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(71) Applicant *(for all designated States except CN)*: **COVESTRO DEUTSCHLAND AG** [DE/DE]; Kaiser-Wilhelm-Allee 60, 51373 Leverkusen (DE).

(71) Applicant *(for CN only)*: **COVESTRO POLYMERS (CHINA) CO. LTD.** [CN/CN]; 82 Muhua Road Shanghai Chemical Industry Park, Caojing, Shanghai 201507 (CN).

(72) Inventors: **ZHANG, Chenxi**; Room 2501, No 6, of Lane 1599, Ding Xiang Road, Pudong, Shanghai 200135 (CN). **LI, Liqiang**; Qin yiao Lu 33, Pudong, Shanghai 201206 (CN).

(74) Agent: **LEVPAT**; Covestro AG, Alfred-Nobel-Str. 10, 40789 Monheim am Rhein (DE).

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(54) **Title**: ISOCYANATE COMPOSITION AND POLYURETHANE RIGID FOAM PREPARED FROM THE SAME

(57) **Abstract**: The present invention relates to an isocyanate composition, comprising: a1) a toluene diisocyanate residue, wherein the toluene diisocyanate residue is selected from the distillation residue of toluene diisocyanate prepared by phosgene method, and wherein the toluene diisocyanate residue has a NCO content of 5-45 wt. %, based on total weight of the toluene diisocyanate residue; and a2) diphenyl methane diisocyanate, poly(diphenyl methane diisocyanate) or a combination thereof. The present invention also relates to a polyurethane rigid foam prepared from the isocyanate composition, wherein the polyurethane rigid foam has favorable insulation property and compression strength.

Isocyanate Composition and Polyurethane Rigid Foam Prepared from the Same

TECHNICAL FIELD

The present invention relates to an isocyanate composition comprising a toluene diisocyanate residue, which can be used for preparing a polyurethane rigid foam having favorable insulation properties and compression strength. The present invention also relates to a polyurethane rigid foam prepared from said isocyanate composition.

BACKGROUD

Toluene diisocyanate (TDI) are usually prepared by reacting toluene diamine (TDA) and phosgene and then purifying the obtained crude product via distillation. In practice, there exists a large amount of high-boiling distillation residues during the distillation process of the crude product of toluene diisocyanate (TDI). These residues are toxic and difficult to dispose; thus disposal of these residues leads to a serious problem in industry, which is not only uneconomical, but also poses a safety risk. Therefore, it is a key process of producing TDI how to deal with and utilize these residues.

These distillation residues are usually treated by a method of incineration, wherein the toxic exhaust gases require additional recycling and processing. CN 1064074A discloses a method of reducing the content of hydrolysable chlorides in toluene diisocyanate (TDI), in particular in its distillation residues, and polymer made by processing the residues.

SUMMARY OF THE INVENTION

The present invention provides an isocyanate composition, comprising:

a1) a toluene diisocyanate residue, wherein the toluene diisocyanate residue is selected from the distillation residue of toluene diisocyanate prepared by phosgene method, and wherein the toluene diisocyanate residue has a NCO content of 5-45 wt.%, based on the total weight of the toluene diisocyanate residue; and

a2) diphenyl methane diisocyanate, poly(diphenyl methane diisocyanate) or a combination thereof.

In one embodiment of the present invention, the isocyanate composition has a NCO content of 30-40 wt.%, based on the total weight of the isocyanate composition.

In a preferred embodiment of the present invention, the toluene diisocyanate residue is selected from the distillation residue of toluene diisocyanate prepared by phosgene method in gas phase.

In another preferred embodiment of the present invention, the toluene diisocyanate residue has a content of 15-40 wt.%, based on the total weight of the isocyanate composition.

In still another preferred embodiment of the present invention, the toluene diisocyanate residue has a content of 20-30 wt.%, based on the total weight of the isocyanate composition.

The present invention also relates to a polyurethane rigid foam, wherein the polyurethane rigid foam is prepared from the above-mentioned isocyanate composition.

DETAINED DESCRIPTION

I. Isocyanate composition

The present invention provides an isocyanate composition, comprising:

a1) a toluene diisocyanate residue, wherein the toluene diisocyanate residue is selected from the distillation residue of toluene diisocyanate prepared by phosgene method, and wherein the toluene diisocyanate residue has a NCO content of 5-45 wt.%, based on the total weight of the toluene diisocyanate residue; and

a2) diphenyl methane diisocyanate, poly(diphenyl methane diisocyanate) or a combination thereof.

In one embodiment of the present invention, the isocyanate composition has a NCO content of 30-40 wt.%, based on the total weight of the isocyanate composition.

In one embodiment of the present invention, the isocyanate composition has a viscosity of 350-1100 mPa·s, preferably 450-1050 mPa·s and more preferably 550-950 mPa·s.

The toluene diisocyanate residue in the isocyanate composition has a content of 15-40 wt.%, preferably 20-30 wt.%, based on the total weight of the isocyanate composition.

In one embodiment of the present invention, the toluene diisocyanate residue is selected from the distillation residue of toluene diisocyanate prepared by phosgene method. The well-known phosgene method for preparing toluene diisocyanate generally consists of four steps:

(1) the reaction of toluene and nitric acid to form dinitro-toluene (DNT);

(2) the reaction of DNT and hydrogen to form toluene diamine (TDA);

(3) the reaction of TDA and phosgene to form toluene diisocyanate (TDI);

(4) purification of TDI by distillation.

The toluene diisocyanate residue used in the present invention is obtained in step (4) of purification by distillation, wherein

the toluene diisocyanate residue has a NCO content of 5-45 wt.%, preferably 10-39 wt.%, more preferably 25-38 wt.%, based on the total weight of the toluene diisocyanate residues.

In a preferred embodiment of the invention, the toluene diisocyanate residue is selected from the distillation residue of toluene diisocyanate prepared by phosgene method in gas phase. Gas-phase phosgene method is characterized in that in said step (3), TDA and phosgene react in gas phase, preferably at a temperature of 200-600 , to obtain the toluene diisocyanate.

Isocyanate composition further comprises diphenyl methane diisocyanate (MDI), poly(diphenyl methane diisocyanate) (PMDI) or a combination thereof, with a content of 60-85%, preferably 70-85%, based on the total weight of the isocyanate composition.

In one embodiment of the present invention, the polyisocyanate composition may also comprise other organic polyisocyanates, such as aliphatic, alicyclic and aromatic diisocyanate(s) and/or polyisocyanate(s). Examples of suitable organic polyisocyanates used in the present invention include, but are not limited to, 1,4-butylene diisocyanate, pentane-1,5-diisocyanate, hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 2,2,4- and/or 2,4,4-trimethylhexamethylene diisocyanate, bis(4,4'-isocyanato-cyclohexyl)methane or mixtures thereof with other isomers, 1,4-cyclohexylene diisocyanate, 1,4-phenylene diisocyanate, 1,5-naphthalene diisocyanate, 1,3- and/or 1,4-tetramethylxylylene diisocyanate (TMXDI), 1,3-xylylene diisocyanate (XDI).

II. Polyurethane rigid foam

The present invention also provides a polyurethane rigid foam prepared from the above-mentioned isocyanate composition. The polyurethane rigid foam system provided by the present invention, preferably a conventional block foam and a plywood, has good insulation properties and compressive strength.

In one embodiment of the present invention, the composition used for preparing the polyurethane rigid foam also comprises an isocyanate-reactive component. The isocyanate-reactive component may comprise one or more polyether and/or polyester polyol(s) having a hydroxyl number of 150-1200 mgKOH/g and a content of 75-95 wt.%, based on the total weight of the isocyanate-reactive component.

The polyether polyols used in the present invention can be prepared by known processes. For example, it can be obtained by the reaction of alkylene oxide and an initiator in the presence of a catalyst. The catalyst is, preferably but not limited to, alkali hydroxides, alkali alkoxides, antimony pentachloride, boron fluoride etherate, or a mixture thereof. The alkylene oxide is, preferably but not limited to, tetrahydrofuran, ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide, styrene oxide, or a mixture thereof; in particular preferably ethylene oxide and/or propylene oxide. The initiator is, preferably but not limited to, a polyhydroxy or polyamine compound. The polyhydroxy compound is, preferably but not limited to, water, ethylene glycol, 1,2-propanediol, 1,3-propanediol, diethylene glycol, trimethylolpropane, glycerol, bisphenol A, bisphenol S or a mixture thereof. The polyamine compound is, preferably but not limited to, ethylene diamine, propylene diamine, butylene diamine, hexamethylene diamine, diethylenetriamine, tolylenediamine or a mixture thereof. The polyether polyol has a functionality of 2-8, preferably 2-5.

The polyester polyol is obtained by the reaction of a dicarboxylic acid or dicarboxylic acid anhydride with a polyol. The dicarboxylic acid is preferably, but not limited to, an aliphatic carboxylic acid containing 2 to 12 carbon atoms, for example, succinic acid, malonic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, capric acid, dodecylic acid, maleic

acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid, and a mixture thereof. The dicarboxylic acid anhydride is preferably, but not limited to, phthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, and a mixture thereof. The polyol is preferably, but not limited to, ethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, dipropylene glycol, methyl-1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,10-decanediol, glycerol, trimethylolpropane, and a mixture thereof. The polyester polyol further includes those prepared from lactones. The polyester polyol prepared from lactones is preferably, but not limited to, ε- caprolactone.

In addition to the above-mentioned polyether polyol and/or polyester polyol, the polyurethane rigid foam according to the present invention may also comprise, but not limited to, a polycarbonate polyol and a polymer polyol.

The polycarbonate polyol is preferably, but not limited to, a polycarbonate diol synthesized by the reaction of a diol with a dialkyl or diaryl carbonate or phosgene. The diol is preferably, but not limited to, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, diethylene glycol, s-Trioxane diol, and a mixture thereof. The dialkyl or diaryl carbonate is preferably, but not limited to, diphenyl carbonate.

The polymer polyol is a stable dispersion formed by solid enhanced particles in a polyol liquid. Any known polymer (or dispersion) polyol in the art can be included in the polyol component according to the present invention. It includes, but is not limited to, SAN polymer polyol, PHD polymer polyol and PIPA polymer polyols. The SAN polymer polyol is made by in-situ polymerization of a mixture of acrylonitrile and styrene in a base polyol; the PHD polymer polyol is made by in-situ

polymerization of a isocyanate mixture and a diamine in a base polyol; the PIIPA polymer polyol is made by in-situ polymerization of a isocyanate mixture and a diol and/or diol-amine in a base polyol.

The measurement of hydroxyl number is known for the skilled as such and described, for example, in Houben Weyl, Methoden der Organischen Chemie, vol. XIV/2 Makromolekulare Stoffe, p. 17, Georg Thieme Verlag; Stuttgart 1963, which is incorporated by reference herein in its entirety.

When used in the present invention, the functionality and hydroxyl number of an organic polyol mean the average functionality and the average hydroxyl number in each case, unless otherwise indicated.

The skilled in the art can add, if needed, a blowing agent, a chain extender, a catalyst, a surfactant, a flame retardant, a filler or other additives suitable for the preparation of the polyurethane rigid foam according to the present invention. The blowing agent according to the present invention may be a variety of physical blowing agents or chemical blowing agents. Examples of said blowing agent are, preferably but not limited to, water, halogenated hydrocarbons, hydrocarbons and gases. The halogenated hydrocarbons are preferably, but not limited to, monochlorodifluoromethane, dichloromonofluoromethane, dichlorofluoromethane, trichlorofluoromethane, or a mixture thereof. The hydrocarbons are preferably, but not limited to, butane, pentane, cyclopentane, hexane, cyclohexane, heptane, or a mixture thereof. The gases are preferably, but not limited to, air, CO_2 or N_2. The blowing agent is particularly preferably water. The amount of the blowing agent is dependent on the desired density of the polyurethane.

The chain extender used in the present invention is usually an active hydrogen atom-containing compound having a molecular weight of less than 800, preferably a molecular weight of 18-400. The active hydrogen atom-containing compound is preferably, but not limited to, alkylene glycols, dialkylene glycols, polyalkylene polyol, or a mixture thereof, for example, ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, diethylene glycol, dipropylene glycol, polyoxyalkylene glycol, or a mixture thereof. The active hydrogen atom-containing compound may also include other grafted or unsaturated alkylene glycol or a mixture thereof, for example, 1,2-propanediol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-butene-1,4-diol, 2-butyne-1,4-diol , alkanol amine, N-alkyl-dialkanol amine. The N-alkyl-dialkanol amine is preferably, but not limited to, ethanol amine, 2-propanol amine, 3-amino-2,2-dimethylpropanol, N-methyl-diethanol amine, N-ethyl-diethanol amine, or a mixture thereof. The active hydrogen atom-containing compound may further include aliphatic amines, aromatic amines, or a mixture thereof. The aliphatic amines and aromatic amines are preferably, but not limited to, 1,2-ethylenediamine, 1,3-propanediamine, 1,4-butanediamine, hexamethylene diamine, isophorone diamine, 1,4-cyclohexane diamine, N,N'-diethyl-phenylenediamine, 2,4-diaminotoluene, 2,6-diaminotoluene, or a mixture thereof. The catalyst according to the present invention is preferably, but not limited to, amine catalysts, organic metal catalysts, or a mixture thereof. Said amine catalysts are preferably, but not limited to, triethylamine, tributylamine, triethylenediamine, N-ethylmorpholine, N,N,N',N'-tetramethyl-ethylene diamine, pentamethyl-diethylene triamine, N,N-methylaniline, N,N-dimethylaniline, or a mixture thereof. Said organic metal catalysts are preferably, but not limited to, organotin compounds, for example, tin(II) acetate, tin(II) octoate, tin

ethylhexanoate, tin laurate, dibutyltin oxide, dibutyltin dichloride, dibutyltin diacetate, dibutyltin maleate, dioctyltin diacetate and a mixture thereof.

The surfactant used in the present invention is preferably, but not limited to, ethylene oxide derivatives of siloxanes.
The flame retardant used in the present invention may be an organic or an inorganic flame retardant. The organic flame retardant is preferably, but not limited to, tris(2-chloroethyl) phosphate (TCEP), tris(2-chloropropyl) phosphate (TCPP), trischloropropyl phosphate (TDCPP), dimethyl methylphosphonate (DMMP), triphenyl phosphate, melamine orthophosphate (MPP) or a mixture thereof. The inorganic flame retardant is preferably, but not limited to, hydrated aluminum hydroxide, hydrated magnesium hydroxide, monoammonium phosphate, diammonium phosphate, ammonium chloride, boric acid, hydrated zinc borate or a mixture thereof.

The filler used in the present invention can be a variety of inorganic fillers or organic fillers. The inorganic filler is preferably, but not limited to, silicate minerals, metal oxides, metal salts, inorganic pigments, natural and synthetic mineral fibers, nano-materials, or a mixture thereof. Non-limiting examples are calcium silicate, calcium carbonate, fumed silica, nano-zinc oxide, barite, zinc sulfide, glass particles and wollastonite. The organic filler is preferably, but not limited to, crystalline wax, polymer polyol, organic microparticles and cork. The inorganic fillers or organic fillers may be used singly or in combination. The filler may serve to enhance the strength of the polyurethane layer, flame retardancy and so on.

The present invention will be further described below in combination with examples. The specific examples and methods disclosed herein are illustrative and not restrictive.

EXAMPLES

The starting materials and devices used in this application are described as follows:

TDI distillation residue: NCO content of about 34 wt.%, a viscosity of about 12000 cps (25°C), available from Bayer MaterialScience AG;
Desmodur 44V20L: PMDI, NCO content of 30.5-32.5 wt.%, available from Bayer MaterialScience AG;
Desmophen 4030 M: polyether polyol, a hydroxyl number of 380, available from Bayer MaterialScience AG;
Desmophen 4034B: polyether polyol, a hydroxyl number of 440, available from Bayer MaterialScience AG;
Arcol 1021: polyether polyol, a hydroxyl number of 56, available from Bayer MaterialScience AG;
L-6920: a foam stabilizer available from Momentive;
Polycat 8: a catalyst available from Air Products;
Polycat 41: a catalyst available from Air Products;
HK 470 Type of conventional high-pressure foaming machine: available from Hennecke company.

The isocyanate-reactive components used in the amounts shown in Table 1 were mixed and then reacted in HK 470 Type of conventional high-pressure foaming machine based on the amounts shown in Table 2. After the reaction, the liquid polyurethane is poured into a mold of 20 cm * 30 cm * 60 cm, the temperature of the mold is controlled between 25-35 , the temperature of raw materials is 25-30 , the mixing pressure of the high-pressure machine is 120-150 bar. The foam rises substantially freely since there is no cover on the mold. After 20 minutes, it was demolded and kept at room temperature for 24 hours, and the top part which is uneven is cut off. The remaining lower part is cut into test samples with desired size in accordance with the foam test standards. A group of five samples were tested in terms of mechanical

properties (according to GB/T 8813-2008) and heat insulation properties (according to GB/T3399-1982). The test data are shown in Table 2.

The polyurethane rigid foams of Examples 2 and 3 have a lower thermal conductivity and therefore better insulation properties. In addition, the polyurethane rigid foams of Examples 2 and 3 have a higher compression strength in the direction vertical to foaming when compared with that of Example 1 having the same density.

Table 1: Isocyanate-reactive components

Components	Unit	Amount
Desmophen 4030 M	pbw	70
Desmophen 4034B	pbw	25
Arcol 1021	pbw	5.0
L-6920	pbw	2.0
Glycerol	pbw	2.0
TCPP	pbw	8.0
Polycat 8	pbw	0.8
Polycat 41	pbw	0.5
Water	pbw	1.2
R-141B	pbw	25

Table 2: Polyurethane rigid foam and the properties thereof

Examples	unit	1*	2	3
isocyanate-reactive component	pbw	100	100	100
Desmodur 44V20L	pbw	100	80	75
TDI residue	pbw	0	20	25
Cream time	second	147	209	215

Tack-free time	second	300	387	398
Foam density	kg/m^3	34.7	34.5	34.7
compression strength (vertical direction)	KPa	131	136	164
Thermal conductivity	mW/m.K	22.27	21.67	21.64

*comparative example

Claims

1. An isocyanate composition, comprising:
a1) a toluene diisocyanate residue, wherein the toluene diisocyanate residue is selected from the distillation residue of toluene diisocyanate prepared by phosgene method, and wherein the toluene diisocyanate residue has a NCO content of 5-45 wt.%, based on total weight of the toluene diisocyanate residue; and
a2) diphenyl methane diisocyanate, poly(diphenyl methane diisocyanate) or a combination thereof.

2. The isocyanate composition according to claim 1, wherein the isocyanate composition has a NCO content of 30-40 wt.%, based on total weight of the isocyanate composition.

3. The isocyanate composition according to claim 1 or 2, wherein the toluene diisocyanate residue is selected from the distillation residue of toluene diisocyanate prepared by phosgene method in gas phase.

4. The isocyanate composition according to claim 3, wherein the toluene diisocyanate residue has a content of 15-40 wt.%, based on total weight of the isocyanate composition.

5. A polyurethane rigid foam, wherein the polyurethane rigid foam is prepared from the isocyanate composition according to any one of claims 1-4.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/18 C08G18/76 C08G18/72 C08G18/48 C08G18/66
C07C263/10 C07C263/20
ADD. C08G101/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C08G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CH 571 544 A5 (BAYER AG) 15 January 1976 (1976-01-15) column 1, line 1 - column 5, line 52 column 5, line 55 - column 8, line 2; examples 1a, 1b,2a, 2b claim 1 -----	1-5
X	GB 1 434 917 A (ICI LTD) 12 May 1976 (1976-05-12) page 1, line 10 - page 2, line 90 claim 1 -----	1-5
X	EP 0 497 538 A2 (DOW CHEMICAL CO [US]) 5 August 1992 (1992-08-05) page 3, line 28 - page 9, line 4 examples 4,6 & CN 1 064 074 A (DOW CHEMICAL CO [US]) 2 September 1992 (1992-09-02) cited in the application -----	1-5

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

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European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Neugebauer, Ute

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CH 571544 A5	15-01-1976	AT 325858 B	10-11-1975
		AU 462594 B2	26-06-1975
		AU 4203172 A	15-11-1973
		BE 783257 A1	10-11-1972
		CH 571544 A5	15-01-1976
		DE 2123183 A1	14-12-1972
		ES 402619 A1	01-04-1975
		FR 2137728 A1	29-12-1972
		GB 1346402 A	13-02-1974
		IT 957771 B	20-10-1973
		NL 7206340 A	14-11-1972
GB 1434917 A	12-05-1976	NONE	
EP 0497538 A2	05-08-1992	BR 9200378 A	13-10-1992
		CN 1064074 A	02-09-1992
		EP 0497538 A2	05-08-1992
		JP H051014 A	08-01-1993