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Preparation and Properties of an Internal Mold Release for Rigid Urethane Foam

By B. G. Parker

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Final Report

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Internal mold releases which can be added to urethane foam resin were synthesized and evaluated. The use of this type of release agent eliminates the repeated cleaning and recoating of molds, a procedure required with surface-applied mold releases. The internal mold releases investigated are the reaction products of a fatty acid ester, containing an active hydrogen, and a monoisocyanate. The use of an internal mold release resulted in urethane foam with good releasability and excellent surface bondability. Several properties of rigid urethane foam formulated with the use of an internal mold release are presented.

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SUMMARY

Most mold release agents used in the molding of rigid polyurethane foam are applied to the internal surfaces of the mold. The commonly used mold release agents include waxes, fluorocarbon materials, soaps, and silicone oils. These materials form a thin layer between the surface of the mold and the foam, allowing for easy release of the molded parts. This type of mold release must be applied prior to each molding operation; and, after repeated use, cleaning of the mold is required. Small amounts of this mold release are transferred to the molded part, resulting in a part with poor surface bondability characteristics.

An internal release agent, which can be mixed in a urethane foam resin was investigated. Internal mold release agents were prepared in the laboratory and evaluated. The internal mold release provided good releasability and resulted in urethane foam that has excellent surface bondability. Thermomechanical and solvent extraction data indicate that no compatibility problems would be expected from the use of this type of release agent.

DISCUSSION

SCOPE AND PURPOSE

Most mold release agents used in the molding of polyurethane foam parts are applied to the internal surfaces of the mold. A portion of this type of release agent is often transferred to the surface of the foam part during the molding operation. The surfaces of the resulting part must be chemically cleaned or plasma etched in order to achieve a good bonding surface prior to further assembly.

The purpose of this project was to synthesize and evaluate internal mold release agents which can be added directly to urethane foam components prior to molding. Use of this type of mold release would eliminate plasma etching or chemical cleaning of the foam surface which requires bonding as part of the next-assembly operation.

PRIOR WORK

In most molding operations the internal surfaces of the mold are coated with a mold release agent to prevent the resulting part from sticking to the mold when removed. Typical mold release agents include waxes, soaps, and silicone oils. These materials form a thin layer between the surface of the mold and the part, adhering to neither the mold nor the part, thus allowing for easy removal of the cured foam. There are several disadvantages associated with the use of this type of release agent. The mold release must be applied prior to each molding operation, which reduces the amount of time the mold is available for production. After repeated use the mold release builds up, reducing surface definition and dimensional control, thus requiring cleaning of the mold. In addition, molded parts become coated with a thin film of the release agent, which reduces surface bondability.

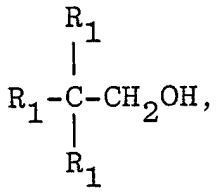
It was disclosed in U.S. Patent 3,726,952 that the addition of a salt of a fatty acid and an amine to a polyurethane foam mixture could eliminate the need for a surface-applied mold release.[1] This type of internal mold release resulted in excellent mold release properties and good flow properties in the mold, as well as providing an antistatic effect on the finished part. Storage of the foam components containing this internal mold release, however, resulted in separation of the mold release from the resin. For this reason, adequate stirring of the reaction components prior to mixing was required.

In addition, U.S. Patent 3,925,527 has disclosed that excellent mold release properties can also be obtained by applying the reaction product of a fatty acid ester, containing an active hydrogen and a monoisocyanate, to a polyurethane foam mixture.[2] This internal mold release remains soluble in the isocyanate side of the reaction mixture and does not react with the prepolymer.

ACTIVITY

Preparation of Internal Release Agents

A three-step reaction process was used in the preparation of internal release agents. The first step was to prepare a fatty acid ester containing one free hydroxyl group on the molecule. As a typical reaction, 846 grams of oleic acid (3 moles), together with 136 grams of pentaerythritol (1 mole), were placed in a 2-liter resin reactor and heated while stirring for 24 hours at 150°C under a nitrogen atmosphere. The mixture was then heated for 8 additional hours at 150°C under vacuum. The reaction product had a hydroxyl number of 48 and an acid number of 6, as determined by ASTM D-1638. The resulting liquid (Compound I) had the following general structure.



Compound I

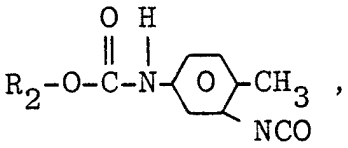
Fatty Acid Ester,

where

$$R_1 = \left[CH_3(CH_2)_7(CH)_2(CH_2)_7 \overset{O}{\overset{\|}{C}}\text{-O-}CH_2 \right] .$$

The second reaction step was the preparation of a monoisocyanate. Tolylene diisocyanate (TDI) (522 grams), 80/20 isomer ratio, was placed in a 2-liter resin reactor and heated to 60°C while purging with dry nitrogen. The TDI was stirred with a magnetic stirrer while 642 grams of tetradecanol was added slowly. The addition rate of tetradecanol was adjusted in order to maintain a reaction

temperature of 60 ± 5°C. After complete addition of the tetradecanol, the reaction mixture was heated for 30 minutes at 60°C, and then was allowed to cool to room temperature. The resulting monoisocyanate (Compound II) had the following general structure.



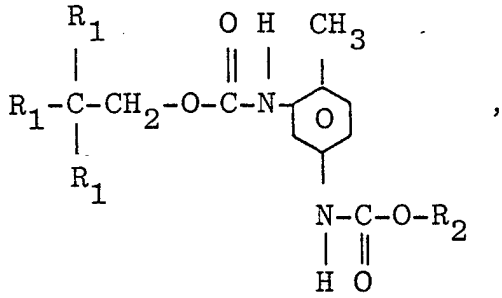
Compound II

Monoisocyanate,

where

$$R_2 = \left[CH_3(CH_2)_{13} \right] - .$$

The final step involved the reaction of the fatty acid ester with the monoisocyanate. Typically, 967 grams of reaction product (Compound I) and 388 grams of reaction product (Compound II) were placed in a 2-liter resin reactor and heated to 60°C while stirring with a magnetic stirrer and purging with dry nitrogen. The reactor temperature was maintained at 60 ± 5°C until absence of isocyanate was observed by infrared analysis; for example, loss of absorption at 2260 cm^{-1}. The resulting mold release (Compound III) had the following general structure.



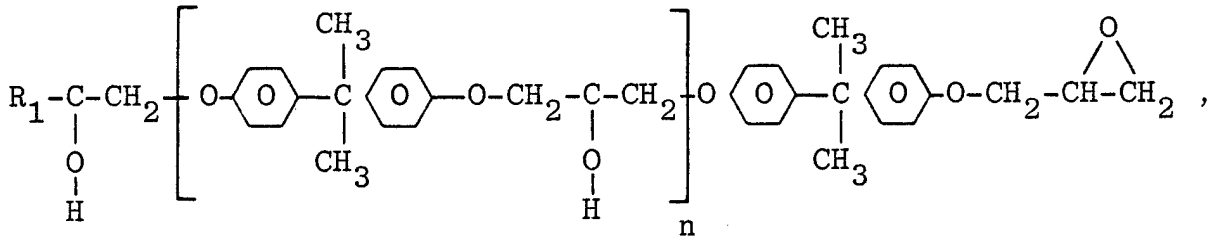
Compound III

Internal Mold Release.

Stearic acid was evaluated as an alternate fatty acid, used in preparing the fatty acid ester, but this resulted in a solid material. Further reaction of this fatty acid ester with the monoisocyanate (Compound II) also resulted in a solid material with lower solubility than the oleic acid ester in the isocyanate side of the foam system. Testing of this release agent was discontinued.

An alternate method for the preparation of the fatty acid ester containing a free hydroxyl group was also investigated. Oleic acid (564 grams) and 760 grams of Epon 828 epoxy were placed in a 2-liter resin reactor, heated to 150 ± 5°C, and stirred under a nitrogen atmosphere for 8 hours. The resulting fatty acid ester (Compound IV) had the following general structure.

Compound IV



Epoxy Fatty Acid Ester,

where

n = 1.

This fatty acid ester, containing epoxy, was reacted with the monoisocyanate (Compound II), as described in the previous procedure. The resulting product was solid at room temperature. It was reasoned that incorporation of reactive epoxy group into the internal mold release structure might result in a urethane foam having good bondability to epoxy adhesives.

Foam Sample Preparation

Varying levels of the internal mold releases were added to BKC 44306-10, a polyarylisocyanate/sucrose-based polyether polyol foam system. Foam specimens were molded in aluminum molds with new aluminum faceplates to yield foam blocks (152.4 by 152.4 by 25.4 mm) for adhesion tests and in aluminum cylinders (44.5 mm by 26.8 mm I.D.) for release tests.

The foam test blocks were prepared from BKC 44306-10, formulated at an isocyanate index of 1.2, molded to a density of 320 kg/m^3 and cured for 8 hours at 163°C. The release test specimens were allowed to cool to room temperature slowly, to prevent excessive foam shrinkage which could influence the foam releasability. The releasing force of some surface-applied release agents was also measured as a comparison with the internal mold releases. Table 1 lists the surface-applied release agents tested, their general composition, and the manufacturers. The surface-applied mold releases were coated on the interior of the 44.5-mm by 26.8-mm-I.D. cylinders and filled with BKC 44306-10 foam system in which no internal mold release was added.

Table 1. Surface-Applied Mold Releases

Mold Release	Manufacturer	Composition
Frekote 11	Frekote, Inc.	Silicone
Frekote 33	Frekote, Inc.	Silicone
MS 136	Miller-Stephenson Chemical Company, Inc.	Fluorocarbon
Camie 666	Camie Company	Silicone
Surfak	Gibraltar, Inc.	Fatty Acid Ester
OSR	Chem-Trend, Inc.	Hydrocarbon Wax

Release Testing

A new test method was developed for measuring the releasability of molded urethane foam samples. A Chatillon model HTCM compression tester was operated at a crosshead speed of 0.31 mm/s when forcing foam plugs from aluminum cylinders as shown in Figure 1.

The shear force required for release of the urethane foam samples having a mold surface area of 37.47 cm^2 was determined by measuring the maximum force required to push the urethane foam plug out of the aluminum cylinder. Use of internal mold releases containing epoxy groups resulted in such a large release force that failure of the urethane foam occurred prior to its release. Additional testing of internal mold releases containing epoxy groups was, therefore, discontinued. The results of the release tests are listed in Table 2 and illustrated in Figure 2.

Increasing the concentration of internal mold release resulted in a decrease in the release force required (Figure 2). Comparing the release forces of a surface-applied mold release (Table 2) with those of internal mold releases indicates that the internal mold release performed as well as, or better than, surface-applied mold releases.

Water Drop Test

A water drop test, used as a relative measure of surface wetability, thereby provided a way of predicting relative bond strengths. Water drop tests were performed on urethane foam samples by placing a 5-μl drop of water on a molded surface and measuring

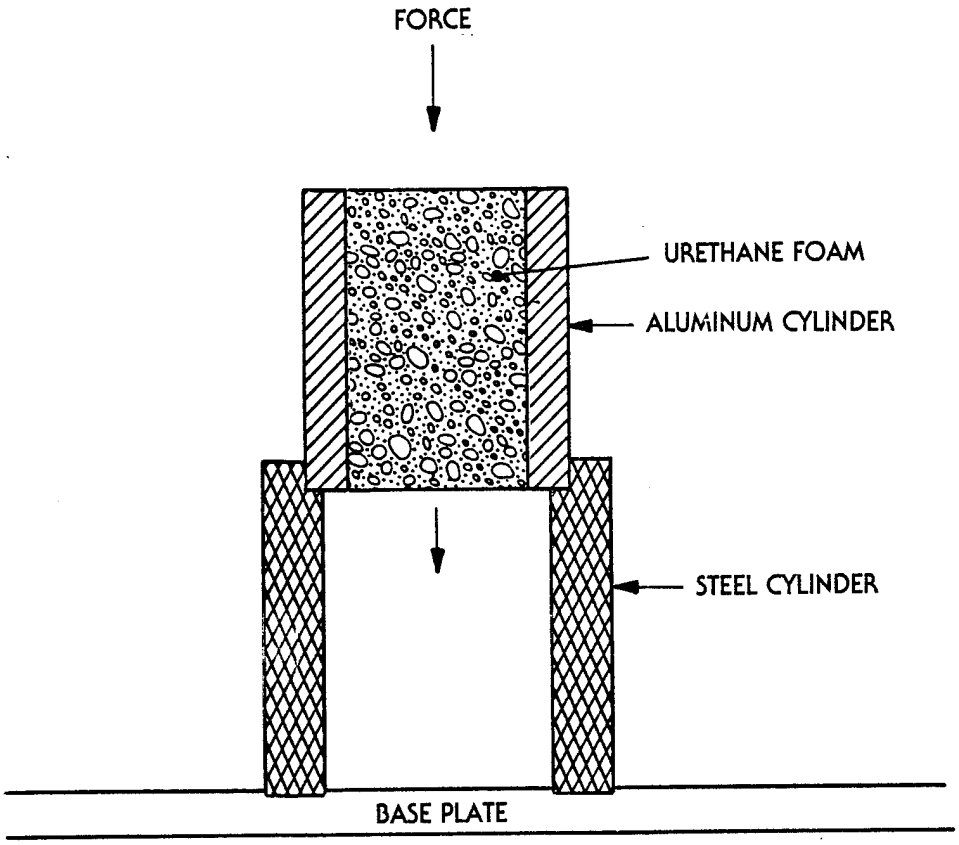


Figure 1. Cross Section of Release Test Fixture for Polyurethane Foam

the diameter of the drop, using an optical microscope. Generally, a large drop diameter is indicative of high tensile strength in an adhesive-bonded specimen. The results of this testing (Figure 3) show a marked decrease in surface wetability when increasing a mold release concentration from 2 parts per hundred resin (phr) to 5 phr. A possible reduction in surface bondability at concentrations above 2 phr is indicated.

Adhesion Testing

Adhesion properties were determined from 28.7-mm-diameter foam cylinders, machined from the 152.4- by 152.4- by 25.4-mm foam blocks. Aluminum end adapters were bonded to both molded surfaces of foam specimens, using a rigid epoxy system mixed in the ratio of 10 parts-by-weight (pbw) Epibond 104 and 1 pbw Hardener 951, manufactured by Furane Plastics, Inc. Tensile properties (Table 3) indicate that there is not an appreciable effect of mold release concentration on the tensile strengths measured even though water drop tests indicated there might be.

Table 2. Releasability of Surface-Applied Mold Releases

Mold Release	Release Shear Force (kPa)
Frekote 11	12
Frekote 33	413*
MS 136	107
Camie 666	408*
Surfak	14
OSR	12
Epoxy-Internal (10 phr)**	333*

NOTE: Average of three samples for each mold release.

*Foam stuck to cylinder wall.
**Internal mold release containing epoxy groups (Compound IV).

Test specimens used in a plasma-treatment study[3] were prepared in the same manner as those just discussed. A comparison of test results from foams prepared with the internal mold release (Table 3) and foams that were plasma-etched (Table 4) shows the tensile strengths to be comparable.

Compatibility Concerns

Internal mold release agents resulted in a urethane foam with good releasability and excellent surface bondability. However, it was reasoned that the large level of relatively inert high-molecular-weight mold release might plasticize the foam and provide a large amount of migratable material which could cause compatibility problems.

Softening temperatures (T_s) (Figure 4) of the foam samples were run on a Perkin Elmer thermomechanical analyzer. These temperatures were measured, using a heating rate of 5°C/minute, with an expansion probe and a 10-gram weight on the sample. A small degree of plasticizing occurred at a mold release level of 10 phr (Figure 4).

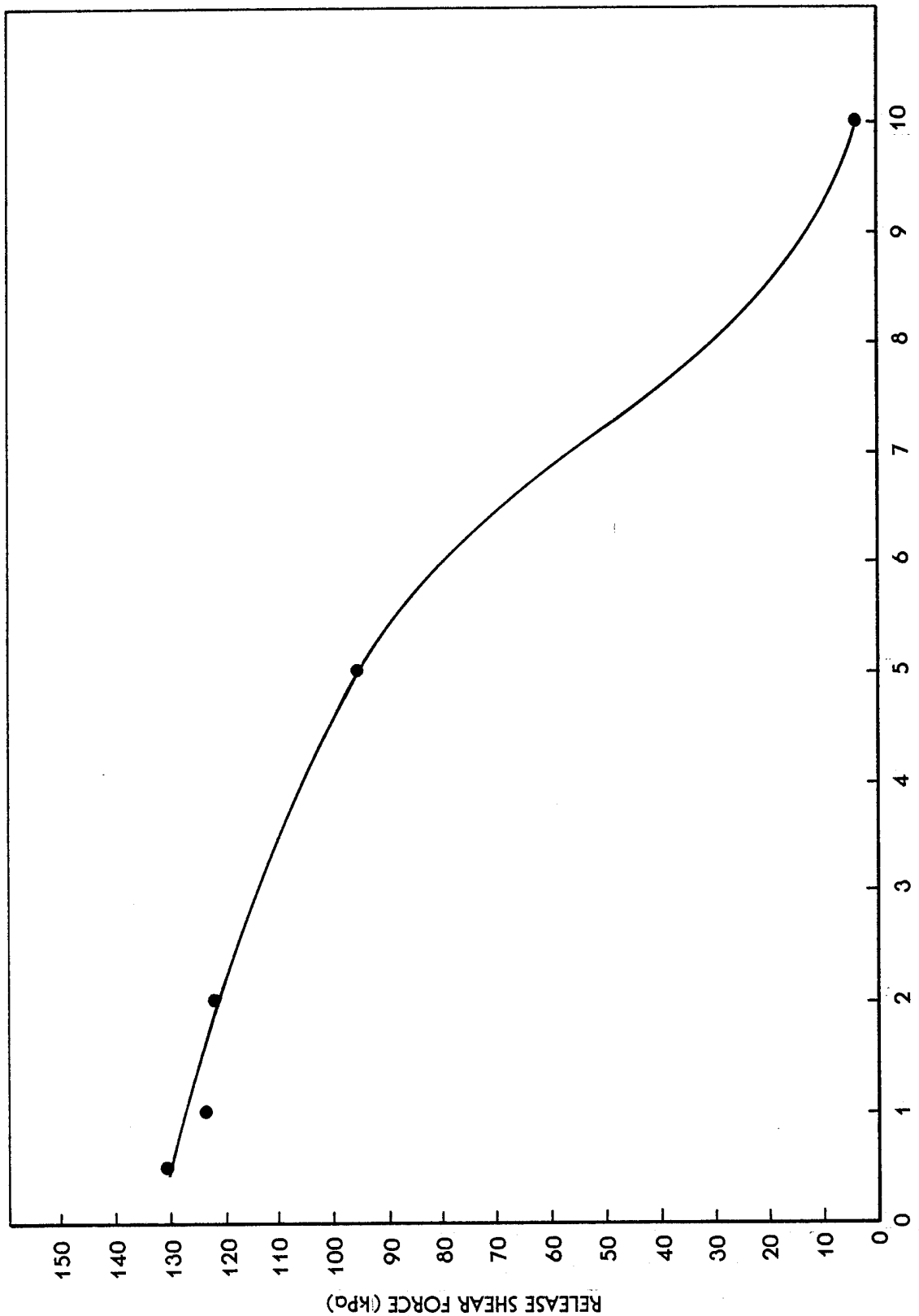


Figure 2. Releasability of Urethane Foam Containing an Internal Mold Release

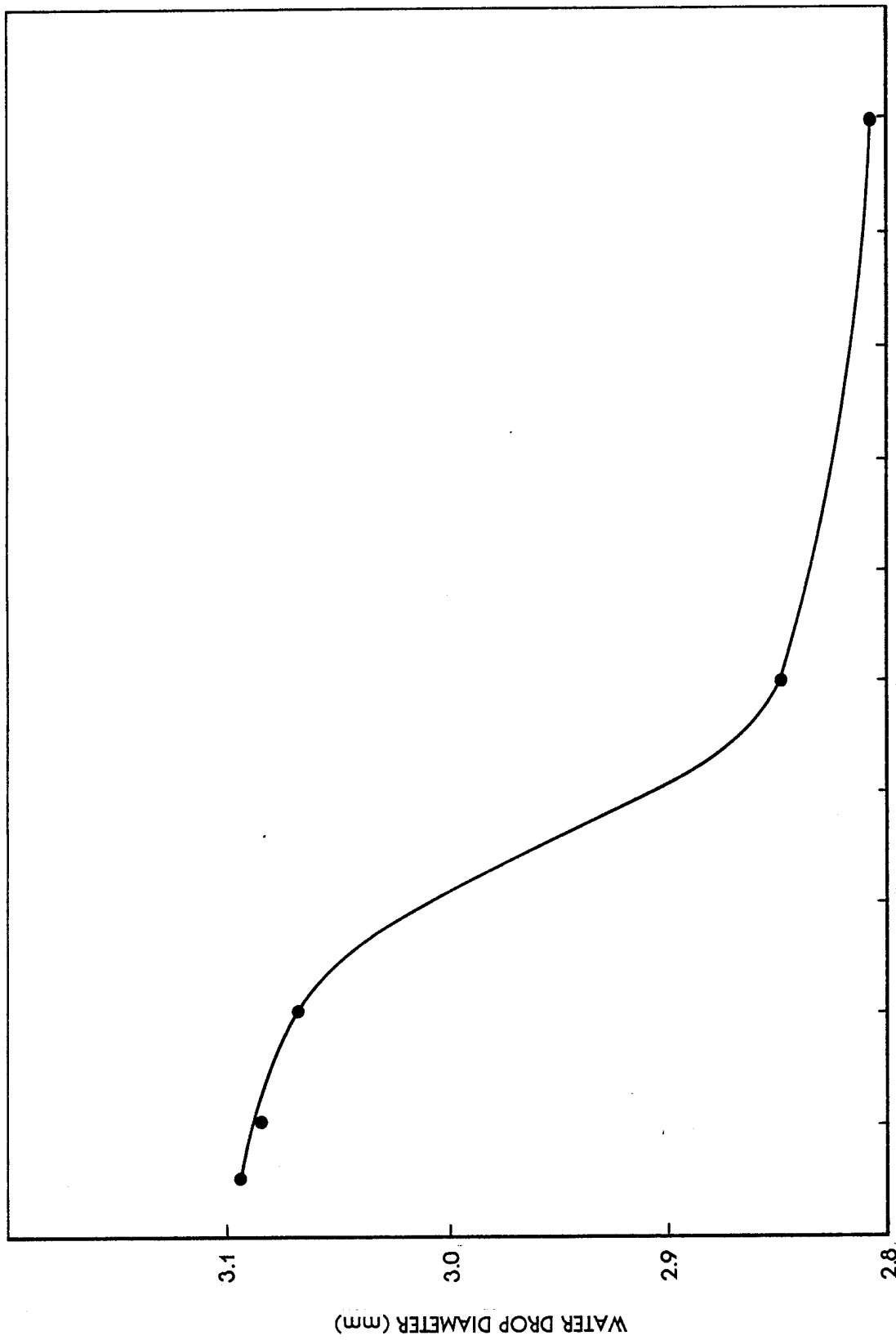


Figure 3. Water Drop Test for Urethane Foam Containing an Internal Mold Release

Table 3. Surface Bondability for Foam Containing an Internal Mold Release

Mold Release Concentration (phr)*	Tensile Strength (MPa)	
	$\bar{X}$	S**
10	2:52	0.18
5	2.39	0.27
2	3.14	0.19
1	2.88	0.29
1/2	2.61	0.60

NOTE: Average values for four samples each.

*Compound III.
**Standard deviation.

Solvent extractions, using toluene and a Soxhlet extractor, were performed on the foam samples for 24 hours. The results (Table 5) showed the amount of extractables to be very low even at a mold release concentration of 10 phr. No compatibility problems were expected with the use of this mold release.

ACCOMPLISHMENTS

Internal mold release agents which can be added to urethane foam components prior to molding were synthesized and evaluated. The use of this type of mold release resulted in urethane foam with very good releasability and bondability, comparable to plasma-etched foam surfaces. At mold release concentrations at or below 5 phr there was no noticeable effect on the softening temperature of the foam, and the level of extractables was below 0.2 percent.

FUTURE WORK

Although there was only a minimal effect at high mold release concentrations on the softening point of the foams, compression tests should also be performed to determine if there are any losses in load-bearing properties with the use of this mold release. If an internal mold release is used in production parts, a scale-up to production quantities of this material would be required in the Polymer Pilot Plant.

Table 4. Bonding Screening Tests With BKC 4003-8 Foam System

	Tensile Strength (MPa)			
	As Molded		Plasma-Treated	
Release System	$\bar{X}$	S*	$\bar{X}$	S*
OSR	1.63	0.75	2.66	0.26
Fatty Acid Ester	2.04	0.34	2.29	0.35
Silicone Oil	2.16	0.49	1.60	0.45
OSR**	- -		2.99	0.73

*Standard deviation.
**BKC 44306-10 foam system.

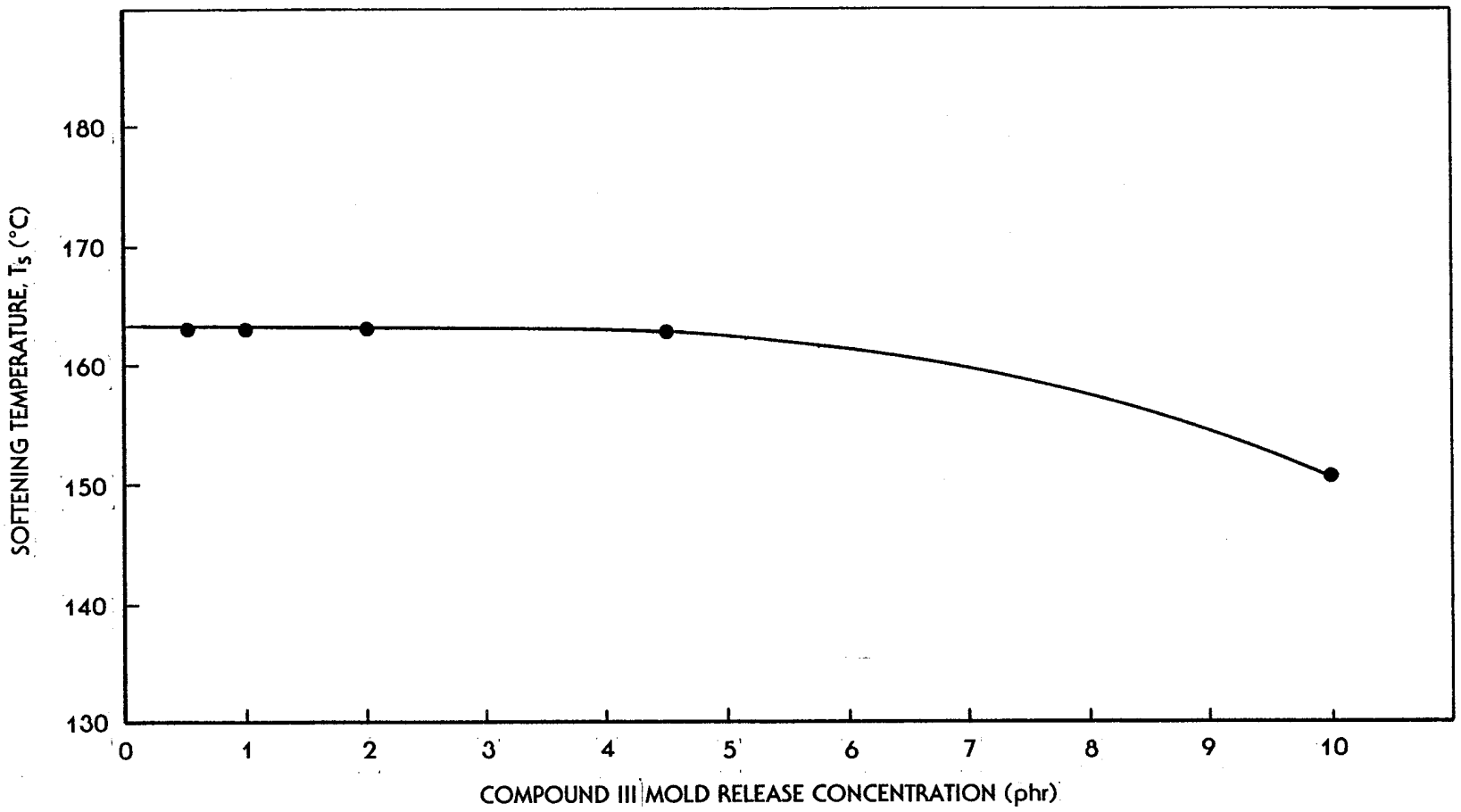


Figure 4. Effect of an Internal Mold Release Concentration on Foam Softening Temperature

Table 5. Extractable Levels for Foam Containing an Internal Mold Release

Mold Release Concentration (phr)*	Extractables (percent)
10	1.35
5	0.138
2	0.184
1	0.002
1/2	0.004
0	0.003

NOTE: Average values for two samples each.

*Compound III.

REFERENCES

[1]Boden, et al, U.S. Patent 3,726,952, 1973.

[2]Kleimann, et al, U.S. Patent 3,925,527, 1975.

[3]S. L. DeGisi and C. H. Smith, Improved Bondability of Molded Rigid Urethane Foam by Plasma Treatment (SPE Conference Paper). UNCLASSIFIED. Bendix Kansas City: BDX-613-1915, November, 1977. (Available From NTIS)

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PLASTICS: Mold Releases

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