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MONSANTO RESEARCH CORPORATION

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Mr. Delmar E. Loewe
University of California
Lawrence Radiation Laboratory
P.O. Box 808
Livermore, California 94551

Attention: William E. Cady

Dear Mr. Loewe:

Enclosed is a copy of an excerpt from Mound Laboratory Progress Reports covering the Research Departments efforts on LRL SANL 311-047, from December 15, 1965 to January 15, 1966. This report is preliminary and the data and conclusions at this time should be treated as such.

If you have any questions concerning this report, do not hesitate to let us know.

Very truly yours,

Original Signed by
RICHARD E. VALLEE

Richard E. Vallée, Manager
Chemistry and Metallurgy Section
Research Department

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SUMMARY

A preliminary evaluation of some chlorobutyl, chlorosulfonated polyethylene, ethylene-propylene, polychloroprene and ethylene-propylene terpolymer elastomers as matrices for crystalline boron particles was conducted.

Seven chlorobutyl elastomers were prepared which contained 70 volume per cent of crystalline boron. None of the samples would cure satisfactorily. Of six chlorobutyl elastomer formulations containing 61.5 volume per cent of crystalline boron, four could be cured to some extent.

A chlorosulfonated polyethylene elastomer formulation was filled with 70, 75 and 80 volume per cent of crystalline boron. All samples molded well and were flexible; the lowest loaded formulation was the most flexible. Seven chlorosulfonated polyethylene elastomers formulations were prepared which contained 61.5 volume per cent of crystalline boron. All samples molded satisfactorily.

Ten ethylene-propylene terpolymer elastomer formulations were filled with 61.5 volume per cent of crystalline boron. Seven of the ten appeared to cure satisfactorily.

Two Neoprene WRT elastomer formulations were prepared which contained 61.5 volume per cent of crystalline boron. Both formulations contained chlorobutyl elastomer as plasticizer. Both formulations appeared to cure satisfactorily.

Nine ethylene-propylene elastomer formulations were prepared which contained 61.5 volume per cent of crystalline boron. Only one sample cured adequately.

Eight unfilled formulations were prepared from EPT 3509 and EPR 404 elastomers. The samples were cured and their densities determined. These values were used to calculate the density expected for filled samples containing 61.5 volume per cent of crystalline boron. The calculated values were in most cases higher than those obtained by direct measurement in filled formulations.

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SECRET

A swelling test for determining the cross link density of cured elastomer formulations was set up and preliminary swelling data obtained.

Two batches were prepared of crystalline boron filled hydrolysed vinyl ester elastomer containing tolylene diisocyanate dimer (TDID) in the specified amount. The sample in which the filler was added after the catalyst would not cure when heated at 255°C for 50 minutes, while the sample in which the filler was added before the catalyst cured satisfactorily. Both uncured samples flowed readily in a compression creep apparatus at 1000 pound loads. Flow measurements, shrinkage in the die, hardness, and density measurements were run on the satisfactory sample.

To study the thermal decomposition of TDID, samples were incorporated into potassium bromide pellets and heated at temperatures ranging from 90 to 140°C. In various periods of time. Infrared spectra on these pellets showed the dimer to be stable for four hours at 105°C. Slight decomposition began after one hour at 115°C and became very extensive at 135°C. None of the spectra examined resembled that of tolylene diisocyanate.

Tolylene diisocyanate dimer (TDID) was treated with an excess of n-hexanol at 130°C for six hours to determine whether the dimer decomposed under these conditions. The only carbamate isolated from the reaction was that of the monomer indicating that depolymerization had occurred. However, when the experiment was repeated using smaller ratios of alcohol to dimer of 1:1, 1:2, and 1:4, other carbamates were obtained indicating that complete depolymerization did not occur under these conditions.

Preliminary evaluation of some of the elastomers specified in the SANL outline was carried out using crystalline boron powder as the filler. The results are summarized as follows:

1. <u>Chlorobutyl Elastomer 10-66 (Enjay)</u>

   a. Seven different recipes were prepared and loaded with 70 volume per cent of crystalline boron (Table 1) none of the samples cured satisfactorily although recipes E and F were better than the others.

   b. Six recipes were prepared and loaded with 61.5 volume per cent of crystalline boron (Table 2). Four of the six recipes cured fairly well; recipes 2 and 4 did not cure.

TABLE 1

BORON-FILLED HT 10-66 FORMULATIONS

Component	Component in Formulation (g)						
	A	B	C	D	E	F	G
Elastomer	3.000	3.000	3.000	3.000	3.000	3.000	3.000
Boron Filler	17.49	17.49	17.49	17.49	17.49	17.49	17.49
ZnO	0.15	0.15	0.15	0.15	---	0.15	0.15
TMTDS[a]	---	0.03	0.03	0.03	---	---	---
MBTS[a]	---	---	0.03	0.03	---	0.03	---
MgO	---	---	0.03	---	0.15	0.15	---
DETA[b]	---	---	---	---	0.06	---	---
Na-22[c]	---	---	---	---	---	0.045	---
Sulfur	---	---	---	0.06	---	---	---
Permalux[c]	---	---	---	---	---	---	0.03
Cure Cycle	30 min/ 307°C	40 min/ 307°C	40 min/ 307°C	45 min/ 307°C	45 min/ 307°C	60 min/ 307°C	30 min/ 307°C

a Monsanto Company
b Diethylenetriamine, Union Carbide Corp.
c E. I. DuPont de Nemours & Co.

TABLE 2

BORON-FILLED HT 10-66 FORMULATIONS

Formulation	Component in Formulation (g)										Cure Cycle (min/°F)
	ZnO	MgO	GMF	MBTS	ZDEDC	TDEDC	AMBEROL ST-137	DETA	NA-22	Sulfur	
1	0.20	---	---	---	---	---	0.200	---	---	---	40/307
2	0.200	---	---	0.040	---	0.040	0.200	---	---	0.060	60/307
3	0.200	---	---	---	0.060	---	---	---	---	---	60/307
4	---	0.400	0.08	0.160	---	---	---	---	---	---	60/307
5	---	0.200	---	---	---	---	---	0.08	---	---	45/307
6	0.200	0.040	---	0.040	---	---	---	---	0.060	---	60/307

NOTE: All formulations contained 4.000 g HT 10-66, 0.040 g stearic acid, and 12.000 g crystalline boron.

GMF = p-quinone dioxime
MBTS = Benzothiozyl disulfide
ZDEDC = Zincdiethyl dithiocarbamate
TDEDC = Tellurium diethyldithiocarbamate
AMBEROL ST-137 = Phenol formaldehyde resin
DETA = Diethyltriamine
NA-22 = 2-mercaptoimidazoline

2. Chlorosulfonated Ethylenes Hypalon 20 and 40 (du Pont)

   a. A recipe of Hypalon 40 was loaded with 70, 75, and 80 volume per cent of crystalline boron (Table 3). All test specimens cured satisfactorily and were flexible. The sample with the least load was the most flexible of the three.

   b. Seven recipes of Hypalon 20 and 40 were prepared which were loaded with 61.5 volume per cent of crystalline boron (Table 4). All recipes molded well, had good appearance and appeared to be well cured.

3. Ethylene - Propylene Terpolymer EPT-3509 (Enjay)

   a. Ten recipes of EPT-3509 were prepared and loaded with 61.5 volume per cent of crystalline boron (Table 5). Seven of the ten recipes cured satisfactorily.

4. Ethylene - Propylene Elastomer EPR-404 (Enjay)

   a. Nine recipes of EPR-404 were prepared and loaded with 61.5 volume per cent of crystalline boron (Table 6). Only one recipe, #2, cured satisfactorily.

5. Chloroprene Elastomer Neoprene WRT (du Pont)

   An LRL recipe and a United Kingdom recipe were prepared and loaded with 61.5 parts by volume of crystalline boron (Table 7). Both samples cured satisfactorily.

   Eight unfilled formulations were prepared from EPT and EPR elastomers. The samples were cured and their densities determined. The densities were used to calculate the theoretical densities for formulations filled with 61.5 volume per cent of crystalline boron (Table 8). The calculated values were in most cases higher than those obtained by direct measurement on filled samples.

TABLE 3

BORON-FILLED HYPALON 40 FORMULATIONS

Material	Composition of Formulation (g) A	B	C
Hypalon-40[a]	3.000	3.000	3.000
DPER[b]	0.114	0.114	0.114
MgO	0.120	0.120	0.120
Tetrone A[a]	0.060	0.060	0.060
Boron Filler	25.225	18,919	14.715

a E. I. du Pont de Nemours & Co.

b Dipentaerythritol, Heyden Newport Corp.

TABLE 4

HYPALON FORMULATIONS

Formulation	Elastomer	DPER	PER	TriPER	MBTS	Quinoxaline	2-3 Dimethylquinoxaline	TMP	MgO
1	Hypalon-40	0.152	---	---	---	---	---	---	0.160
2	Hypalon-20	0.152	---	---	---	---	---	---	0.160
3	Hypalon-40	---	---	---	---	---	---	0.176	0.160
4	Hypalon-40	---	---	---	0.030	0.200	---	---	---
5	Hypalon-40	---	---	---	0.030	---	0.248	---	---
6	Hypalon-40	---	---	0.164	0.020	---	---	---	0.080
7	Hypalon-40	---	0.120	---	0.020	---	---	---	0.080

NOTES: All formulations contained 4.000 g Hypalon elastomer, 12.000 g crystalline boron, and 0.080 g Tetrone A.

Cure Cycle: 20 min. at 320°F.

DPER = Dipentaerythritol
PER = Pentaerythritol
TriPER = Tripentaerythritol
MBTS = Benzothiazyl disulfide
TMP = Trimethylol propane
Hypalon = Chlorosulfonated polyethylene
Tetrone A = Dipentamethylenethiuram tetrasulfide

TABLE 6

EPT-3509 FORMULATIONS

Formulations	Component in Formulation (g)														
	MBTS	Sulfur	MBT	TMTMS	TMTDS	CDEDC	TDEDC	DTDM	Calcium Stearate	t-butyl peroctoate	GMF	PbO	AMBEROL ST-137	HT 10-66	Di-Cup-40C
1	---	0.060	0.020	0.060	---	---	---	---	---	---	---	---	---	---	---
2	---	0.060	0.020	---	0.060	---	---	---	---	---	---	---	---	---	---
3	0.020	0.060	---	---	---	0.060	---	---	---	---	---	---	---	---	---
4	0.020	0.020	---	---	---	0.150	---	---	---	---	---	---	---	---	---
5	---	0.020	---	---	0.040	---	0.040	---	---	---	---	---	---	---	---
6	---	---	---	---	0.080	---	---	0.080	---	---	---	---	---	---	---
7	---	---	---	---	---	---	---	---	0.040	---	---	---	---	---	0.040
8	---	---	---	---	---	---	---	---	0.040	0.040	---	---	---	---	---
9	0.040	---	---	---	---	---	---	---	---	---	0.160	0.080	---	---	---
10	---	---	---	---	---	---	---	---	---	---	---	---	0.400	0.400	---

Notes: All formulations contained 4.000 g EPT-3509 elastomer, 12.000 g crystalline boron, 0.200 g ZnO, and 0.040 g stearic acid (in first 6 only).

Cure cycle: 20 min at 320°F, except 7 and 8 which were cured 25 min at 320°F.

MBTS = Benzothiazyl disulfide
MBT = 2-mercaptobenzathiazole
TMTMS = Tetramethylthiuram monosulfide
TMTDS = Tetramethylthiuram disulfide
CDEDC = Cadmium diethyldithiocarbamate
TDEDC = Tellurium diethyldithiocarbamate
DTDM = 4.4'-dithiomorpholine
GMF = p-quinonedioxime
AMBEROL ST-137 = phenol, formaldehyde resin
HT 10-66 = chlorobutyl rubber
DiCup-40C = dicumyl peroxide

TABLE 6

BORON-FILLED EPR 404 FORMULATIONS

Sample No.	Ingredients added to Master Batch,[a] g									Cure Schedule Minutes and Temp. °F
	Dicup R[b]	Sulfur	Diallyl Melamine	Divinyl Benzene	t-butyl perbenzoate	Buton 150[c]	Dicup 40C[b]	Luperco 101 X L[d]	S-890[b]	
1	0.078	0.009	---	---	---	---	---	---	---	30/300
2	0.078	---	0.150	---	---	---	---	---	---	30/300
3	0.078	---	---	0.150	---	---	---	---	---	30/300
4	---	0.009	---	---	---	---	---	---	0.09	20/320
5	---	0.018	---	---	0.116	---	---	---	---	30/200
6	---	0.010	---	---	---	---	0.203	---	---	30/320
7	---	---	---	---	---	0.150	---	---	---	30/320
8	---	0.010	---	---	---	---	---	0.210	---	30/320
9	---	---	---	---	---	0.150	---	0.090	---	30/320

a Master batch contained 3.00 g EPR 404, 12.826 g crystalline boron and 0.03 g of calcium stearate.

b Hercules Powder Co.

c Enjay Company

d Wallace and Tierman Corp.

TABLE 7

NEOPRENE FORMULATIONS: TYPE WRT

Formulation	Component in Formulation (g)									
	Filler	HT 10-66	MgO	Neozone D	Stearic Acid	TMTMS	DOTG	NA-22	ZnO	Sulfur
1	21.574	1.714	0.171	0.114	0.029	0.029	0.029	0.029	0.285	0.057
3	15.493	0.801	0.160	---	0.016	---	---	0.016	0.163	---

NOTES: 4.000 g Neoprene WRT elastomer in both formulations.

Cure Cycle: 40 min. at 307°F.

Formulation 1: United Kingdom formulation.
Formulation 3: Special LRL formulation.
HT-10-66 = Chlorobutyl
Neozone D = Phenyl-B-napthylamine
TMTMS = Tetramethylthiuram monosulfide
DOTG = N,N[1]-Di-ortho-tolyguanidine
Na-22 = 2-mercaptoimidazoline

Table 8

UNFILLED FORMULATIONS USING EPT AND EPR ELASTOMERS[a]

Formulations	Curatives[b]											Measured Density of Unfilled Elastomer (g/cc)	Measured Density of Boron-filled Elastomer (g/cc)	Calculated Boron-filled Density (g/cc)
	Sulfur	MBT	TMTMS	TMTDS	MBTS	CDEDC	TDEDC	Sulfasan R	Di-Cup 40C	Diallyl Melamine	Calcium Stearate			
1	0.180	0.060	0.060	--	--	--	--	--	--	--	--	0.873	1.6719	1.6895
2	0.180	0.060	--	0.180	--	--	--	--	--	--	--	0.875	1.6568	1.6901
3	0.180	--	--	--	0.060	0.180	--	--	--	--	--	0.874	1.657	1.6898
4	0.060	--	--	--	0.060	0.450	--	--	--	--	--	0.874	1.653	1.6898
5	0.180	--	--	0.120	--	--	0.120	--	--	--	--	0.869	1.6858	1.6882
6	--	--	--	0.240	--	--	--	0.240	--	--	--	0.876	1.661	1.6904
7	--	--	--	--	--	--	--	--	0.120	--	0.120	0.867	1.5699	1.6876
8	--	--	--	--	--	--	--	--	0.312	0.600	0.120	0.882	1.7850	1.7600

[a] Formulations 1-6 contain 12.000 g EPT-3509, 0.060 g ZnO and 0.120 g stearic acid in addition to the listed ingredients. Formulation 7 contains the above ingredients with the exception of stearic acid. Formulation 8 contains 12.000 g EPR-404 in addition to the listed ingredients.

[b] MBT = 2-mercaptobenzothiazole

TMTMS = tetramethyl thiuram monosulfide

TMTDS = tetramethyl thiuram disulfide

MBTS = benzothiazyl disulfide

CDEDC = cadmium diethyl dithiocarbamate

TDEDC = tellurium diethyl dithiocarbamate

Sulfasan R = 4,4' dithiodimorpholine

Di-Cup 40C = dicumyl peroxide (40% inert filler)

Swell Index Measurements Swell index measurements were made on cured chlorosulfonated polyethylene and ethylene propylene terpolymer formulations by the method of Smith and Magnusson[1] to evaluate the degrees of cure and the times necessary for the samples to attain equilibrium with the solvent. The procedure was as follows: Samples (0.5 x 0.5 in.) of the cured elastomer were weighed, placed in a flask, and 100 ml of benzene was added. The flasks were placed in a water bath maintained at 30°C. Two samples of each formulation were removed periodically, blotted with filter paper, and reweighed. The benzene absorbed by the sample was then removed by heating at 65°C under vacuum overnight, and the samples were weighed again. The swell index was calculated using the formula

$$V/V_O = [W_i/D_e + (W_r - W_v)/D_s]/(W_v/D_e),$$

where V = volume of the swollen sample,

V_O = volume of the unswollen sample after removal of the solvent,

W_i = initial sample weight,

W_r = sample weight upon removal from solvent,

W_v = sample weight after removal of solvent,

D_e = density of elastomer sample, and

D_s = density of solvent.

The swell index is a measure of cross link density,[2] i.e., the lower the swell index, the greater the crosslink density. The data obtained for formulations using Hypalon elastomers

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1 T. L. Smith and A. B. Magnusson, J. Poly. Sci., 42, 391 (1960).

2 S. D. Gehman, Industrial and Engineering Chemistry, 44 730 (1952).

are shown in Figure 1. Formulations 1 and 2 show the lowest swell index and thus appear to have a higher degree of cure than the other formulations. Also, the figure shows that equilibrium was attained after 19 hr. immersion.

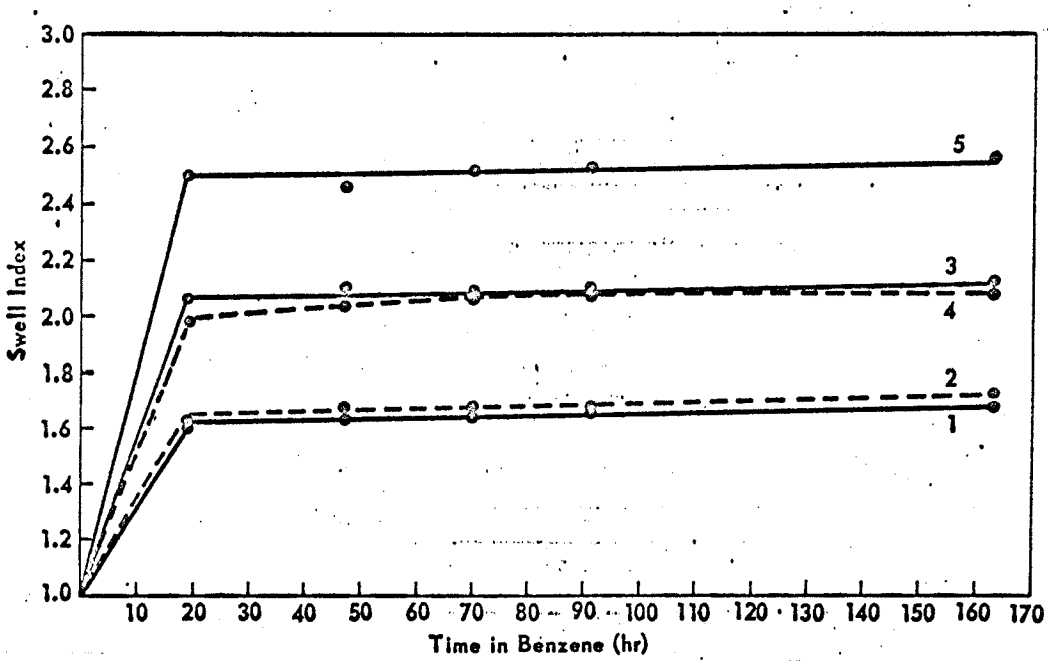

Figure 1

SWELL INDEX OF FILLED HYPALON ELASTOMERS IN BENZENE AT 30°C

Table 9 gives the swell index data obtained for a series of formulations using EPT elastomers. Formulation 5 had lost cohesiveness, and the swell index could not be determined. Figure 2 shows a sample of this formulation after a 23-hour immersion. By comparing the size of the sample with the 0.5 inch line in the photograph (initial sample dimensions were 0.5 x 0.5 in.) it can be seen that the sample was extremely swollen. This formulation had not cured adequately.

The procedure described above gave relatively good precision. Although the method used was not ideal, i.e., the complete removal of solvent from the swollen sample is not guaranteed, and the densities used in the calculations do not necessarily remain constant, the data are sufficiently accurate for this application. In future work, toluene, rather than benzene will be used as the swelling solvent.

TABLE 9

SWELL INDEX OF FILLED
EPT ELASTOMERS IN
BENZENE AT 30°C

Sample	Immersion Time (hr)	Swell Index
1	22.6	1.66 ± 0.015
2	22.7	1.58 ± 0.035
3	22.7	1.60 ± 0.025
4	22.8	1.62 ± 0.005
5	23.0	---

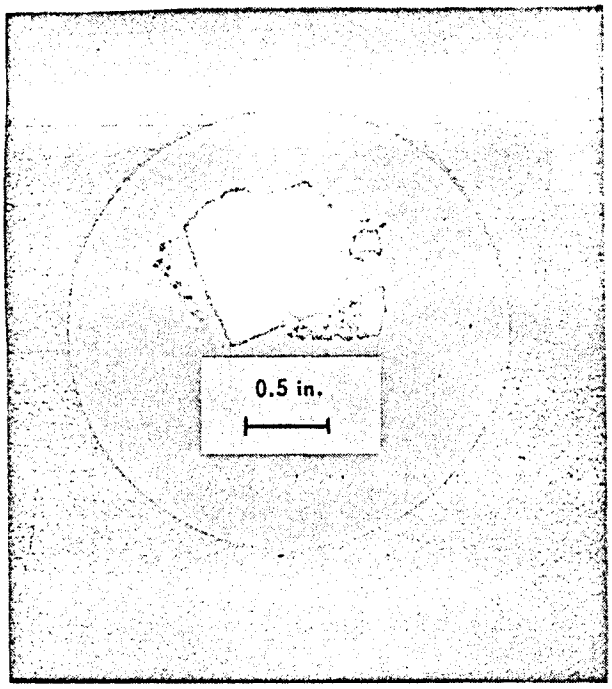

Figure 2

SAMPLE OF FORMULATION 5 (Table 9)
AFTER A 23-HR. IMMERSION IN BENZENE AT 30°C

Two batches of crystalline boron filled hydrolysed vinyl ester copolymer elastomer were prepared which contained tolylene diisocyanate dimer (TDID) as the curing agent. The sample to which the filler was added after the catalyst (A) would not cure while that to which the filler was added before the catalyst cured satisfactory. The formulation was as follows:

Hydrolysed vinyl ester copolymer elastomer (VCD 43.2/1.03)	8.0 gm
Witco cosmetic grade zinc stearate	0.16 gm
Tolylene diisocyanate dimer	0.116 gm
Crystalline boron powder	22.713 gm

cured @ 255°F for 50 minutes.

Freshly milled one inch in diameter uncured samples flowed readily when placed in a compression creep apparatus under 1000 pound load. Deflections versus time as shown. Flow was greater in B sample than in A.

	A (TDID added 1st)	B (Boron added first)
	Minutes under 1000 lbs. load	
(0)	80.3	81.0
(30)	64.0	53.6
(60)	62.3	51.0
wt. sample -	1.6443	1.6240

When similar samples were pressed in a compression cage with a pressure of 5000 pounds as suggested by Lawrence Radiation Laboratory, there was essentially no flow after 15 minute.

Samples of each batch milled to about 80 mils thickness were cut to approximately 5" x 1/2" and cured under 14000 pounds pressure in a hot die at 255°F for 50 minutes. The mold was cooled to about 125°F before removal of the sample.

The density of the cured B sample was 1.736 g/cc; the theoretical density calculated from the density of the unfilled elastomer was 1.793 g/cc. The hardness of the cured B sample was 93 on the Shore A scale. The appearance of the molding was good. The cured 5" sample was 0.015 inches longer than the die from which it was molded.

Tolylene diisocyanate dimer (TDID) was incorporated into potassium bromide pellets and heated under various conditions of time and temperature. Infrared spectra of the pellets were then obtained to determine the extent ot decomposition. Results are listed in Table 10.

None of the spectra obtained resembled that of 2,4-tolylene diisocyanate.

To more closely approximate the reaction conditions between TDID and hydroxylated polymers a sample of TDID was heated at 130°C for six hours in the presence of an excess of n-hexanol to determine whether the TDID would depolymerize under these conditions. The only carbamate isolated from this reaction was that of the monomer indicating that depolymerization had occurred. However, when the experiment was repeated using molar ratios of n-hexanol to TDID of 1:1, 1:2, and 1:4, other carbamates were obtained indicating that completee depolymerization did not occur under these conditions.

TABLE 10

EFFECT OF TEMPERATURE ON THE DECOMPOSITION OF TOLYLENE DIISOCYANATE DIMER

Temperature °C	Time of Heating Hours	Extent of Decomposition
90	24	None
100	4	None
105	4	None
115	1	None
	2	Very Slight
	4	Very Slight
120	3	Slight
125	1/2	Slight
135	1	Extensive
145	1	Extensive

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