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SYNTHESIS OF
TOLUENE
DIISOCYANATE DIMER
(TDID)

BDX-613-506

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KANSAS CITY DIVISION

KANSAS CITY, MISSOURI

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ABSTRACT

The procedure developed at Bendix Kansas City for the synthesis of a toluene diisocyanate dimer (TDID) is discussed. This development provides a second source for a curing agent formerly available only from a non-domestic source.

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SUMMARY

A method for synthesizing toluene diisocyanate dimer (TDID), a curing catalyst required for the manufacture of the Rattan and Caribou filled elastomer parts used in the Delta Program, was developed in the Polymer Laboratory at Bendix Kansas City. The TDID will be produced in the required quantities in the Bendix Pilot Plant. This production capability will provide a second source for the TDID which was formerly available only from a foreign supplier (Farben Fabriken Bayer AG, Leverkusen, Germany) as Desmodur TT.¹

The basic reaction for this synthesis involves the dimerization of toluene diisocyanate (TDI) in dry toluene using pyridine as a catalyst.

Information available in the literature on the dissociation theory of the TDID was useful in the development of a procedure for analyzing the purity of the TDID compound. The procedure is based on the dissociation of the dimer into monomeric free isocyanate groups, the number of which constitute the degree (percent) of purity.

Analysis of a scaled-up quantity of the TDID which had been produced in the Bendix Pilot Plant confirmed the product to be chemically and physically comparable to the Desmodur TT. The purity of the Bendix TDID was found to be 97.6 percent.

Qualitative analysis by Soxhlet extraction was used to identify free monomeric TDI as part of the impurity present in the TDID.

Material Standard 4612102 now designates the Bendix Pilot Plant as a qualified source. On this basis the Pilot Plant will supply the material for production.

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DISCUSSION

SCOPE AND PURPOSE

The purpose of this activity was to develop the capability at Bendix Kansas City to synthesize toluene diisocyanate dimer (TDID), the curing agent for two different filled elastomer parts used in current production programs. Prior to this development, the TDID was available only from a German supplier (Bayer) as Desmodur TT.

PRIOR WORK

Prior work in 1966 at Bendix Kansas City resulted in the development of a crude TDID. Because the purity of the dimer was below that required for production, the work was terminated.

ACTIVITY

The literature on the basic chemical characteristics of isocyanates was surveyed to provide background information for the synthesis of a TDID compound. The survey encompassed the chemistry of isocyanates, the reaction of dimerization, and the mechanism of pyridine catalysis. The information obtained was used to establish an experimental program which began with the chemical synthesis of TDID.

The basic reaction (Equation 1) involves the dimerization of toluene diisocyanate in dry toluene using pyridine as a catalyst.

Equation 1.

The product formed is known as a uretidine dione or, more commonly, as the toluene diisocyanate dimer (TDID).

The dissociation of the dimer to the toluene diisocyanate monomer occurs only at elevated temperatures.³ This dissociation principle was useful in determining the percent purity of TDID. Since the temperature at which the dimer dissociates is approximately 170°C, boiling ortho-dichlorobenzene (boiling point 180°C) was chosen as the solvent for dissolving and dissociating the dimer.

The basic method used to determine the free monomeric isocyanate groups involved an excess amount of dibutylamine in the dissociating solvent. The amount of dibutylamine which does not selectively react with all free isocyanate groups is determined by back-titration with standardized hydrochloric acid, as shown by the reaction in Equation 2.

Equation 2.

A procedure documented at Lawrence Radiation Laboratories by Mr. Robert Lim⁴ was also considered for this type of analysis, but reproducible results employing this method were unobtainable in the Bendix Polymer Laboratory. A combination of Mr. Lim's procedure and another method specified in ASTM D-1638 was used to develop a procedure suitable for determining the purity of the dimer (percentage of monomeric free isocyanate groups

Figure 1. Comparison by Sectional Differential Scanning Calorimetry of Desmodur TT and Bendix TDID Compounds

Table 1. Comparison of Results Obtained From Purity Analysis of Desmodur TT and BKC TDID Compounds

Product	Crystalline Color*	Melting Point** (°C)	Assay*** (Percent)
Desmodur TT	White	161 to 162	97.79
TDID Produced in Bendix Polymer Lab	White	161.5 to 162	99.99
TDID Produced at Pilot Plant	First Batch	160.5 to 162	96.52
	Second Batch	162.5 to 163	97.04
	Third Batch	163 to 163.5	97.56
Desmodur TT Received October, 1970	White	161.5 to 162	96.69
<p>*Crystalline color quality determined by visual analysis.</p> <p>**Melting Point determined with Fisher-Johns Melting Point Appartus.</p> <p>***Assay performed by procedure given in Appendix A (developed in Bendix Polymer Laboratory).</p>			

present in the dimer). A typical example of the analytical procedure developed at Bendix is presented in Appendix A.

This assay proved beneficial in monitoring the percent purity of the dimer products which resulted from various reaction conditions. Based on the information obtained on the crystalline quality and melting point of the dimer, a procedure was developed which yielded a TDID meeting the requirements of Material Standard 4612102 and exceeding the quality of the commercially available Desmodur TT compound. An example of the preparation technique is summarized in Appendix B.

The dimer was successfully synthesized in the Bendix Polymer Laboratory up to quantities of three liters. Since the Pilot Plant will be responsible for synthesizing monthly quantities of from 3 to 4 pounds of TDID to satisfy production requirements at Bendix, an investigation was made to verify such a capability. Although the initial attempts at the Pilot Plant to scale-up the dimer resulted in low yields and relatively impure end products, the use of an 18-liter glass reaction vessel finally facilitated the manufacture of 3 to 5 pound quantities of the material. Refinements of the experimental techniques and the use of higher quality starting materials permitted production in the Pilot Plant of a dimer which consistently fulfilled the requirement specified in Material Standard 4612102 for a TDID having a purity of 97 percent minimum.

Given in Table 1 is a comparison of the purity analyses performed on the commercially prepared Desmodur TT, the material produced in the Bendix Polymer Laboratory, and the Pilot Plant products.

The three compounds were also analyzed by differential scanning calorimetry (DSC). The curves shown in Figure 1 indicate the transition which each compound undergoes during its melting endotherm. The area between the melting point curve and the tangent lines indicates the relative amount of impurity in each dimer.

Qualitative Soxhlet extraction was used to characterize the 2 to 3 percent impurity present in the TDID. The extracting solvent was absolute methyl alcohol.

The Pilot Plant material and the Desmodur TT were subjected to identical conditions, and a finely divided white powder was extracted in both instances. Infrared spectroscopy correlations indicated the material extracted from both products to be a urethane. This finding was confirmed by a comparison of the extract with the model compound formed from the reaction of TDI and methyl alcohol⁵ (Equation 3).

Equation 3.

Compared in Figure 2 are the sectional infrared spectra of the extracted materials showing their respective urethane carbonyl absorptions at 5.88 microns; the urethane carbonyl absorption of the TDI-methanol model compound; and the absorption of the uretidine dione ring structure of the TDID compound. As shown by the figure, no uretidine dione ring structure (absorption at 5.61 microns) is present in the extracted materials. This fact indicates that the urethane formed from the reaction between the TDID and the methanol (Equation 4) is insoluble in the methanol extracting solvent and, therefore, does not appear as part of the extracted material. On the other hand, the model urethane compound (Equation 3) appears to be structurally identical to the extracted material. The explanation for this is that the free monomeric TDI in Desmodur TT and Bendix TDID reacted with the methyl alcohol to form the urethane.

Equation 4.

It follows then that free monomeric toluene diisocyanate accounts for part of the impurity in the TDI dimer.

The results of the purity assay revealed the impurity in the TDID to be at least 2 to 3 percent (determined by TDID converting to monomeric TDI by dissociation). While the free TDI, as previously stated, is present in the dimer as a part of the impurity, no qualitative or quantitative method of identifying the remaining impurity has been successfully developed. That is, if the only impurity were TDI, the dissociated dimer would be

Figure 2. Sectional Infrared Spectra Comparison of TDID-Methanol Extracts, TDI-Methanol Model Compound, and TDID

theoretically analyzed by the prescribed method as 100 percent pure. However, the 2 to 3 percent impurity indicated by this method suggests that a portion of the impurity is of a nature different from TDI. The literature on isocyanate reactions emphasizes that the reaction between an isocyanate and water form a urea and biuret,⁶ both of which could explain the identity of the impurity in the TDID (Equation 5).

Equation 5.

The commercial Desmodur TT and the Bendix TDID were compared to determine the processability of each. Processing consisted of milling the catalyst into filled and unfilled ethylene/vinyl acetate/vinyl alcohol terpolymer (VCE). The properties evaluated (Table 2) were the coefficient of thermal expansion, weight change after toluene swell, tensile strength, and ultimate elongation.⁷

Table 2. TDID Test Results on Filled and Unfilled (VCE) Polymers

Test	Filled (VCE) Polymer		Unfilled (VCE) Polymer	
	Bendix TDID	Desmodur TT	Bendix TDID	Desmodur TT
Thermal Expansion, In./In. (°F); Two-point test, 30 to 130°F	22.4 x 10 ⁻⁶	25.7 x 10 ⁻⁶	146.3 x 10 ⁻⁶	149 x 10 ⁻⁶
Density (g/cc)	14.45	15.22	1.009	1.006
Toluene Swell (Percent Weight Increase)	2.43 2.46 <u>2.40</u>	2.16 2.18 <u>2.18</u>	150.8 150.2 <u>148.0</u>	150.8 153.2 <u>153.1</u>
Averages	2.43	2.18	149.7	152.4
Density	14.09 <u>14.09</u>	14.63 <u>14.64</u>	1.013 <u>1.013</u>	1.013 <u>1.012</u>
Averages	14.09	14.64	1.013	1.013

Table 2 is continued on next page.

Table 2 Continued. TDID Test Results on Filled and Unfilled (VCE) Polymers

Test	Filled (VCE) Polymer		Unfilled (VCE) Polymer	
	Bendix TDID	Desmodur TT	Bendix TDID	Desmodur TT
Tensile Strength (psi), Die C	1669	1670	423	606
	1685	1716	448	464
	1616	1651	463	442
	1685	1702	476	445
	<u>1603</u>	<u>1742</u>	<u>463</u>	<u>370</u>
Averages	1652	1692	455	465
Ultimate Elongation (Percent)	2.20	1.83	60	70
	2.60	2.91	60	70
	2.20	2.02	60	70
	2.23	2.67	60	70
	<u>2.62</u>	<u>3.14</u>	<u>60</u>	<u>50</u>
Averages	2.37	2.51	60	66

A comparison of the results given in Table 2 for both the filled and unfilled polymers shows no significant differences between the two products.

ACCOMPLISHMENTS

A toluene diisocyanate dimer was successfully synthesized by the dimerization of TDI in dry toluene using pyridine as a catalyst. It has been proposed that the Pilot Plant produce the TDID by the procedure developed at Bendix Kansas City.⁸ Such production will supply a TDID comparable to the commercial Desmodur TT. The product will be of acceptable purity and meet the requirements of Material Specification 4612102.

By a Soxhlet extraction procedure, it was possible to confirm that free monomeric toluene diisocyanate is a part of the impurity in the TDID compound.

FUTURE WORK

No further development work is anticipated for this project. Production of the TDID will be undertaken.

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Appendix A

METHOD FOR DETERMINING TOTAL ISOCYANATE IN TOLUENE DIISOCYANATE DIMER

PROCEDURE

Using a 250 ml round bottom flask:

1. Weigh out sample to nearest 0.1 mg.
2. Add 40.0 ml of ortho-dichlorobenzene.
3. Pipette exactly 20.0 ml of 2 N dibutylamine and allow pipette to drain exactly 30 seconds.
4. Heat the solution under reflux at 180°C for 90 minutes.
5. Add 100.0 ml of absolute methyl alcohol.
6. Titrate with 1 N HCl to a 5.4 pH end point.
7. Run a blank determination by omitting Step 1.

CALCULATION

$$\text{Assay (Percent)} = \frac{(B-A) (N) (E)}{(W)} \times 1000$$

where

A = Milliliters of HCl required for titration of sample;

B = Milliliters of HCl required for titration of blank;

N = Normality of HCl;

E = Equivalent weight of toluene diisocyanate (87.08); and

W = Milligrams of sample used.

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Appendix B

SYNTHESIS FORMULATION FOR TOLUENE DIISOCYANATE DIMER

<u>Materials</u>	<u>Parts by Weight (Percent)</u>
Toluene diisocyanate	80.64
CP Grade Dry Toluene	16.13
Reagent Grade Pyridine	3.23

PROCEDURE

1. Into a reaction vessel fitted with a stirring mechanism and reflux condenser, charge toluene diisocyanate and dry toluene.

NOTE: Toluene is stored for 24 hours over molecular sieves (a drying agent).

2. Purge reaction vessel with blanket of dry nitrogen.
3. Add pyridine drop-wise to the stirring mixture.
4. Stir for approximately 5 hours.
5. Stop agitation and allow crystallization to proceed until complete.
6. Filter product from mother liquor and wash up to four times with dry toluene.
7. Collect crystals and place in vacuum oven at 100°F for approximately 24 hours.
8. Crush crystals into fine powder and place in amber bottles flushed with dry nitrogen.