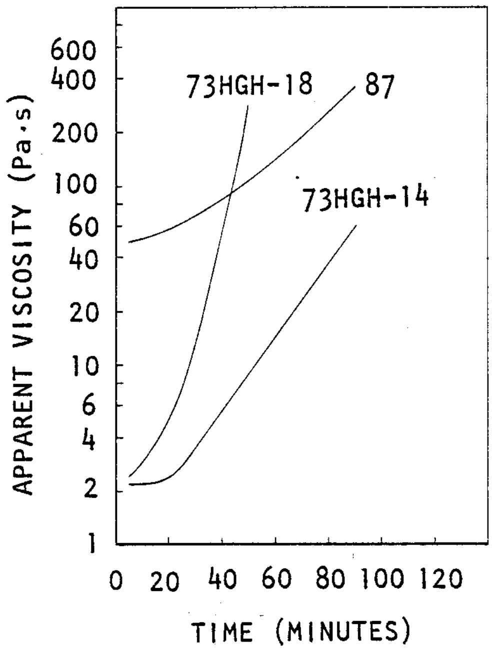



Figure 1. Pot Life of Halthane Adhesives

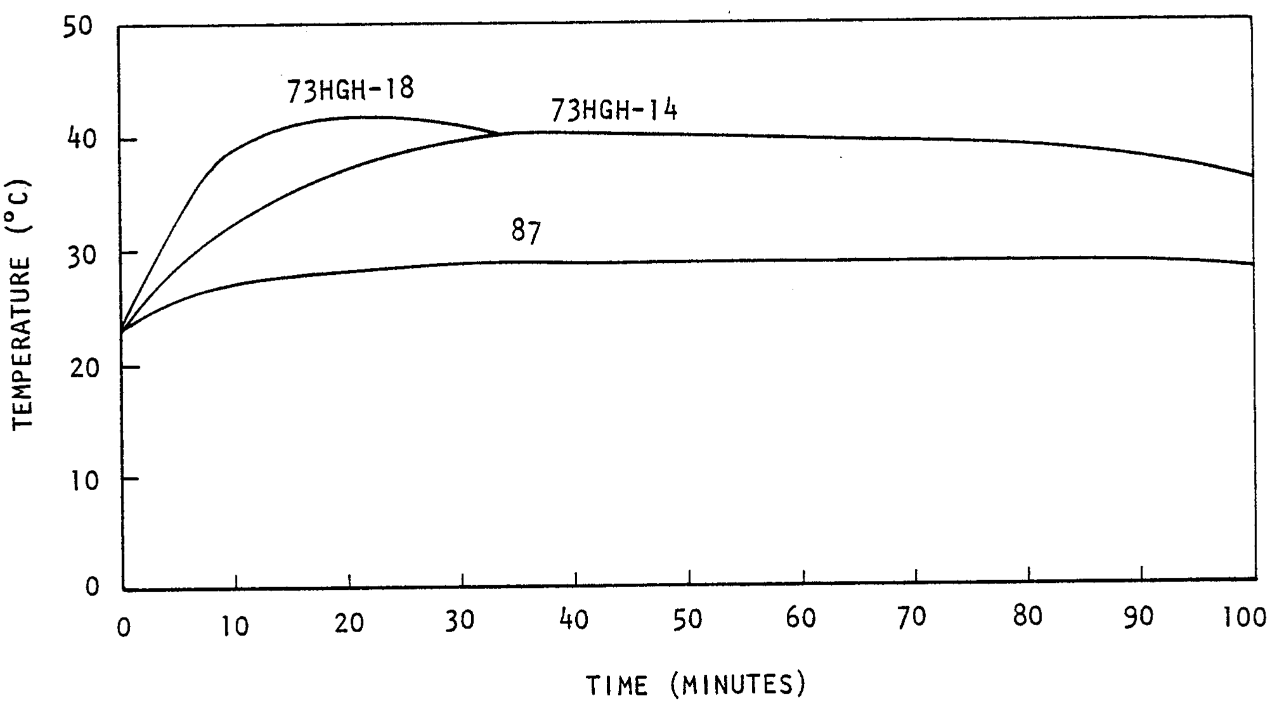



Figure 2. Exotherm of 350 Gram Samples of Halthane Adhesives

Table 1. Properties of Halthane 73 Prepolymer

| | Lot Number | | | | |
|---|---|---|---|---|---|
| Property | 2 | 3 | 4 | 5 | 6 |
| Batch Size (kg) | 1 | 4 | 4 | 27 | 27 |
| Percent Free MDI | 20 | 19 | 20.4 | 21.4 | 21.7 |
| Percent NCO | 10.29 | 10.29 | 10.44 | 10.22 | 10.43 |
| Viscosity* (Pa•s) | 9.1 | 9.2 | 9.28 | 10.6 | 7 |
| Spindle Number | 3 | 3 | 3 | 1 | 1 |
| RPM (rad/s) | 10 (1.0) | 10 | 10 | 5 (0.52) | 5 |
| Temperature (°C) | 24 | 24 | 24 | 25 | 25 |

*Brookfield HBF Viscometer

## Preparation of Samples

Samples of cured adhesives for testing shear storage modulus were prepared by vacuum mixing the prepolymer and curing system together and transferring them to Teflon coated aluminum molds for 16 hours at room temperature. In addition, some of the specimens were cured at 74°C for 16 hours to see what effect cure at elevated temperature had on the final properties of the adhesives.

Cured samples were prepared using prepolymers synthesized in both the laboratory and pilot plant for comparison of the two materials. The conditions used in preparing the test specimens are shown in Table 6.

Results of shear storage modulus with temperature are shown in Figure 3. One of the samples (123) was divided into two parts. One part was stored in a desiccator having very low relative humidity and the other part was allowed to be exposed to atmospheric humidity in the laboratory. After shear modulus versus temperature tests were performed on both parts, the one stored in the desiccator was removed and exposed to atmospheric humidity. The results are shown in Figure 3 (Halthane 73-14, RT Cure). The shear modulus of the sample left in the desiccator falls off more rapidly with temperature than the sample that wasn't placed in

Table 2. Properties of Halthane 87 Prepolymer

| Property | Lot Number 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| Batch Size (kg) | 1 | 4 | 4 | 5 | 27 | 27 |
| Percent Free $H_{12}MDI$ | 6.5 | 6 | 6.7 | 9.9 (7.6)* | 10.4 (9) | 16.6 |
| After Prep. (Days) | 10 | 14 | 13 | 6 (13) | 5 (11) | 4 (10) |
| Percent NCO | 3.91 | 4.04 | 3.86 | 4.30 (4.06) | 4.06 (3.88) | 4.88 (3.85) |
| Viscosity (Pa•s)** | 54.8 | 55.2 | 54.7 | 18.1 | 6.78 | 7.68 (47) |
| Spindle Number | 3 | 3 | 4 | 3 (2) | 2 | 2 (2) |
| RPM (rad/s) | 10 (1.04) | 10 | 10 | 10 (10) | 10 | 10 (2) |
| Temp. (°C) | 24 | 24 | 24 | 24 (25) | 25 | 25 (25) |

*Second test
**Brookfield HBF Viscometer

Table 3. Properties of Halthane 87, Lot 7

| Days | NCO (Percent) | Viscosity (Pa•s) |
|---|---|---|
| 4 | 4.88 | 7.68 |
| 5 | 4.27 | 18.6 |
| 10 | 3.85 | 47 |
| 17 | 3.85 | 47 |

Table 4. Room Temperature Shelf Life Stability of Halthane Prepolymers

| Halthane Prepolymer | Lot Number | Amine Equivalent | | |
|---|---|---|---|---|
| | | Initial | 1 Month | 3 Months |
| 73 | 2 | 408 | 408.3 | 409.2 |
| 73 | 3 | 408.1 | 409.2 | 414.2 |
| 73 | 4 | 402.3 | 403 | 403.4 |
| 73 | 5 | 411.1 | 411 | 413.8 |
| 73 | 6 | 402.7 | 402.6 | 403 |
| 87 | 2 | 1073 | 1078 | 1082 |
| 87 | 3 | 1040 | 1058 | 1062 |
| 87 | 4 | 1087 | 1096 | 1096 |
| 87 | 5 | 1131 | 1150 | 1155 |
| 87 | 6 | 1083 | 1082 | |
| 87 | 7 | 1090 | 1097 | 1102 |

Table 5. Curing Agents for Halthane 73 and 87 Adhesive Systems

| | | Weight Percent | | |
|---|---|---|---|---|
| Adhesive | Hardener | 1,4 butanediol | Polymeg 1000 | Quadrol |
| 73 | HGH-14 | 10 | 90 | |
| | HGH-18 | 10 | 85 | 5 |
| 87 | Tonox 60/40 | 40 percent meta-phenylene diamine, 36 percent 4,4'-methylene dianiline, 8 percent 2,4-methylene dianiline, and 16 percent polymeric aromatic amines | | |

the desiccator. Also, after the sample was removed from the desiccator and exposed to atmospheric moisture for 2 weeks, its shear modulus versus temperature matched the sample that was not placed in the desiccator. This indicates that some degree of cure might be taking place due to reaction with atmospheric moisture.

## ACCOMPLISHMENTS

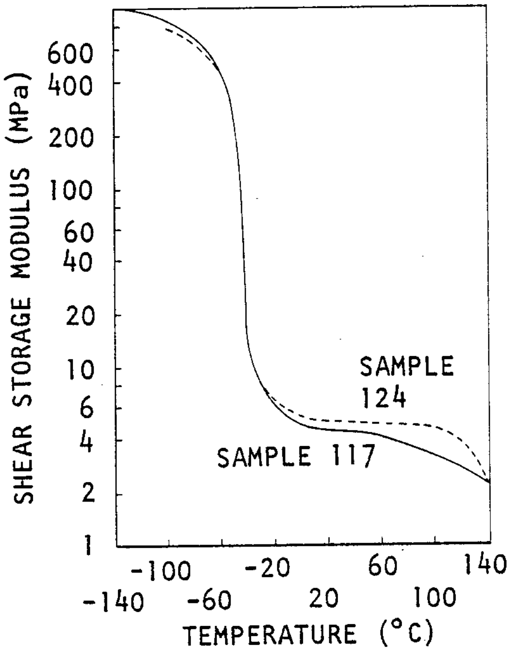
The preparation of Halthane 73 and Halthane 87 prepolymers was scaled-up to provide 27 kg quantities of the prepolymer for each batch having properties identical to the laboratory product. The stability of the prepolymers was measured over several months with both the Halthane 73 and the Halthane 87 showing good shelf-life stability. As a result of this work, Bendix Kansas City has developed the capability to produce material to support the Halthane 73 and 87 adhesive systems.

## FUTURE WORK

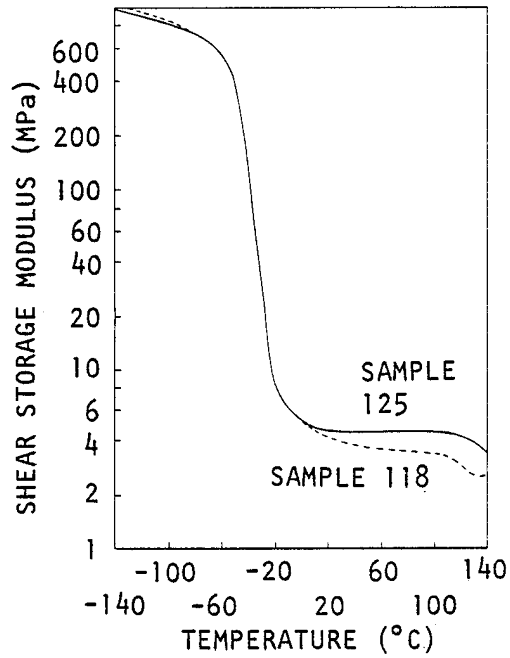
Modification of the pilot plant reactors is being investigated. This modification would allow the addition of both the isocyanate and polyol to be metered into the reactor at a controlled rate and with total exclusion of atmospheric moisture.

Table 6. Shear Modulus Test Specimens

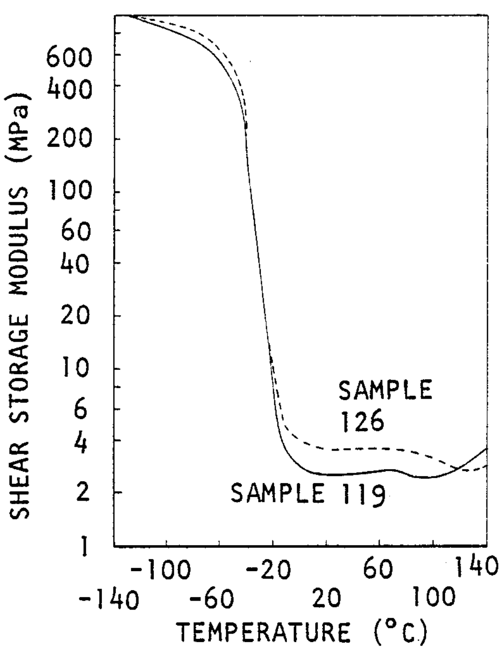
| Sample Number | Date Prepared | Date Shear Modulus Run | Halthane Resin | Lot Number | Curing System | Cure Time, Hours | Cure Temperature |
|---|---|---|---|---|---|---|---|
| 116 | 8/7/75 | 12/1/75 | 73 | 2 | HGH-14 | 16 | RT |
| 117 | 8/7/75 | 12/2/75 | 73 | 2 | HGH-14 | 16 | 74°C |
| 118 | 8/8/74 | 12/3/75 | 73 | 2 | HGH-18 | 16 | RT |
| 119 | 8/8/75 | 12/4/75 | 73 | 2 | HGH-18 | 8 | 74°C |
| 123 | 10/16/75 | 11/18/75 | 73 | 7 | HGH-14 | 16 | RT |
| 124 | 10/16/75 | 11/19/75 | 73 | 7 | HGH-14 | 8 | 74°C |
| 125 | 10/17/75 | 11/20/75 | 73 | 7 | HGH-18 | 16 | RT |
| 126 | 10/17/75 | 11/21/75 | 73 | 7 | HGH-18 | 8 | 74°C |
| 127 | 11/11/75 | 11/24/75 | 87 | 2 | Tonox 60/40 | 16 | RT |
| 128 | 11/11/75 | 11/25/75 | 87 | 5 | Tonox 60/40 | 16 | RT |



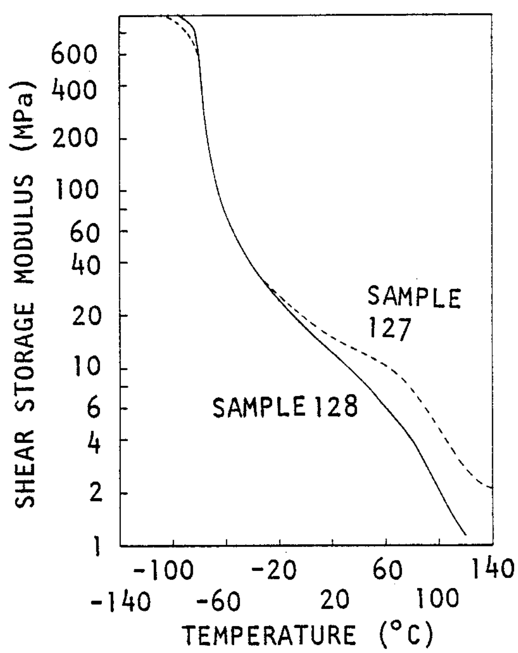

HALTHANE 73-14, 74°C CURE




HALTHANE 73-18, RT CURE

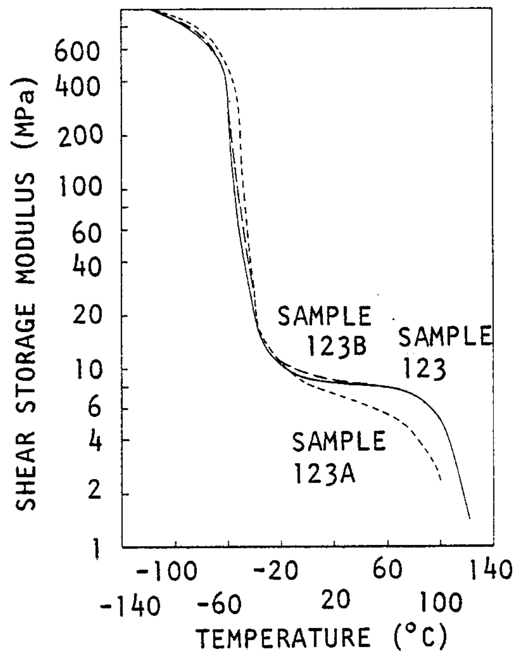



HALTHANE 73-18, 74°C CURE




HALTHANE 87-TONOX 60/40, RT CURE

Figure 3. Shear Storage Modulus




HALTHANE 73-14, RT CURE

Figure 3. Continued.
Shear Storage Modulus

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