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(72) Inventors YUTAKA MATSUI and JUGO GOTO

(54) A METHOD FOR PRODUCING ISOCYANATE TRIMERS

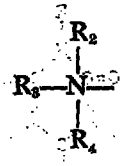
(71) We, TAKEDA CHEMICAL INDUSTRIES LIMITED, a Company organised under the Laws of Japan, of 27, Doshomachi 2-chome, Higashi-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for producing isocyanate trimers.

The isocyanate trimer is useful as a starting material for the preparation of paints, coating agents, adhesive agents, elastomers and plastic. It has been proposed to trimerize an isocyanate compound in the presence of a catalyst to produce the corresponding isocyanate trimer, and hitherto, various kinds of catalyst have been proposed. However, these previously proposed catalysts have low catalytic activity and therefore, must be used in a large quantity. Moreover, it takes rather a long period of time to complete the trimerization.

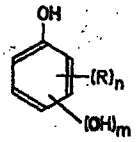
According to the invention there is provided a method for producing isocyanate trimers or elastomers in which the repeating units are cross-linked trimers comprising trimerizing an isocyanate compound in the presence of a catalyst, said catalyst comprising:

A) a quaternary ammonium hydroxide of the general formula Y — R_1 OH .....(1) in which Y may be a pyridinium radical or



R_1, R_2, R_3 and R_4 may be the same or different and represent an alkyl radical having from 1 to 6 carbon atoms, a hydroxy alkyl radical having from 1 to 6 carbon atoms, a cycloalkyl radical having — 5 or 6 carbon atoms, a benzyl radical or a phenyl radical and,

B) a phenol of the general formula



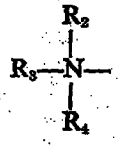
.....(2)

in which R represents a halogen, methyl or amino radical n is 0 or an integer of from 1 to 3 and m is 0 or 1 and when m is 1 the two OH groups occupy meta and para positions in the benzene ring, or an oxime having from 2 to 6 carbon atoms, or methanol.

The invention also provides a catalyst composition for trimerization of an isocyanate compound, comprising 1 part by weight of quaternary ammonium hydroxide of the general formula:

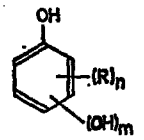
$$Y—R_1OH \qquad .....(I)$$

in which Y may be a pyridinium radical or



R_1, R_2, R_3 and R_4 may be the same or different and represent an alkyl radical having from 1 to 6 carbon atoms, a hydroxy alkyl radical having from 1 to 6 carbon atoms, a cycloalkyl radical having 5 or 6 carbon atoms, a benzyl

radical or phenyl radical and from 5 to 100 parts by weight of a phenol of the formula:



.....(II)

in which R represents a halogen, methyl or amino radical n is 0 or integer of from 1 to 3, m is 0 or 1, and when m is 1 the two OH groups occupy meta or para positions on the benzene ring; or an oxime of 2 to 6 carbon atoms or methanol.

In the aforementioned general formula (I) the alkyl radical may be for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, 3-methyl pentyl, 3,3-dimethylbutyl or n-hexyl; the cycloalkyl radical may be for example, cyclopentyl or cyclohexyl, and the hydroxy alkyl radical may be for example hydroxy ethyl, 1-hydroxypropyl or 1-hydroxy, n-butyl.

Typical compounds represented by the formula (I) are:

1) tetramethylammonium hydroxide
2) tetraethylammonium hydroxide
3) trimethylbenzylammonium hydroxide
4) trimethylcyclohexylammonium hydroxide
5) trimethyl-n-hexylammonium hydroxide
6) β - hydroxyethyltrimethylammonium hydroxide
7) N-ethylpyridinium hydroxide.

The phenol compounds of formula (II) may be for example phenol, cresol, resorcinol, hydroquinone, o-chlorophenol, m-chlorophenol, p-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol or o-aminophenol.

The oxime compounds are those having from 2 to 6 carbon atoms, examples being acetoxime, aldoxime, methyl ethyl ketoxime, dimethyl glyoxime, diethyl glyoxime, methylethyl glyoxime or cyclohexanonoxime.

Examples of isocyanate compounds suitable for trimerization are aromatic isocyanates such as phenylisocyanate, benzylisocyanate, 1 - chloro - 2,4 - phenylene diisocyanate, 1 -methoxy - 2,4 - phenylene diisocyanate, 1 - ethoxy-2,4 - phenylene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, phenylene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), naphthylene diisocyanate, ω,ω' - dimethylbenzene diisocyanate (XDI), ω,ω' - diethylbenzene diisocyanate, ω,ω - diethylxylene diisocyanate, dicyclohexylmethane - 4,4' - di - isocyanate; aliphatic isocyanates such as hexamethylene diisocyanate (HDI), tetramethylene diisocyanate, dichlorohexylmethane - 4,4' - di - isocyanate. Isocyanate compounds suitable for trimerization may also be addition products having terminal-NCO groups, which are obtained by the reaction between an excess of an isocyanate, a polyol such as ethylene glycol, propylene glycol, glycerol, hexane triol, trimethylol propane, pentaerythritol, diethylene glycol, dipropylene glycol or other conventional polyether polyols or polyester polyols having rather high molecular weight.

The method according to the invention is preferably carried out by contacting an isocyanate compound with the catalyst composition at a room temperature, under cooling or under heating.

The temperature is suitably selected in accordance with the isocyanate compound and/or catalyst composition, and is generally from about 0 to 150°C, more particularly from 0 to 60°C.

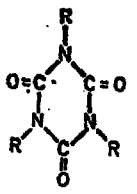
The reaction may be carried out in an organic solvent or without any solvent. Examples of suitable solvents are esters (e.g. ethoxyethyl acetate, ethylacetate, butylacetate), ketones, (acetone, methylethyl ketone, methyl isobutyl ketone), ethers (e.g. di-ethylether, dioxane,) and aromatic compounds (e.g. benzene, xylene, toluene).

The amount of the quaternary ammonium hydroxide to be used is preferably from 0.005 to 0.5 more preferably from 0.01 to 0.1 parts by weight per 100 parts by weight of organic isocyanate compound, and the phenols, oximes or methanol are preferably used in an amount of about 0.001 to about 5.0, more preferably about 0.01 to about 1.0 parts by weight of organic isocyanate compound.

A suitable ratio of phenols, oximes or methanol relative to the quaternary ammonium hydroxide is from 5 to 500 (weight/weight ratio), advantageously from 5 to 100, and preferably from 10 to 50.

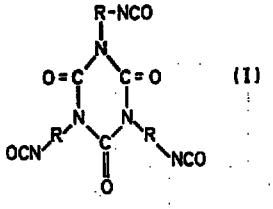
The quaternary ammonium hydroxide is advantageously added to the reaction system in a solution prepared by dissolving it in a solvent as mentioned above or other solvents such as water, methanol, dimethylsulfoxide or dimethylformamide.

In the present method, when monoisocyanate (R—NCO) is used, the corresponding trimer



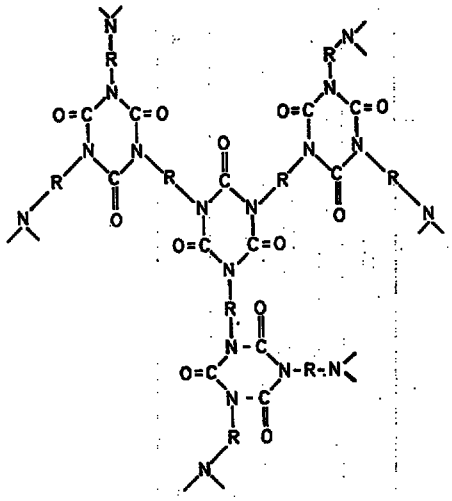
is produced, but when di- or polyisocyanate is

used there is produced the corresponding trimer (e.g. OCN—R—NCO ⟶



(I)

The isocyanate groups of trimer (I) concurrently react to produce a cross-linked elastomer(II)



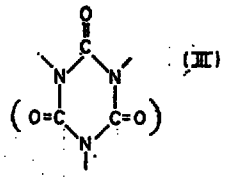
cross-linked elastomer

(II)

In the latter case, when only the trimer (I) is desired, a so-called catalyst poison such as benzoylchloride or phosphoric acid may be added to the reaction system before gelation occurs, so that the trimerization of the trimer (I) may be terminated.

When it is intended by the present method to produce the trimer of a so-called addition product having two or more terminal NCO groups which is prepared by a reaction between an excess of low molecular weight di- or polyisocyanate and a polyol, the addition product may be directly subjected to trimerization, or the excess low molecular weight di- or polyisocyanate and the polyol may separately be added to the reaction system to contact both of them with the catalyst composition.

When the addition of both components is effected separately, besides the trimer (I) is produced a cross-linked elastomer (elastomer (III)) in which the repeating units are cross-linked trimers having isocyanuric linkages, as illustrated below:—



(III)

elastomer

Urethane formation occurs between the di- or polyisocyanate and the polyol concurrently with the trimerization of the di- or polyisocyanate *per se* and the thus-produced polyurethane having urethane linkage is cross-linked with the trimer (I). Also in this case, the trimer (I) alone, can be obtained by adding a catalyst poison, as mentioned above, to the reaction system before gelation occurs.

The following examples further illustrate the invention. In the examples, parts by weight bear the same relation to parts by volume as do grams to milliliters.

As the trimerization of an isocyanate proceeds, gelation is observed if no catalyst poison is added to the reaction system. Therefore, the activities of catalyst composition for trimerizing an isocyanate compound can be determined by measuring the gelation time of the reaction system, containing isocyanate compound and the catalyst composition for trimerizing the isocyanate compounds.

EXAMPLE 1.

Three parts by weight of ethylacetate, 3 parts by weight of tolylene diisocyanate (a mixture of 80 weight % of 2,4-isomer and 20 weight % of 2,6-isomer) and a catalyst composition were homogeneously admixed, and the whole mixture kept standing at room temperature.

The time required for causing gelation of the whole mixture was measured and the results summarized in Table 1.

TABLE 1

		Catalyst Composition				Gelation time (min)
		Catalyst		Co-catalyst		
		Compound	Amount parts by weight	Compound	Amount parts by weight	
Present invention	(1)	Trimethylbenzyl-ammoniumhydroxide	0.0024	Phenol	0.15	15
Control	(2)	"	"	—	—	150
	(3)	1,4-Diazabicyclo 2,2,2-octane	0.006	—	—	>1000
	(4)	"	"	Phenol	0.15	>1000
	(5)	"	"	Propylene oxide (molecular weight)	"	90
	(6)	Calcium naphthenate	"	Phenol	"	>1000
	(7)	lead 2-ethylhexoate	"	Methanol	"	>1000

EXAMPLE 2.

Five parts by volume of butylacetate, 0.05 part by volume of a 10% ethoxyethyl acetate solution containing 0.005 part by weight of trimethylbenzylammonium hydroxide, five parts by weight of tolylene diisocyanate (a mixture of 2,4-isomer 80 weight % and 2,6-isomer 20 weight %) and 0.1 part by weight of a co-catalyst were homogeneously admixed, and the mixture kept standing at 25°C.

The time required for causing gelation of the whole mixture was determined and the results summarized in the Table 2.

TABLE 2

Co-catalyst	Gelation time (sec.)
—	6300
Phenol	30
o-Chlorophenol	30
m-Chlorophenol	15
p-Chlorophenol	15
2,4-Dichlorophenol	30
2,4-Trichlorophenol	60
Resorcinol	25
Hydroquinone	20
o-Aminophenol	720
Methanol	60
Acetoxime	50
Methyl ethyl ketoxime	125
Dimethyl Glyoxime	720

EXAMPLE 3.

Using 5 parts by weight of various isocyanate compounds and various catalyst compositions, the reaction was carried out in a similar manner to the preceding Examples.

The results are summarized in Table 3.

TABLE 3

Isocyanate	Catalyst Composition				Gelation time (min)
	Catalyst		Co-catalyst		
	Compound	Amount parts by weight	Compound	Amount parts by weight	
MDI	Trimethylbenzyl-ammonium hydroxide	0.005	p-Chlorophenol	0.1	0.5
"	"	"	—	—	>60
HDI	"	0.025	o-Chlorophenol	0.1	94
"	"	"	—	—	>4320
XDI	"	0.005	o-Chlorophenol	0.1	8
TDI	β-Hydroxyethyl trimethyl Ammonium Hydroxide	"	"	0.1	8
"	"	"	—	—	>4320
"	Tetraethyl ammonium hydroxide	"	o-Chlorophenol	0.1	360
"	"	"	—	—	>4320

MDI: 4,4-Diphenylmethanediisocyanate

HDI: Hexamethylenediisocyanate

XDI: *w,w'*-Dimethylbenzenediisocyanate

TDI: Mixture of 80% by weight of 2,4-tolylene diisocyanate and 20% by weight of 2,6-tolylene diisocyanate.

EXAMPLE 4.

Ten parts by weight of benzene, 0.05 part by weight of an ethoxyethyl acetate solution containing 0.005 part by weight of trimethylbenzylammonium hydroxide and 0.1 part by weight of p-chlorophenol were homogeneously admixed, and to the mixture were added 10 parts by weight of phenylisocyanate under agitation. The mixture reacted exothermically and a precipitate was formed. After filtration, the precipitate was washed with benzene to yield 9.7 parts by weight of white powder melting at 274°C.

The white powder was analysed by IR spectrum to reveal a significant absorption band at 1710 cm^{-1}, which corresponds to an absorption by an isocyanuric linkage, and no significant absorption band at 2250cm^{-1}, which corresponds to an absorption by an isocyanate group. The result of the analysis by IR spectrum and the melting point of 274°C prove that the white powder is a trimer of phenylisocyanate.

EXAMPLE 5.

90 parts by weight of butyl acetate, 0.008 parts by weight of a 40% methanol solution of trimethylbenzylammonium hydroxide and 0.5 parts by weight of o - chlorophenol were homogeneously admixed, and to the mixture were added 60 parts by weight of tolylene diisocyanate (a mixture of 80 weight % 2,4-isomer and 20 weight % 2,6-isomer). The whole mixture was kept at 25°C with agitation to allow a reaction to take place, while measuring the amine equivalent of the reaction mixture.

When the amine equivalent was about 700, 0.1 parts by weight of phosphoric acid were added to the reaction mixture to terminate the reaction. A viscous liquid having an amine equivalent 728 was obtained.

The liquid was shown to be a trimer of the isomers of tolylene diisocyanate by IR spectrum analysis. The liquid can be used as an isocyanate component in the so-called two-can type coating composition.

EXAMPLE 6.

2.5 parts by weight of polypropylene glycol (molecular weight 600), 2.5 parts by weight of polypropylene glycol (molecular weight 200), 0.005 parts by weight of a 40% methanol solution of trimethylbenzylammonium hydroxide and acetoxime, were homogeneously admixed, followed by degassing under vacuum. To the treated mixture were added 3.9 parts by weight of ω,ω'-diisocyanate dimethylbenzene under stirring, followed by degassing under vacuum. The whole mixture was left standing at room temperature for half an hour to allow a reaction to take place, whereby a colorless transparent cured elastomer was produced.

EXAMPLE 7.

To a mixture of 306 parts by weight of butyl acetate and 261 parts by weight of tolylene diisocyanate (a mixture of 80 weight % 2,4-isomer and 20 weight % 2,6-isomer) were added 45 parts by weight of 1,3-butylene glycol, and the mixture was heated at 70°C for 12 hours, followed by cooling at 25°C. To the reaction mixture was added a mixture of 2 parts by weight of p-chlorophenol and 0.06 parts by weight of an ethoxyethyl acetate solution containing 0.006 part by weight of trimethylbenzylammonium hydroxide.

The whole mixture was kept at 25°C with agitation to allow a reaction to take place, while measuring the amine equivalent of the reaction mixture. When the amine euivalent was about 614, 0.3 parts by weight of benzoylchloride were added to the reaction mixture to terminate the reaction. A high viscosity liquid was obtained.

The product had isocyanuric linkage and urethane linkages in its molecule, and is useful as an isocyanate component in the so-called two-can-type coating composition.

EXAMPLE 8.

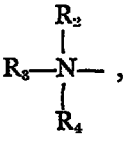
To a mixture of 134.8 parts by weight of butyl acetate and 34.8 parts by weight of tolylene diisocyanate (a mixture of 80 weight % 2.4-isomer and 20 weight % 2,6-isomer) were added 100 parts of polypropylene glycol (molecular weight of about 2000), and the mixture heated at 70°C for 2 hours, followed by cooling at 25°C. To the reaction mixture were then added a mixture of 1 part by weight of p-chlorophenol and 0.03 parts by weight of ethoxyethyl acetate solution containing 0.003 parts by weight of trimethylbenzylammonium hydroxide. The whole mixture was kept at 25°C with agitation to allow a reaction to take place, while measuring amine equivalent of the reaction mixture. When the amine equivalent was about 1800, 0.14 parts by weight of benzoylchloride were added to the reaction mixture to terminate the reaction. A high viscosity liquid was obtained. The product had isocyanuric linkages and urethane linkages in its molecule, and can be used as a one-component moisture-cure type coating agent.

WHAT WE CLAIM IS:—

1. A method for producing isocyanate trimers or elastomers in which the repeating units are crosslinked trimers comprising trimerizing an isocyanate compound in the presence of a catalyst comprising:

A) a quaternary ammonium hydroxide of the general formula Y—R_1 OH ..... (I)

in which Y may be a pyridinium radical or



R_1, R_2, R_3 and R_4 may be the same or different and represent an alkyl radical having from

EXAMPLE 4.

Ten parts by weight of benzene, 0.05 part by weight of an ethoxyethyl acetate solution containing 0.005 part by weight of trimethylbenzylammonium hydroxide and 0.1 part by weight of p-chlorophenol were homogeneously admixed, and to the mixture were added 10 parts by weight of phenylisocyanate under agitation. The mixture reacted exothermically and a precipitate was formed. After filtration, the precipitate was washed with benzene to yield 9.7 parts by weight of white powder melting at 274°C.

The white powder was analysed by IR spectrum to reveal a significant absorption band at 1710 cm^{-1}, which corresponds to an absorption by an isocyanuric linkage, and no significant absorption band at 2250cm^{-1}, which corresponds to an absorption by an isocyanate group. The result of the analysis by IR spectrum and the melting point of 274°C prove that the white powder is a trimer of phenylisocyanate.

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EXAMPLE 8.

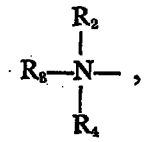
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A) a quaternary ammonium hydroxide of the general formula Y—R_1 OH ..... (I)

in which Y may be a pyridinium radical or

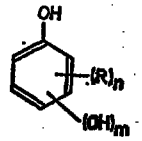


R_1, R_2, R_3 and R_4 may be the same or different and represent an alkyl radical having from

* C L M S *

1 to 6 carbon atoms, a hydroxy alkyl radical having from 1 to 6 carbon atoms, a cycloalkyl radical having 5 or 6 carbon atoms, a benzyl radical or a phenyl radical, and

B) a phenol of the general formula



(II)

in which R represents a halogen, methyl or amino radical,

n is 0 or an integer of from 1 to 3 and m is 0 or 1 and when m is 1 the two OH groups occupy meta and para positions on the benzene ring,

or an oxime having from 2 to 6 carbon atoms, or methanol.

2. A method as claimed in Claim 1, wherein the quaternary ammonium hydroxide is present in an amount of from 0.005 to 0.5 parts by weight per 100 parts by weight of isocyanate, the ratio of the phenol, oxime or methanol relative to the quaternary ammonium hydroxide (weight/weight ratio) being from 5 to 500.

3. A method as claimed in Claim 2, wherein the ratio of phenol, oxime or methanol relative to the quaternary ammonium hydroxide is from 5 to 100.

4. A method as claimed in claim 2, wherein the ratio of phenol, oxime, or methanol relative to the quaternary ammonium hydroxide is from 10 to 50.

5. A method as claimed in Claim 3, wherein the catalyst comprises 1 part by weight of trimethylbenzyl ammonium hydroxide and from 5 to 100 parts by weight of phenol, o-chlorophenol, m-chlorophenol or p-chlorophenol.

6. A method as claimed in Claim 3, wherein the catalyst comprises 1 part by weight of trimethylbenzyl ammonium hydroxide and from 5 to 100 parts by weight of methanol., acetoxime or methyl ethyl ketone oxime.

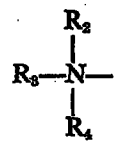
7. A method according to claim 1 for producing isocyanate trimers or elastomers in which the repeating units are cross-linked trimers substantially as described herein with reference to any one of Examples 1 to 8.

8. Isocyanate trimers or elastomers in which the reacting units are cross-linked trimers produced by the method as claimed in any preceding claim.

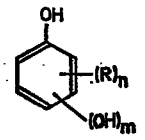
9. A catalyst composition for trimerization of an isocyanate compound comprising 1 part by weight of quaternary ammonium hydroxide of the general formula:

$$Y—R_1\ OH \qquad (I)$$

in which Y may be a pyridinium radical or,



R_1, R_2, R_3 and R_4 may be the same or different and represent an alkyl radical having from 1 to 6 carbon atoms, a hydroxy alkyl radical having from 1 to 6 carbon atoms, a cycloalkyl radical having 5 or 6 carbon atoms, a benzyl radical or a phenyl radical and from 5 to 100 parts by weight of a phenol of the formula:



in which R represents a halogen, methyl or amino radical, n is 0 or integer of from 1 to 3, m is 0 or 1, and when m is 1, the two OH groups occupy meta or para positions on the benzene ring, or an oxime of 2 to 6 carbon atoms or methanol.

10. A catalyst composition for trimerization of an isocyanate compound comprising 1 part by weight of trimethylbenzyl ammonium hydroxide and from 5 to 100 parts by weight of phenol, o-chlorophenol, m-chlorophenol or p-chlorophenol.

11. A catalyst composition for trimerization of an isocyanate compound comprising 1 part by weight of trimethylbenzyl ammonium hydroxide and from 5 to 100 parts by weight of methanol, acetoxime or methyl ethyl ketoxime.

12. A catalyst composition according to claim 8 for trimerization of an isocyanate compound substantially as described herein with reference to any one of examples 1 to 8.

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