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PREPARATION AND PROPERTIES OF
BLOCKED DIISOCYANATES

Final Report

B. G. Parker, Project Leader

Project Team:
M. F. Radford

Published March 1978

Prepared for the United States Department of Energy
Under Contract Number EY-76-C-04-0613.

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Department 814

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Prepared by B. G. Parker, D/814

The preparation and scaleup for production of phenol blocked 4,4'-methylenebis(phenylisocyanate) (Hylene MP) (Du Pont Corporation) was investigated. Hylene MP is a single source material used as the curing agent for some filled VCE (ethylene/vinyl acetate/vinyl alcohol) product.

In addition to developing a backup capability for Hylene MP, other blocked isocyanates were synthesized. Several physical and chemical properties of reagents suitable for use as blocking agents and the resulting blocked diisocyanates prepared from these materials are presented.

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CONTENTS

Section	Page
SUMMARY.	5
DISCUSSION	6
SCOPE AND PURPOSE.	6
ACTIVITY	6
<u>Preparation of Blocked Isocyanates</u>	6
<u>Determination of the Thermal Dissociation</u> <u>Temperature.</u>	7
<u>Interpretation of Data</u>	10
<u>Scaleup of Phenol Blocked MDI.</u>	17
ACCOMPLISHMENTS.	17
FUTURE WORK.	17
REFERENCES	20
DISTRIBUTION	21

ILLUSTRATIONS

Figure		Page
1	Differential Scanning Calorimetry Thermogram of Phenol/MDI Adduct	10
2	Infrared Transmittance and Millivolts Versus Time.	11
3	Infrared Transmittance Versus Temperature at Fixed Wave Number	12
4	Formation of Isocyanate Band in Infrared Spectra.	13
5	Infrared Spectrum of Hylene MP	18
6	Infrared Spectrum of Bendix Phenol Blocked MDI.	18

TABLES

Number		Page
1	Chemical Properties of Compounds Used to Synthesize Blocked 4,4'-methylenebis- (phenylisocyanate)	8
2	Melting Points of Blocked 4,4'- methylenebis(phenylisocyanate)	9
3	Dissociation Temperatures of Blocked 4,4'- methylenebis(phenylisocyanate)	14

SUMMARY

Blocked isocyanates (ASTM Type III Urethanes) are materials which contain no free isocyanates at room temperature and are relatively inert. At elevated temperatures the blocking agent is released and these compounds behave like conventional isocyanates. The blocking agent can be any compound containing active hydrogens such as phenols, oximes, mercaptans, secondary amines, imides, 1,3-dicarbonyl compounds, hydrogen cyanide or alcohols.¹

The dissociation of N-monosubstituted urethane has been shown to proceed through dissociation to give the free isocyanate.² This reaction is shown in the following equation:

The preparation of diphenyl-4,4'-methylenebis(phenylcarbamate) (Hylene MP) (Du Pont Corporation) is described by Iwakura and Hayashi.³ This blocked diisocyanate was prepared by refluxing a 2 to 1 molar ratio of phenol with 4,4'-methylenebis(phenylisocyanate)(MDI) in toluene for 2 hours. The product was then recrystallized from hot ethanol and gave a melting point of 143° to 145°C.

The preparation and scaleup of production quantities of Hylene MP was investigated. This is a single source material used as a curing agent for filled VCE (ethylene/vinyl acetate/vinyl alcohol) parts.

Additional blocking agents such as halogen substituted phenols, cresols, oximes, and alcohols were reacted with MDI to yield various adducts. The dissociation temperatures of these blocked isocyanates were determined using infrared spectroscopy and differential scanning calorimetry. A mechanism was proposed which helps explain the dissociation reaction.

DISCUSSION

SCOPE AND PURPOSE

Hylene MP, used as the curing agent for filled VCE parts, is only available from a single source. This project was undertaken to develop the capability of producing and supplying a chemical equivalent to Hylene MP.

In addition to developing a backup source for Hylene MP, the syntheses of alternate blocked isocyanates which have potentially improved processing characteristics were investigated.

ACTIVITY

Preparation of Blocked Isocyanates

The blocking agents used were dried over 4A Linde molecular sieves (Union Carbide Corporation) to remove any water present in the materials. The 4,4'-methylenebis(phenylisocyanate) (MDI) was purified by first melting and then filtering the diisocyanate prior to use to remove any urea type reaction products or dimers present.

In preparing the blocked isocyanates, a very slight excess of blocking agent was used to ensure complete reaction of the isocyanate groups. As a typical reaction, 50 g of purified MDI was dissolved in 100 ml of toluene in a 500 ml resin reactor equipped with a thermometer, a mechanical stirrer, and a nitrogen inlet. The reactor was purged with dry nitrogen and heated to 60°C while stirring. The dried phenol (40 g) dissolved in 100 ml of toluene was slowly added to the reactor.

The reaction temperature was kept at or below 60°C by controlling the rate of addition of the phenol. After all of the phenol was added, heating was continued until no isocyanate was present as determined by infrared analysis. The reaction mixture was then allowed to cool to room temperature and the product was collected by filtration. The phenol blocked isocyanate was washed with toluene and then recrystallized from hot methyl ethyl ketone (MEK).

The procedure yielded white crystals having a melting point of 198°C compared to a melting point of 201°C for Hylene MP. A literature reference listed a melting point of 143° to 145°C for the phenol blocked MDI recrystallized from hot ethanol.³ It was determined by gel permeation chromatography, however, recrystallizing of the blocked MDI from hot ethanol yielded a less pure material. The purity of one batch of the product went from 87

to 45 percent after recrystallization from hot ethanol. The impurity was identified using mass spectroscopy to be an ethanol/MDI adduct.

Recrystallization of the phenol blocked MDI from hot MEK yielded the product with the greatest purity. It was found the phenol must be thoroughly dried and the MDI purified before use in order to prevent the formation of urea compounds which are difficult to separate by a recrystallization process.

In addition to using phenol as a blocking agent, various substituted phenols and other active hydrogen compounds which might exhibit improved processibility were also investigated (Table 1).⁴

The same general procedure previously described was used in preparing the additional blocked isocyanates. In some cases, when the reaction was found to proceed very slowly a small amount of stannous octoate was added in order to catalyze the reaction.

Melting point determinations were performed on all the blocked isocyanates using a Fisher-Johns melting point apparatus. A list of melting points for these prepared compounds is given in Table 2.

Determination of the Thermal Dissociation Temperature

Two methods were employed in the determination of the thermal dissociation temperature of the blocked diisocyanates. The methods were infrared spectroscopy (IR) and differential scanning calorimetry (DSC). Using the DSC method, a 9 mg sample was heated at a programmed temperature rise of 10°C/minute in a nitrogen atmosphere with a Du Pont 990 DSC thermal analyzer. A typical DSC thermogram for an unblocking reaction is shown in Figure 1.

Point B is normally chosen as the transition temperature on DSC curves, however, Point A, the first deviation from the tangent, was found to be in better agreement with the IR method. All dissociation temperatures listed in Table 2 under DSC method were evaluated in this manner. The DSC method proved to be more difficult to interpret and less reliable than the IR method.

For the IR method, a Perkin-Elmer Corporation Model 457 grating infrared spectrophotometer equipped with a Model 124 hot cell attachment was used. One channel of a 2-pen recorder was connected to the external output of the spectrophotometer while the other channel was connected to a compensated chromel-alumel thermocouple attached to the hot cell equipment. Samples were prepared by first mixing the adduct thoroughly in Nujol (Plogh Incorporated) or VCE. The mixture was then transferred to a potassium bromide (KBr) window and placed in the hot cell.

Table 1. Chemical Properties of Compounds Used to Synthesize Blocked 4,4'-methylenebis-(phenylisocyanate)

Blocking Agent	Specific Gravity	Boiling Point, (°C)	Melting Point, (°C)
4-acetamidophenol (p-hydroxy-acetanilide)	1.293		169-171
acetone oxime	0.911	134.8 (728 mm)	61
p-bromophenol	1.84	238	66.4
2-butanoneoxime	0.923	152-153	-29.5
BHT	0.894	265 (760 mm) 136 (10 mm)	71
1-butanol	0.81	117	-89.5
2-butanol	0.806	99.5	-114.7
t-butanol	0.789	82.2	25.5
m-cresol	1.034	202.2	11.5
o-cresol	1.027	191	30.9
p-cresol	1.019	202	34.8
m-chlorophenol	1.268	214	33
o-chlorophenol	1.263	174.9	9.0
p-chlorophenol	1.265	219.8	43.2-43.7
E-caprolactam		139 (12 mm)	69-71
p-fluorophenol		185	48
phenol	1.072	181.75 (760 mm) 70.86 (10 mm)	43

Table 2. Melting Points of Blocked
4,4'-methylenebis-
(phenylisocyanate)

Blocking Agent	MDI/Adduct (°C)
4-acetamidophenol	128-130
acetone oxime	128-130
p-bromophenol	205-224
2-butanone oxime	liquid at RT
BHT	187-195
1-butanol	102-105
2-butanol	58-60
tert-butanol	186-187
E-caprolactam	180-184
m-chlorophenol	160
p-chlorophenol	160-163
o-chlorophenol	156-160
m-cresol	158
p-cresol	170
o-cresol	194-197
p-fluorophenol	186-191
phenol:	201 Hylene MP 198 Bendix

The infrared spectrophotometer was locked in at 2260 cm^{-1} and the hot cell was then heated at an approximate rate of $5^{\circ}\text{C}/\text{minute}$. The result of a typical temperature scan is shown in Figure 2. Converting the thermocouple reading to degrees centigrade and replotting gives a more easily interpreted curve (Figure 3) showing the temperature at which the adduct unblocks.

At the unblocking temperature there is a rapid change in absorbance caused by the formation of the isocyanate group. This proved to be a very sensitive and highly reliable method of evaluating the unblocking temperature. Periodic scans of the region from 2400 cm^{-1} to 2200 cm^{-1} were made at temperatures above and below

Figure 1. Differential Scanning Calorimetry Thermogram of Phenol/MDI Adduct

the observed unblocking temperature as shown in Figure 4. This was done to ensure the isocyanate group was indeed forming and not just a change in cell path length due to the heating of the cell. Table 3 shows the results of both DSC and IR methods.

Interpretation of Data

As evident from the data in Table 3, the dissociation of blocked isocyanates is affected by both steric and electronic effects. Griffin and Willwerth suggested that the ease with which a blocked isocyanate

will dissociate is dependent upon the strength of the bond between Z and the carbonyl group.⁵ They further stated, the greater the

Figure 2. Infrared Transmittance and Millivolts Versus Time

change difference between the carbonyl carbon and Z, the greater the expected strength, and therefore, the higher the unblocking temperature. To support this mechanism they observed that electron withdrawing substituents such as chlorine in the ortho or para position on the phenol ring result in a lower unblocking temperature. They reasoned that the electron withdrawing group was reducing the charge on the ether oxygen resulting in a lower charge difference between it and the slightly positive carbonyl carbon.

Figure 3. Infrared Transmittance Versus Temperature at Fixed Wave Number

This lowering of the unblocking temperature is not limited to electron withdrawing substituents on phenol since the cresols, as shown in Table 3, also exhibit a lower unblocking temperature. From the work of Griffin and Willwerth, one would expect that electron donating groups on phenol, as in the case of the cresols, would result in a higher unblocking temperature, however, this is not the case.

The following is a proposed alternate mechanism showing the effects of substituents on the phenol ring:

Figure 4. Formation of Isocyanate Band in Infrared Spectra

Table 3. Dissociation Temperatures of Blocked 4,4'-
methylenebis(phenylisocyanate)

Blocking Agent	Detection Using IR		Detection Using DSC	
	With Nujol (°C)	With VCE (°C)	Neat (°C)	With VCE (°C)
4,-acetamidophenol	97	116	120	90
acetone oxime	112	114	128	110
p-bromophenol	161	138	160	150
2-butanone oxime	119	115	120	115
BHT	188	148	186	160
1-butanol	183	184	216	202
2-butanol	177	183	208	186
tert-butanol	161	137	176	132
E-caprolactam	162	147	171	142
m-chlorophenol	148	70	152	122
o-chlorophenol	134	89	138	96
p-chlorophenol	135	107	196	162
m-cresol	133	115	138	135
o-cresol	101	85	134	120
p-cresol	150	138	160	168
p-fluorophenol	65	60	175	138
phenol: Bendix	178	158	186	151
Hylene MP	181	162	183	150

Any group such as a halogen or an alkyl group in the ortho or para position would result in an increased negative charge on the ether oxygen. This would result in a lowering of the unblocking temperature by internal abstraction of the amido hydrogen.

At first glance a possible anomaly to this mechanism would be the 2,6-ditertiarybutyl-p-cresol (BHT). The BHT would be expected to have an even lower unblocking temperature than ortho or para cresol since the BHT has alkyl groups in both ortho positions and the para position. However, this is not the case. The reason is probably due to steric hinderance of the two bulky tertiary butyl groups in the ortho positions. The two ortho side groups on BHT block the abstraction of the amido hydrogen resulting in an increased dissociation temperature. However, when the BHT/MDI adduct is mixed in VCE, the unblocking temperature is again lower than the phenol/MDI adduct.

In most cases the unblocking temperature is lower in the VCE than in the Nujol. This is probably due to the reactive OH groups in the VCE which are not present in the Nujol. The following shows the chemical structure of VCE:

The following proposed mechanisms illustrate the possible catalytic effect that an active hydrogen group, in this case -OH, can have on the dissociation of a blocked isocyanate:

These mechanisms help explain the lower unblocking temperatures found in VCE and why active hydrogen compounds such as ethanol cannot be used as a recrystallization solvent.

In addition to the phenols, other active hydrogen materials were evaluated as blocking agents. Aliphatic alcohols, such as butanol, unblocked in the order, t-butanol (lowest), then 2-butanol, and finally 1-butanol (highest). This again suggests that groups which induce a slight negative charge on the oxygen result in a lower unblocking temperature for the blocked isocyanate.

Unlike the toluene diisocyanate/t-butanol adduct reported to thermally decompose giving isobutylene, carbon dioxide, and toluene diamine (no isocyanate),⁵ the MDI/t-butanol adduct did yield at least some free isocyanate upon heating as seen in the IR results.

Only two of the various blocked isocyanates investigated had unblocking temperature in VCE in the same general area as did Hylene MP. These two blocking agents, BHT and 2-oxahexamethyleneimine, have higher boiling points than phenol and would prove harder to remove in the postcure operation used to free molded parts of the blocking agent.

Scaleup of Phenol Blocked MDI

The preparation of phenol blocked MDI was scaled from the 80 g laboratory batches to approximately 2 kg quantities using the following procedure. One kg of purified phenol dissolved in 1 liter of toluene was placed in a 4-liter reactor equipped with a nitrogen inlet, a reflux column, a thermometer, and an addition funnel. The reaction mixture was stirred with a magnetic stirring bar and heated to 60°C while being purged with dry nitrogen. A mixture of 800 g of dried phenol in 800 ml of toluene was placed in an addition funnel and added to the reactor over a 1-hour period. Heating was continued until all isocyanate had disappeared (loss of IR adsorption at 2260 cm^{-1}). The reactor was then allowed to cool and the product collected by filtration.

This material was washed with fresh toluene and then recrystallized from hot MEK. The purified phenol blocked MDI had a melting point of 198°C and a purity of greater than 99 percent by GPC analysis. The amine equivalent of both the Hylene MP and the Bendix material was determined by refluxing in a dibutylamine/toluene solution. The theoretical amine equivalent for the phenol-blocked MDI is 219. Hylene MP had an amine equivalent of 217 and the Bendix product had an amine equivalent of 218.2. The two materials, Hylene MP and the Bendix phenol blocked MDI, had identical IR spectras (Figures 5 and 6).

ACCOMPLISHMENTS

The preparation of phenol blocked MDI was scaled up and the capability to produce sufficient quantities to support production was developed. The purity of the material was identical to Hylene MP and could be used interchangeably without any change in processing procedures. As a result of this work, the capability has been developed to produce material to support production.

Additional blocked/MDI adducts were synthesized and some of their properties evaluated. None of the adducts prepared which had dissociation temperatures in the range of Hylene MP had a higher volatility than phenol.

A mechanism was proposed which would help explain the unblocking reaction and the role VCE has in lowering the dissociation temperature.

FUTURE WORK

Several of the blocking agents investigated have a higher volatility than phenol, however the unblocking temperatures of these

Figure 5. Infrared Spectrum of Hylene MP

Figure 6. Infrared Spectrum of Bendix Phenol Blocked MDI

adducts were lower than the phenol/MDI adduct. Although not within the scope of this investigation, actual molded parts should be prepared using these adducts, in order to evaluate their processibility at various molding temperatures and pressures.

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PLASTICS: Curing Agents

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