

Polyisocyanurate Adhesives

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Synopsis

The preparation of polyisocyanurates by the polytrimerization of isocyanate prepolymers in the presence of organometallic catalysts leads to an increase in adhesive strength at 400°F. for bonding aluminum-to-aluminum. The trimerization efficiency of several other catalysts is briefly described.

INTRODUCTION

In an attempt to modify the polyurethane adhesives,¹ based on polyether polyols, to give improved tensile shear strength at 400°F. it was found that polytrimerization to polyisocyanurates was an effective method.

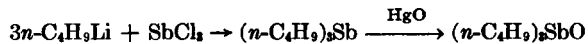
An earlier investigation of polyisocyanurate adhesives was reported by Kansen,² who mentioned the work of Gilman et al.³ under a government contract.

EXPERIMENTAL

The preparation of prepolymers is similar to that described for the polyurethanes in an earlier investigation.¹ A few model preparations are given below.

The trimerization agent used in the initial phase of this investigation was a calcium naphthenate solution obtained from the Harshaw Chemical Co. and abbreviated as Ca-liq.

Tri-*n*-Butylantimony Oxide



n-Butyllithium (15% in hexane, 0.3*m*) was added slowly to antimony trichloride (0.1*m*) in 100 ml. tetrahydrofuran at 5°C. and stirred for 1 hr. The liquid was decanted and kept cold while mercuric oxide (0.1*m*) was added with stirring, then 200 ml. ethanol was added and the solids were removed by filtration.⁴ Solvents were removed by water suction on a hot water bath. The product (40% yield) was a viscous liquid.

Preparation of Polyurethane Prepolymers (452-3-3)

A 500-ml. kettle equipped with stirrer, condenser, thermometer, and a 250-ml. dropping funnel was purged with nitrogen for 10 min. Toluene

diisocyanate (Du Pont, Hylene T, 0.4*m*, 69.6 g.) and 0.7 ml. benzoyl chloride were placed in the kettle and heated to 45°C. Polytetramethylene ether glycol (Quaker Oats, PTMEG 1000, M.W. 1103, 0.14*m*, 154.4 g.) and polyether PR 1000 (Dover Chemical, M.W. 588, 0.06*m*, 35.3 g.) were mixed together while warm and the uniform mixture was placed in the funnel and added dropwise during 2 hr., maintaining the pot temperature to 50–60°C. Stirring was continued for 1 hr. after final addition while the pot reached room temperature. 80 g. of the product and 12.2 g. toluene diisocyanate were mixed together in an atmosphere of nitrogen for 15 min. Per cent NCO calculated = 12.0.

Preparation of Polyurethane Prepolymer (452-5-3)

A 500-ml. kettle equipped with stirrer, condenser, thermometer, and a 250-ml. dropping funnel was purged with nitrogen for 10 min. Diphenylmethane diisocyanate (Nacconate 300, National Aniline, 0.20*m*, 50.0 g.) and 0.4 ml. benzoyl chloride were placed in the kettle and heated with stirring to 45°C. Polytetramethylene ether glycol (Quaker Oats PTMEG 1000, M.W. 1103, 0.07*m*, 77.2 g.) and polyether PR 1000 (Dover Chemical, M.W. 588, 0.03*m*, 17.6 g.) were mixed together while warm and the uniform mixture was placed in the funnel and added dropwise during 2 hr. maintaining the pot temperature at 50–60°C. Stirring was continued for 1 hr. after final addition while the pot reached room temperature. 40 g. of the product and 11.5 g. diphenylmethane diisocyanate were mixed together at 45°C. in an atmosphere of nitrogen for 15 min. Per cent NCO calculated = 12.0.

Preparation of Polyurethane Prepolymer (439-77-2)

A 500-ml. resin kettle equipped with stirrer, condenser, thermometer, and a 250-ml. dropping funnel purged with nitrogen for 10 min. Diphenylmethane diisocyanate (Nacconate 300, National Aniline, 0.24*m*, 60 g.) and 0.6 ml. *o*-chlorobenzoyl chloride were placed in the kettle and heated with stirring to 45°C. Polytetramethylene ether glycol (Quaker Oats PTMEG, M.W. 1103, 0.12*m*, 132 g.) was placed in the funnel and added dropwise during 2 hr. maintaining the pot temperature at 50–60°C. Stirring was continued for 1 hr. after final addition while the pot reached room temperature. 50 g. of the product and 2.1 g. toluene diisocyanate (Du Pont, Hylene T) were mixed together in an atmosphere of nitrogen for 15 min. Per cent NCO calculated = 7.0.

DISCUSSION

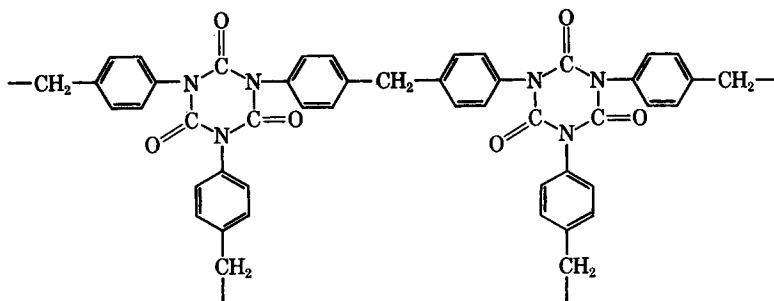
The polytrimerization of 4,4'-diphenylmethane diisocyanate by means of calcium naphthenate has yielded a novel adhesive showing good strength over the range of -320 to +400°F. (Sample 1, Table I.)

TABLE I
Physical Evaluation of Polyisocyanurate Adhesives

Sample No.	Composition	Tensile shear strength, psi ^a at °F. on aluminum				
		-453°	-320°	73°	250°	400°
1	1.0 g. diphenylmethane diisocyanate (DPMDI) + 7 drops 0.5% soln. of calcium naphthenate in petroleum ether (Harshaw)	1230	1260	1165	1510	804
2	452-5-3 ^b + DPMDI + Ca-liq. (0.3/2.7/3 drops)	—	1155	996	1030	812
3	452-5-3 + DPMDI + Ca-liq. (0.6/2.4 g/3 drops)	—	1650	1550	1380	1090
4	452-5-3 + DPMDI + Ca-liq. (0.9/2.1/3 drops)	—	1535	1330	971	833
5	452-5-3 + DPMDI + Ca-liq. (0.2/1.8/3 drops)	—	1935	857	871	624
6	452-5-3 + DPMDI + Ca-liq. (1.5/1.5/3 drops)	—	2490	1132	885	794
7	452-3-3 ^b + DPMDI + Ca-liq. (0.5/1.5/0.04 ml.)	—	1630	1530	1410	1410
8	439-77-2 ^b + DPMDI + Ca-liq. (0.5/2.5/0.05 ml.)	—	1460	1630	1450	1300

^a The samples were cured for 2 hr. at 165°C. An average of three determinations is shown.

^b See experimental section for a description of this polyurethane prepolymer.



The polyisocyanurates of Table I show a large improvement over the earlier reported¹ polyurethanes in adhesion at 400°F. The polyurethanes gave strength of 0-200 psi at 400°F. whereas the polyisocyanurates exhibit strength in the range of 800-1400 psi.

It was thought that incorporation of polyisocyanurate structure with the polyether prepolymers may likewise cause an increase in tensile shear strength at 250 and 400°F. Brittleness can not be the main problem in the polyisocyanurates since they still exhibit tensile shear strength of 1260 psi at -320°F. as seen in the polyisocyanurate formed from diphenylmethane diisocyanate (Sample 1, Table I).

Infrared spectra of Sample 6 (Table I) has shown that the isocyanurate group is present as evidenced by the strong absorption band at 7.10μ . The latter band is also found in triphenylisocyanurate.

Incorporation of the polyether group into the polyisocyanurates is shown in Table I, where the polyether prepolymer 452-5-3 is added in 10% intervals until 50% concentration has been reached. The low temperature strength shows an increasing trend as compared to the first sample of Table I which is the polyisocyanurate formed by the self-condensation of diphenylmethane diisocyanate. The only disadvantage at present is that the systems are cured at 165°C . Experiments to reduce the cure temperature indicated that a temperature of 165° is necessary to obtain the maximum adhesion using calcium naphthenate. As a result of this finding other catalysts were explored with the hope of being able to lower the cure temperature.

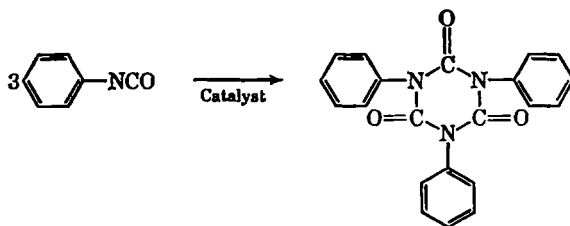


TABLE II
Trimerization of Phenylisocyanate ($0.005M$) by Various Catalysts ($0.0001M$)

Catalyst	Trimer observed ^a		
	23°C.	50°C.	M.p., °C. ^c
Triphenylarsine	N.R. ^b	N.R.	—
Bis(tri- <i>n</i> -butyl)oxide	24 hr.	7 hr.	275-81
Dibutyltin oxide	24 hr.	—	—
Tricresyl phosphate	N.R.	N.R.	—
Antimony chloride	N.R.	N.R.	—
Bismuth trioxide	N.R.	N.R.	—
Bismuth oxychloride	N.R.	N.R.	—
Triphenyltin hydroxide	N.R.	N.R.	—
Tributyltin chloride	N.R.	N.R.	—
Triethylamine	N.R.	N.R.	—
Calcium naphthenate	N.R.	24 hr.	270-75
Dibutyltin dilaurate	N.R.	7 hr.	—
Stannous octoate	24 hr.	5 hr.	275-81
Aluminum isopropylate	N.R.	24 hr.	275-81
Sodium methoxide	48 hr.	—	272-78
Calcium oxide	N.R.	N.R.	—
Tri- <i>n</i> -butylantimony oxide	15 min.	—	265-75

^a The times listed are the times for complete solidification of the triphenylisocyanate.

^b No reaction.

^c Literature value for the m.p. of triphenylisocyanurate is $280-281^\circ\text{C}$.

In a recently published paper⁵ it is reported that the trimerization of some isocyanates is effected at room temperature by organometallics such as tri-*n*-butylantimony and triisobutylarsenic oxides. The antimony compound was prepared and compared with other metal salts in their catalytic effect on phenylisocyanate trimerization shown above. Both tri-*n*-butylantimony oxide and stannous octoate produced a white, sticky, spongy material when added to a polyurethane prepolymer terminated with isocyanate groups; however, in the case of the faster catalyst, the pot-life of such a compound is too short for usefulness in adhesive applications. Adhesives similar to those of Table I were prepared using tri-*n*-butylantimony oxide and yielded adhesives of lower strength than those obtained with Ca-liq. Therefore, the room-temperature-formed polyisocyanurates appear to be of lower adhesive strength. The latter result may be due to the lower degree of polymerization and crosslinking at room temperature as compared to that obtained at 165°C.

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References

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Résumé

La préparation de polyisocyanurates par polytrimérisation de prépolymères isocyanés en présence de catalyseurs organométalliques permet d'obtenir un accroissement de la force d'adhésion à 400°F. pour le lien aluminium-aluminium. L'efficacité de trimérisation de nombreux autres catalyseurs est brièvement discutée.

Zusammenfassung

Die Darstellung von Polyisocyanuraten durch Polytrimerisation von Isocyanatpräpolymeren in Gegenwart metallorganischer Katalysatoren führt zu einer Zunahme der Klebefestigkeit bei der Verklebung von Aluminium an Aluminium bei 400°F. Die Wirksamkeit einiger anderer Katalysatoren bei der Trimerisierung wird kurz beschrieben.

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