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THIOKOL SPECIALTY CHEMICALS DIVISION
TRENTON, NEW JERSEY
RESEARCH DEPARTMENT

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J20-17
September 15, 1980
DATA CONTAINED HEREIN
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HEXAMETHYLENE GLYCOL POLYFORMAL
COPOLYMERS FOR INSULATING GLASS
AND BUILDING SEALANTS

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Hexamethylene Glycol Polyformal Copolymers For Insulating Glass & Building Sealants

SUMMARY

A) Isocyanate Terminated

Polyformals based on Hexamethylene Glycol with a co-Diol such as 1,4-Butanediol were easily prepared under mildly acidic conditions. These polyols were smoothly converted to NCO prepolymers with TDI. The resulting prepolymers were readily cured with trimethylol propane, ambient moisture or quadrol, giving elastomers with good hardness, elasticity and tensile. When slightly alkaline the elastomers showed excellent thermal stability. Evaluation of these polymers for insulating glass sealants is recommended.

B) Mercapto Terminated

These materials were synthesized in a two step sequence involving initially the addition of allyl alcohol during the polyformal reaction. The resulting allyl capped polyformals were then reacted with an equivalent amount of dimercaptan initiated by Vazo-64. These materials did not cure with lead dioxide, probably due to low molecular weight and residual hydroxyl terminals. Removal of residual hydroxyl with TDI or addition of suitable crosslinkers such as trimethylol propane triacrylate or triallyl cyanurate gave curable prepolymers. The elastomers showed good compression set and hardness but very poor elasticity. The marginal properties, increased complexity and cost of these prepolymers render evaluation for insulating glass sealants unwarranted.

INTRODUCTION

Research was initiated to determine the feasibility of rubbers derived from hexamethylene glycol polyformal polymers as sealants. Obvious advantages of the polyols are low odor and cheap manufacture. Two approaches were taken. The first involved conversion of the polyol to the toluene diisocyanate (TDI) urethane prepolymer. Such a prepolymer could then be utilized either in a two package sealant with a polyol cure or as a one package sealant utilizing either a thermal or ambient moisture curative. Since the inherent moisture sensitivity of these prepolymers may be a problem during compounding or storage a second approach was

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investigated. Mercapto terminated polyformals, in principle curable with lead or manganese dioxide, were synthesized. These are insensitive to moisture, but require additional production steps and costs.

EXPERIMENTAL PROCEDURES

a) Hexamethylene Glycol Polyformal Copolymers

Hexamethylene glycol/formaldehyde polymer is a room temperature solid. To depress the melting point a series of OH terminated liquid polymers were made using hexamethylene glycol and 10-20 mole % of an appropriate diol. These glycol mixtures were converted to polyformals with para formaldehyde using p-toluene sulfonic acid catalyst and a toluene azeotrope to remove the water. The results are summarized in Table 1. Yields were essentially quantitative except for F-1867-6 and F-1867-8. F-1867-6 showed only 3 mole % hexylene glycol incorporation, probably due to butyl dioxolane formation. Since it also crystallized further investigation of F-1867-6 was abandoned. F-1867-8 showed ~10 mole % neopentyl glycol incorporation.

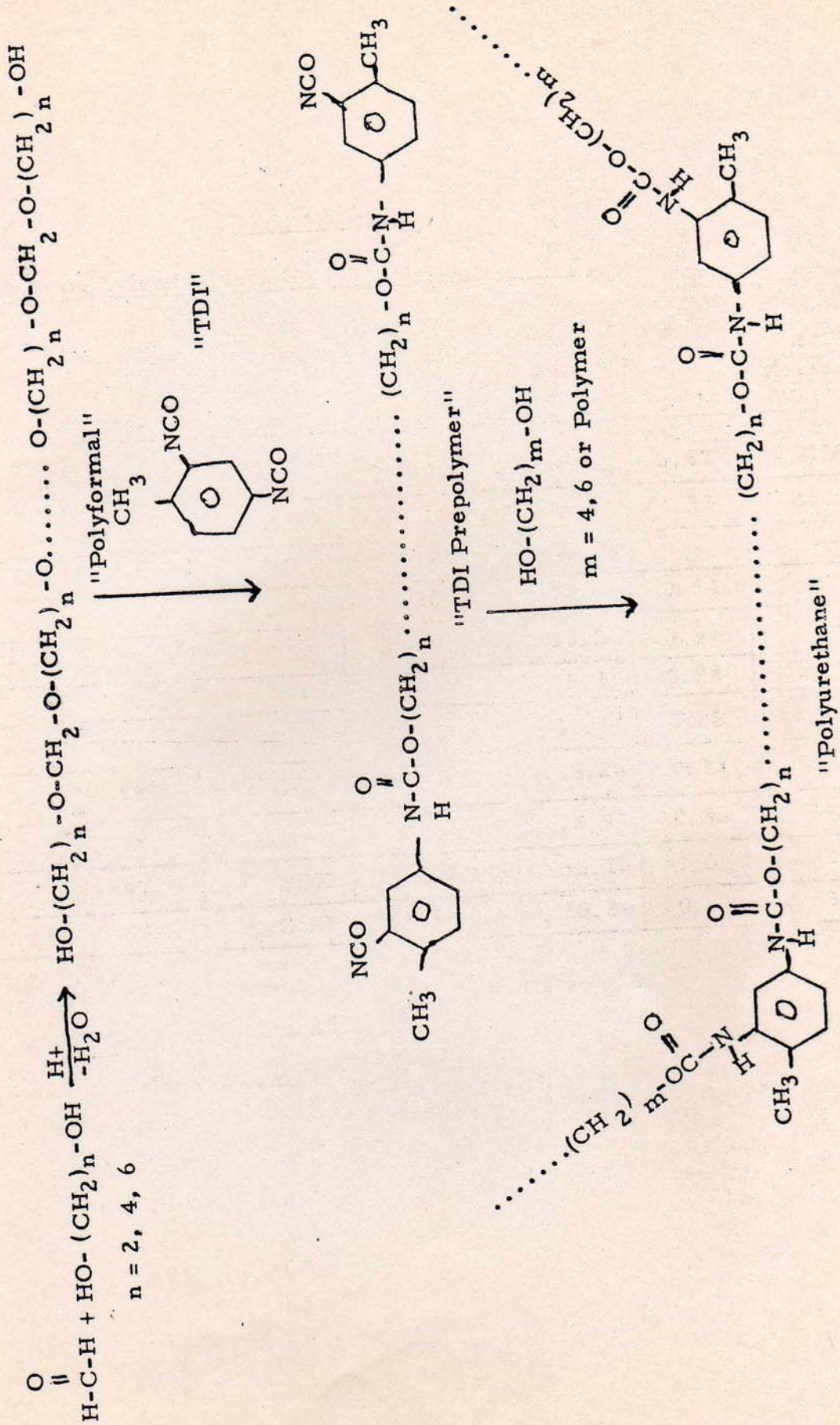
F-1867-1 proved ~50% crystalline, probably due to the lesser mole % of diol. A 20 mole % tetramethylene glycol polyformal (F-1867-34) was a liquid as were all polyformals described in Table 1. The molecular weights ranged from ~2600 to ~6800, based on OH content. No correlation was found between molecular weight and diol structure or reaction conditions. The chemistry involved in these syntheses is summarized in equation #1.

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EQUATION #1

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TABLE 1

Hexamethylene Glycol Polyformal Copolymers

Notebook Ref.	% Yield	Diol Diluent	Mol Ratio HMG/Diol	OH #	% OH	Av. Molecular Weight
F 1867-1	95	BD	90:10	22.1	0.67	5200
F 1867-4	98	EG	80:20	43.95	1.33	2600
F 1867-6	82	HG	80:20	--	--	--
F 1867-8	90	NPG	80:20	17.8	0.54	6800
F 1867-10	99	DEG	80:20	30.0	0.91	3800
F 1867-12	99.7	--	--	29.1	0.88	3900
F 1867-24	98	EG	80:20	28.44	0.86	4000
F 1867-34	98	BD	80:20	25.24	0.73	4700
F 1867-45	99.9	TDE	70:30	28.99	0.88	3900
F 1469-10	97	TDE	100 TDE	35.16	1.06	3240
F 1469-12	99.9	CHD	70:30	18.29	0.55	6350

Abbreviations

HMG	Hexamethylene Glycol
BD	1,4 Butanediol
EG	Ethylene Glycol
HG	Hexylene Glycol
NPG	Neopentyl Glycol
DEG	Diethylene Glycol
TDE	2,2' Thiodiethanol
CHD	1,4-Cyclohexanedimethanol

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b) Hexamethylene Glycol Polyformal TDI Prepolymers

The polyformals were smoothly converted to NCO terminated urethane prepolymers by heating with TDI at $\sim 85^{\circ}\text{C}$ for two hours. Further heating must be avoided or extensive trimerization of the isocyanate group occurs giving brittle solids. The prepolymers were brown viscous liquids with isocyanate percentages close to the theoretical values. The results are summarized in Table 2.

c) Hexamethylene Glycol Polyformal Urethane Rubbers

The TDI prepolymers cured in ~ 20 hrs. at room temperature with "Quadrol", in ~ 4 days under ambient conditions with moisture and in ~ 7 hrs. at 110°C with trimethylol propane. Thermally the rubbers are quite stable if the prepolymer is made alkaline with excess CaCO_3 filler prior to cure. With standard formulations the prepolymers cured with ambient moisture to acceptable hardness (Shore A Duro ~ 40). Incorporation of 2,2'-thiodiethanol (TDE) resulted in both poorer physicals and thermal stability. Also standard formulations incorporating TDE polyformals when moisture cured showed substantial swelling due to gas retention. Table 3 shows typical physical properties and thermal stabilities of the elastomers cured with trimethylolpropane. The moisture vapor transmittance of several cured sheets was also measured. The results are given in Table 4. In general, the polyformal urethane rubbers showed transmission of moisture some 6-10 times more facile than for methyl mercaptan polybutadiene adduct films (See Bertozzi, Cameron, Report #J 31-3, March 24, 1980), and ~ 3 times more facile than for OH terminated LP-32 cured with TDI.

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TABLE 2

Hexamethylene Glycol Polyformal TDI Prepolymers

Note Book Ref.	Polyformal	Reaction Conditions	% NCO	
			Theor.	Found
F 1867-16	F 1867-4	1.7 Hr. 85°C	2.87	2.92
F 1867-19	F 1867-10	2.25 Hr. 85°C	2.05	1.70
F 1867-25	F 1867-24	1.25 Hr. 85°C	1.95	2.16
F 1867-36	F 1867-34	2 Hr. 85°C	1.68	1.62
F 1867-42	F 1867-8	1.7 Hr. 80°C	1.17	1.10
F 1867-48	F 1867-45	1.7 Hr. 85°C	2.00	2.15
F 1469-15	F 1469-10	2 Hr. 85°C	2.34	1.90
F 1469-50	F 1867-34	2 Hr. 85°C	1.68	1.30

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TABLE 3Physical Properties, Thermal Stabilities, Polyformal
Urethane Rubbers, Trimethylolpropane Cure

Note Book Ref.	Film Identification	Elongation	Shore A Duro	Film Weight Change 24 Hrs. 150°C
F 1867-20	HMG/EG/TDI F 1867-16	300	50	- 10.6% ^a - 1.6% ^b
F 1867-39	HMG/BD/TDI F 1867-36	400	40	- 1.1%
F 1867-49	HMG/TDE/TDI F 1867-48	200	55	- 1.3%
F 1469-17	TDE/TDI F 1469-15	100	50	- 4.47%

Abbreviations: See Table 1

a) Untreated with CaCO₃ prior to cureb) CaCO₃ treatedF 1867-39, 49 and F 1467-17 CaCO₃ treated prior to cure.

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TABLE 4

MVT Properties, Polyformal Urethane Rubbers

Film #	Film a) Identification	Sample Thickness(Mills)	MVT	Permeance	Permeability
F 1867-20	HMG/EG/TDI	77	23.03	0.975	0.191
F 1867-39	HMG/BD/TDI	78	32.79	1.290	0.255
F 1867-49	HMG/TDE/TDI	87	28.43	1.115	0.246
F 1469-17	TDE/TDI	100	20.56	0.840	0.213

Abbreviations: See Table 1

a) All prepolymers cured with trimethylol propane.

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d) Hexamethylene Glycol Based Mercapto Terminated Polyformals

These materials were synthesized in a two step sequence involving the initial capping of the polyformals with allyl groups. Addition of excess allyl alcohol during the reaction gave low molecular weight (~ 700) polyformals $\sim 98\%$ end capped with unsaturation. In several cases small amounts of trimethylol propane (TMP) were also added in hopes of giving the polymer additional functionality. Reduction of the quantity of allyl alcohol added gave slightly higher molecular weights and less end capping. Table 5 summarizes these results.

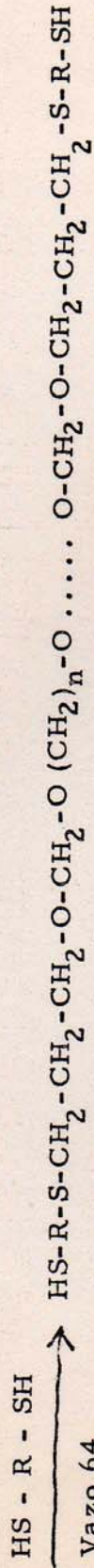
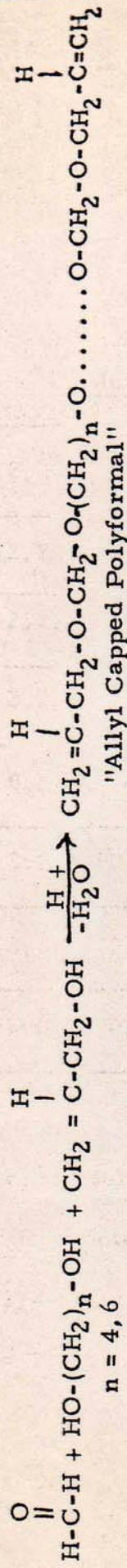
The allyl capped polyformals were then reacted with sufficient dimer-captodiethyl ether, $\text{HS-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-SH}$, to remove all unsaturation, i.e. an equivalent amount. The best conditions for complete addition to the double bond were 2-4 hrs. at $95\text{-}100^\circ\text{C}$ under slightly alkaline conditions with 1-2% Vazo-64 initiator. A slightly alkaline medium was necessary to prevent sulfur-oxygen interchange in the polymer backbone. Potassium hydroxide/ethanol proved effective for this purpose. Table 6 summarizes the results obtained on synthesis of mercapto terminated polyformals. The chemical reactions involved are summarized in Equation #2.

e) Curing of Mercapto Terminated Hexamethylene Glycol Polyformals

The prepolymers obtained by addition of dimercapto diethyl ether to $\sim 98\%$ allyl end capped polyformals failed to cure with lead dioxide, probably due to residual hydroxyl terminals acting as chain stoppers. The low molecular weights of the prepolymers were also a problem. Those prepolymers containing TMP also failed to cure, probably due to formation of "dead" cyclic acetal terminals.

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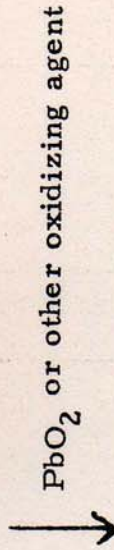
EQUATION #2



"Mercapto Terminated Polyformal"

R = CH₂-CH₂

or CH₂-CH₂-O-CH₂-CH₂



"Elastomer"

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TABLE 5

Allyl Capped Polyformals

Note Book Ref.	F	Moles		TMP	Allyl Alc.	% OH	Unsat. Equiv.	Av. Mol. Wt.	% End Capped
		HMG	BD						
F 1469-21	4.5	2.4	0.6	--	3.0	0.120	0.33	670	98
F 1469-26	4.5	2.22	0.56	0.15	3.0	0.184	0.36	560	97
F 1469-40	4.5	2.22	0.56	0.15	3.0	0.070	0.32	630	99
F 1469-41	4.5	2.22	0.56	0.15	3.0	0.035	0.32	670	99
F 1469-46	1.88	0.88	--	0.25	1.25	~ 0	0.24	820	--
F 1469-49	3.5	2.8	0.7	--	1.0	0.836	0.27	740	82
F 1490-10	3.5	2.8	0.7	--	0.5	0.390	0.13	1500	48
F 1490-13	3.5	2.8	0.7	--	0.5	0.480	0.13	1500	48

Abbreviations: F = Formaldehyde (Paraform)

HMG=Hexamethylene Glycol

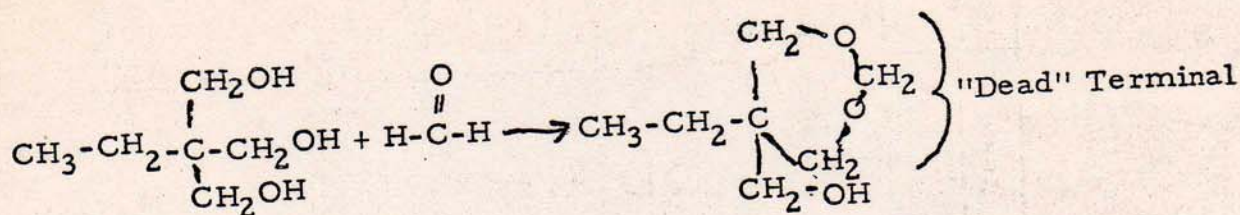
BD = 1,4-Butanediol

TMP = Trimethylol Propane

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EQUATION #3



Two crosslinking agents were found effective for curing these prepolymers. The base catalyzed addition of trimethylol propane triacrylate (TMPTA) to the prepolymers gave cured rubbers of acceptable hardness. They possessed the undesirable features of extreme shortness and hydrolytically unstable ester linkages. Another effective crosslinking agent was triallyl cyanurate (TAC). Addition of 15-20 wt. % TAC to the 98% allyl capped polyformal, followed by Vazo 64 induced addition of dithiol to the double bonds gave prepolymers which cured to Shore A 70 with lead dioxide. While possessing excellent compression set, they were extremely short. Table 6 summarizes the results of attempted curing of these prepolymers.

Another technique which proved successful for curing these prepolymers involved reaction of the residual hydroxyl groups with a stoichiometric amount of TDI, i. e. 0.5 times the molar amount of hydroxyl. 8 hours at 100°C usually served to react all residual hydroxyl. These allyl capped materials, now devoid of hydroxyl chain stoppers, were then reacted with dithiol by the standard technique. To increase the probability of cure, partially end capped polyformals of slightly higher molecular weight (F 1469-49, F 1490-10, 13) were employed. The prepolymers cured to Shore A 35 with lead dioxide with good compression set but poor elasticity. The rubbers could be hardened considerably by addition of 5-20 wt. % TAC to the allyl capped polyformal. Table 6 summarizes curing by this technique. Table 7 shows the effect of TAC addition on Shore A duro.

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Analytical and Curing Data, Mercapto Terminated Hexamethylene Glycol Polyformals
Allyl

Note Book Ref.	Capped Reactant	Reaction Time 95°C	% SH		Curable ?	Shore A Duro	% Elongation
			Theor.	Found			
F 1469-28	F 1469-21	4 hrs.	7.49	8.12	PbO ₂ No	---	---
..	TMPTA/ET ₃ N Yes	30	Short
..	30% TMPTA/ET ₃ N then PbO ₂ , Yes	15	75
..	PAPI 135 Yes	30	Short
..	PAPI 135/TDI Yes	40	Short
F 1469-33a)	F 1469-26	7 hrs.	7.68	6.84	PbO ₂ No	--	--
F 1469-42	F 1469-40	4 hrs.	7.2	7.9	PbO ₂ No	--	--
F 1490-2	F 1469-46	6 hrs.	5.8	6.5	PbO ₂ No	--	--
F 1490-8 ^{b,c} ,	F 1469-49	4.5 hrs.	4.9	6.99	PbO ₂ Yes	35	75
..	Epon 128 Yes	100	---
F 1490-14	TDI prepolymer of F1867-36, capped with allyl alcohol	3 hrs. with HS-CH ₂ -CH ₂ -OH			PbO ₂ Poor	5, gummy	--
F 1490-15	..	Overnight 70°C	--	--	PbO ₂ , Poor	..	--
F 1490-20 ^b	F 1490-13	2 hrs.	--	--	PbO ₂ , Yes	35	50

a) Residual hydroxyl reacted with Molar amount TDI

b) Residual hydroxyl reacted with 0.5 molar amount TDI

c) ~10% excess dimercaptan added

TMPTA = Trimethylol Propane Triacrylate

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TABLE 7
Effect of Triallyl Cyanurate (TAC) Concentration
on Elastomer Hardness

Note Book Ref.	Prepolymer	% TAC	Shore A Duro
F 1490-20	F 1490-20	0	35
F 1490-25	F 1490-10 ^a	2.5	40
F 1490-25	..	5.0	42
F 1490-25	..	10.0	50
F 1490-26	..	16.9	62
F 1490-27	..	20.0	75
F 1490-26	..	10.0	Tacky
F 1490-28	F 1469-21 ^b	15.0	70
F 1490-29	..	20.0	75
F 1490-28	..		

a) Allyl capped polyformal + TDI + Dimercapto diethyl ether + TAC
 See F 1490-24

b) Allyl capped polyformal + Dimercapto diethyl ether + TAC

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DISCUSSIONa) Isocyanate Terminated Hexamethylene Glycol Polyformal Copolymers

The urethane rubbers obtained by curing these prepolymers show acceptable properties, except for their three fold higher permeability to moisture than for polysulfide polymers and eight fold higher permeability than for the methyl mercaptan polybutadiene adduct polymers. These properties are consistent with the more polar polyformal backbone. This apparent drawback may be an advantage in the ambient moisture cure. These prepolymers cure in \sim 4 days with ambient moisture while NCO terminated polysulfides fail to completely cure even after two weeks or more. The good thermal stability with alkaline filler to weight loss and retention of properties is noteworthy. Under acidic conditions the rubbers degrade badly, probably due to catalyzed dehydration and chain cleavage with moisture. Since most fillers are basic the instability of the formal link to hydrolysis under acid conditions should present no problems. Addition of small quantities of an antioxidant should further enhance thermal stability.

b) Mercapto Terminated Hexamethylene Glycol Polyformal Copolymers

While these materials can be induced, with some effort, to cure, the marginal properties of the rubbers so obtained make further development difficult to justify. Good hardness and compression set are offset by their consistent extreme shortness. The very low molecular weights of the allyl capped polyformals (compare Tables 1 and 5) may be in part responsible. Higher molecular weights could be obtained by further reduction in the molar ratio of allyl alcohol. However, the higher levels of hydroxyl would lead to unacceptable viscosities when reacted with TDI. Heating of the polyformals to high temperature under vacuum to increase the molecular weight has been attempted. However, only a modest increase (Mol. Wt. \sim 1000) was observed (Ref. F 1469-44). Thus it appears that we have reached the limits of this approach.

CONCLUSIONS AND RECOMMENDATIONSa) Isocyanate terminated Hexamethylene Glycol Polyformal Copolymers

These prepolymers cure to elastomers with excellent physical properties and thermal stability albeit with relatively poorer barriers to moisture than for the polysulfides. Despite the latter property the good cures and physical properties, coupled with cheap starting materials and ease of manufacture, lead us to recommend evaluation of these materials as

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insulating glass sealants. Moisture vapor transmission is no longer regarded as the overriding property if not unreasonably high. Good adhesion to glass and metal, which is just as important, may well be present in these elastomers.

b) Merapto Terminated Hexamethylene Glycol Polyformal Copolymers

These materials can be cured to rubbers with good hardness and compression set but very poor elasticity. Their marginal properties together with complexity and cost of manufacture make evaluation as insulating glass sealants unjustified.

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