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(54) Titre : POLYESTER POLYOL DE POLYETHYLENE NAPHTALATE ET MOUSSES RIGIDES DE POLYURETHANE
OBTENUES A L'AIDE DE CETTE SUBSTANCE
(54) Title: POLYETHYLENE NAPHTHALATE POLYESTER POLYOL AND RIGID POLYURETHANE FOAMS OBTAINED
THEREFROM

(57) **Abrégé/Abstract:**

Process for preparing a poly(alkylene polyaromatic dicarboxylate)ester based polyester polyol comprising the steps of a) depolymerising poly(alkylene polyaromatic dicarboxylate) in the presence of a glycol and b) transesterifying the obtained product by addition of polycarboxylic acids, anhydrides or esters and/or polyhydric alcohols and use of the thus obtained polyester polyol in the manufacture of rigid polyurethane and urethane-modified polyisocyanurate foams.



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(21) International Application Number: PCT/EP99/07520 (22) International Filing Date: 7 October 1999 (07.10.99) (30) Priority Data: 98121285.5 9 November 1998 (09.11.98) EP (71) Applicant (for all designated States except US): HUNTSMAN ICI CHEMICALS LLC [US/US]; 500 Huntsman Way, Salt Lake City, UT 84108 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): BONAPERSONA, Vittorio [IT/CH]; Ch. Marc Emery 7, CH-1293 Collex Bossy (CH). (74) Agents: SWINNEN, Anne, Marie et al.; Huntsman ICI Europe Ltd., Intellectual Property Department, Everslaan 45, B-3078 Everberg (BE).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: POLYETHYLENE NAPHTHALATE POLYESTER POLYOL AND RIGID POLYURETHANE FOAMS OBTAINED THEREFROM (57) Abstract Process for preparing a poly(alkylene polyaromatic dicarboxylate)ester based polyester polyol comprising the steps of a) depolymerising poly(alkylene polyaromatic dicarboxylate) in the presence of a glycol and b) transesterifying the obtained product by addition of polycarboxylic acids, anhydrides or esters and/or polyhydric alcohols and use of the thus obtained polyester polyol in the manufacture of rigid polyurethane and urethane-modified polyisocyanurate foams.		

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DESCRIPTION

POLYETHYLENE NAPHTHALATE POLYESTER POLYOL AND RIGID POLYURETHANE FOAMS
OBTAINED THEREFROM

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This invention relates to the preparation of poly(alkylene polyaromatic dicarboxylate) ester based polyester polyols and the use thereof in the preparation of rigid polyurethane and polyisocyanurate foams.

The invention more specifically relates to polyester polyols produced from reacting polyethylene naphthalate.

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The preparation of a rigid polyurethane (PUR) and polyisocyanurate (PIR) foam by the reaction of a polyisocyanate, a polyol and a blowing agent in the presence of a catalyst is well known. A wide variety of polyols have been used as one of the components in the preparation of rigid polyurethane foams, including polyols from different waste streams.

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The polyols are usually polyether alcohols or polyester alcohols, or a mixture of the two. Both aliphatic and aromatic polyester polyalcohols are in use. They are the reaction products of an esterification of a dicarboxylic acid or an anhydride with glycols (primary/secondary). More often a transesterification process is used. Aromatic polyester polyols used in rigid PUR/PIR foams are typically based on production waste streams of dimethyl terephthalate (DMT). Polyethylene terephthalate (PET) scrap is also a source of aromatic carboxylates. Depolymerization of production waste streams or post consumer waste from e.g. PET bottles is a known method in the preparation of a polyester polyol.

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Presently available polyols made from scrap PET or DMT process residue suffer from a variety of disadvantages such as the lack of compatibility with blowing agents commonly used in the manufacture of rigid PUR/PIR foams. Foams prepared from these polyols are sometimes deficient in compressive strength and/or thermal insulation capacity and/or flame resistance.

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It has now been found that poly(ethylene naphthalate) (PEN) can easily be depolymerized and that a polyester polyol with high aromatic content can be made based on this depolymerization product. Rigid polyurethane or polyisocyanurate foams made using this polyester polyol show excellent mechanical stability, good fire performance and low smoke generation together with a low thermal conductivity.

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The poly(alkylene polyaromatic dicarboxylate) ester preferably used in the present invention is poly(ethylene 2,6-naphthalate). Other isomers of this polymer, or copolymers with e.g. poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) or poly(butylene naphthalate) can also be employed, as well as the polyesters based on dicarboxylates with a multi ring structure (e.g. anthracene, phenantrene) and their copolymers.

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The polyester polyol is prepared by a two step process.

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In a first step, the polyester is depolymerised in the presence of a glycol. This can be, for example, 1,4-butanediol, diethyleneglycol (DEG) or dipropyleneglycol (DPG). Most suitable as the diol is DEG and it is preferably used in an amount in excess of that required for digestion. Although the reaction takes place in the

absence of catalysts, the reaction times are significantly shortened by use of the appropriate catalysts. The preferred catalyst is tetra-N-butyltitanate (TBT). Zinc oxide or manganese acetate can also be employed.

The depolymerization is carried out at such temperature that the polyester dissociates and the core units are obtained. This is typically in the temperature range of 150 to 350°C, preferably about 240°C. The process is typically carried out at atmospheric pressure. However, it will be obvious that pressures higher than atmospheric can be used. At higher pressures the reaction temperature can be increased significantly, thus shortening the reaction time. The obtained reaction mixture contains the esterification product from the polyaromatic dicarboxylate and the used glycol, together with the diol of the alkylene chain between the aromatic rings. Very often, excess glycols are present. When starting with PEN, the product from this first step contains naphthalate polyols, unreacted glycols and ethylene glycol from the PEN. During the depolymerisation and esterification, removal of the formed ethylene glycol by vacuum distillation is possible. This normally results in a lower OH value of the final polyester polyol, together with a reduction of the aliphatic content, which is reflected in the fire performance of the obtained foam. In the present invention the ethylene glycol was not removed, with no detrimental effects on the final rigid foam properties.

In a second step, the mixture is further transesterified by addition of other polycarboxylic acids, anhydrides or esters and a polyhydric alcohol. This further esterification brings the final polyester polyol in the desired viscosity range. The total content of polyester polymer used in the synthesis of the polyester polyol is typically in the range 5 to 50 wt%, preferably 10 to 40 wt%. The polycarboxylic acid and the polyhydric alcohol are added at a temperature in the range of 80 to 240°C, preferably 100 to 180°C.

Suitable examples of the polycarboxylic acid component or its derivatives are adipic acid, glutaric acid and anhydride, succinic acid, oxalic acid, malonic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, phthalic anhydride, pyromellitic anhydride. As polyfunctional alcohol, glycols are preferred. They can be a simple glycol of general formula $C_nH_{2n}(OH)_2$ or polyglycols with intervening ether linkages, as represented in the general formula $C_nH_{2n}O_x(OH)_2$. They also may contain heteroatoms.

The polycarboxylic component and polyhydric alcohol may include substituents which are inert in the reaction, e.g. chlorine and bromine substituents, and/or may be unsaturated. Examples of suitable polyhydric alcohols are alkylene glycols and oxyalkylene glycols, such as ethylene glycol, diethylene glycol and higher polyethylene glycols, propylene glycol, dipropyleneglycol and higher propylene glycols, glycerol, pentaerythritol, trimethylolpropane, sorbitol and mannitol.

The two steps described above can also be carried out in a single step process. The depolymerisation of the polyester polymer is more complete and faster when using a two step process.

The final polyol mixture for use in the present invention has an average functionality of 1.5 to 8, preferably 2 to 3. The hydroxyl number is generally between 200 and 550 mg KOH/g polyol. The molecular weight of the polyesters is generally in the range 200 to 3000, preferably 200 to 1000, most preferably 200 to 800.

The term polyester polyol as used herein includes any minor amounts of unreacted polyol remaining after the

preparation of the polyester polyol and/or unesterified polyol.

The polyester polyol according to the present invention is used to make polyurethane-based rigid foam. In the processing of polyurethane and polyisocyanurate foams, the polyisocyanates and the mixture of isocyanate-
5 reactive components are generally mixed in a one-shot method. Both high and low-pressure techniques can be employed in the mixing step. The ratio of the NCO/OH groups generally falls within the range 0.85 to 1.40, preferably 0.95 to 1.2 for polyurethane foam, and within the range 50 to 1, preferably 8 to 1 for polyisocyanurate foam.

Besides the PEN based polyester polyol of the present invention other isocyanate-reactive compounds can be
10 used in the process for making rigid polyurethane or urethane-modified polyisocyanurate foams. Suitable isocyanate-reactive compounds include any of that known in the art for the production of rigid polyurethane foam, especially polyether polyols and other types of polyester polyols.

In general the PEN based polyester polyol of the present invention constitutes between 60 and 100 % by weight of total isocyanate-reactive compounds.

15 The isocyanate-reactive mixture generally contains the polyhydric alcohols and other optional additives such as blowing agents, fire retardants, fillers, stabilizers, catalysts and surfactants. Preferred catalysts for the polyurethane formation are amines, most preferably tertiary amines. Dibutyl tin dilaurate is an example of a non-amine based polyurethane catalyst. Preferred polyisocyanurate catalysts are alkali metal carboxylates
20 and quaternary ammonium carboxylates.

Any of the blowing agents known in the art for the preparation of rigid polyurethane or urethane-modified polyisocyanurate foams can be used in the process of the present invention. Both physical and chemical blowing agents can be used, singly or in mixtures.

25 Suitable physical blowing agents are, for example, hydrocarbons, dialkyl ethers, alkyl alkanoates, aliphatic and cycloaliphatic hydrofluorocarbons, hydrochlorofluorocarbons, chlorofluorocarbons, hydrochlorocarbons, fluorine-containing ethers and carbon dioxide. Examples of preferred blowing agents are isomers of pentane such as cyclopentane, n-pentane and isopentane, and mixtures thereof, 1,1-dichloro-2-fluoroethane (HCFC 141b), 1,1,1-trifluoro-2-fluoroethane (HFC 134a), chlorodifluoromethane (HCFC 22), 1,1-difluoro-3,3,3-
30 trifluoropropane (HFC 245fa).

Carbon dioxide releasing products can be used as chemical blowing agent. Water, which releases carbon dioxide upon reaction with isocyanate, is widely known as a chemical blowing agent.

The total quantity of blowing agent is typically from 0.1 to 25% by weight based on the total reaction system.

35 Both aliphatic and aromatic polyisocyanates can be used. Preferred are the aromatic polyisocyanates such as diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI) or prepolymers thereof. Mixtures of isomers and oligomers can be employed. Most preferred is the polymeric form of MDI.

The polyisocyanate can be uretonimine or carbodiimide modified.

The invention is illustrated by, but not limited to, the following examples.

Example 1-3: Synthesis of the polyester.

5 In a two-liter flask equipped with an efficient agitator, thermocouple and distillation set-up, diethylene glycol and polyethylene 2,6-naphthalate was charged. 10 ppm of TBT was added. The content was heated to 240°C under efficient stirring and a nitrogen atmosphere. After 2 to 3 hours, the temperature was lowered to 160°C and adipic acid and glycerol were charged (quantities see table 1), together with 10 ppm TBT. The mixture was heated slowly to 180°C and water was removed by distillation. To complete the esterification, the
10 temperature was further increased to 200°C until the theoretical stoichiometric amount of water was removed by distillation under vacuum. When the distillation rate flattened out, an acid value titration was performed. Acid values of 2 mg KOH/gram are acceptable.

The specifications of the obtained polyesters are shown in Table 1.

15 Table 1

	Example 1: polyol A	Example 2: polyol B	Example 3: polyol C
PEN (gram)	311.00	420.00	532.00
DEG (gram)	583.00	538.00	492.00
glycerol (gram)	133.00	134.00	136.00
adipic acid (gram)	473.00	407.00	340.00
OH value (mg KOH/gram)	351.00	357.00	363.00
Viscosity (cPs at 25°C)	2100.00	4100.00	12900.00
Free glycols			
MEG (%)	1.10	1.60	1.90
DEG (%)	8.30	7.30	6.30
glycerol (%)	3.30	6.60	3.50

Example 4-7

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Rigid urethane-modified polyisocyanurate foams were prepared from the polyesters made according to examples 1 to 3 above. The formulation components (400 gram) were mixed at 5000 rpm with a small-scale lab mixing unit and poured into a 20x20x30 cm open mould. HCFC 141b was used as blowing agent. After standing at room temperature for at least 24 hours, physical properties of the foams were tested. Ingredients
25 (amounts in parts by weight) and foam physical properties obtained with polyols A, B and C and a

comparative example based on a PET polyol are listed in Table 2.

PET polyol: polyester polyol based on scrap PET, OH value 350 mg KOH/gram.

Tegostab B 8406: silicone based surfactant available from Goldschmidt.

5 TEP: triethylphosphate fire retardant.

DMEA: dimethylethanolamine catalyst.

NiAx A1: bis(dimethylamino ethylether) catalyst.

Dabco K15: potassium octoate catalyst.

10 SUPRASEC 2085: polymeric MDI available from Huntsman Polyurethanes (SUPRASEC is a trademark of Huntsman ICI Chemicals LLC).

CT: cream time, which is the time from mixing to the change of appearance of the mixed chemicals, which indicates the onset of the expansion.

ST: string time, which is the time from mixing to the instant at which it is possible to pull a string of polymer from the reacting mixture using a spatula.

15 ER: end-of-rise time, which is the time from mixing to the end of expansion of the foam.

TF: tack-free time which is the time from mixing to when the surface of the foam no longer sticks to a spatula when light pressure is applied.

Density was measured according to standard DIN 53420.

Thermal conductivity was measured according to standard ISO 2581.

20 Compression strength was measured according to standard DIN 53421.

Kleinbrenner values were determined according to standard DIN 4102.

Limited O₂ index was determined according to standard ASTM 2863.

NBS Smoke values were determined according to standard ASTM E 662.

25 Example 8-11

Rigid urethane-modified polyisocyanurate foams were prepared from the polyesters made according to examples 1 to 3 above. The formulation components (400 gram) were mixed at 5000 rpm and poured into a 20x20x30 cm open mould. Isopentane was used as blowing agent. After standing at room temperature for at
30 least 24 hours, the physical properties of the obtained foams were tested. Ingredients (amounts in parts by weight) and foam physical properties obtained using polyols A, B and C and a comparative PET based polyol are listed in Table 3.

Table 2

	Example 4	Example 5	Example 6	Example 7
PET polyol	100.00			
polyol A		100.00		
polyol B			100.00	
polyol C				100.00
Tegostab B 8406	2.00	2.00	2.00	2.00
TEP	15.00	15.00	15.00	15.00
DMEA	2.40	2.50	2.50	2.50
Niax A1	0.13	0.13	0.13	0.13
Dabco K15	1.80	1.90	1.90	1.90
water	2.30	2.30	2.30	2.30
HCFC 141b	21.00	25.00	25.00	25.00
SUPRASEC 2085	312.00	312.00	312.00	312.00
Index (%)	250.00	250.00	250.00	250.00
Reaction profile				
CT (sec)	14.00	14.00	14.00	14.00
ST (sec)	35.00	40.00	40.00	40.00
ER (sec)	50.00	75.00	75.00	75.00
TF (sec)	60.00	75.00	75.00	75.00
Density (kg/m ³)	35.00	33.00	33.00	34.00
Thermal conductivity (mW/m K)				
initially	22.70	22.10	21.40	21.20
1 week	28.70	27.80	27.10	26.70
3 weeks	29.80	29.40	28.40	28.50
5 weeks	29.70	29.80	29.30	28.70
Compression strength (kPa)				
parallel to rise	312.00	270.00	270.00	299.00
perpendicular to rise	97.00	87.60	82.70	94.30
Isotropic 33 kg/m ³	130.00	127.00	122.00	131.00
Kleinbrenner				
Ext. time (s)	15.00	15.00	15.00	15.00
Flame Height (cm)	9.00	8.00	7.00	7.00
Limited O ₂ index (%)	28.0	28.1	28.1	28.1
NBS Smoke				
mass loss (%)	49.00	44.00	44.00	43.00
optical density	126.00	106.00	93.00	119.00

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Table 3

	Example 8	Example 9	Example 10	Example 11
PET polyol	100.00			
polyol A		100.00		
polyol B			100.00	
polyol C				100.00
Tegostab B 8406	2.00	2.00	2.00	2.00
TEP	15.00	15.00	15.00	15.00
DMEA	2.40	2.40	2.40	2.40
Niax A1	0.13	0.13	0.13	0.13
Dabco K15	1.80	1.80	1.80	1.80
water	2.30	2.30	2.30	2.30
i-pentane	15.00	15.00	15.00	15.00
SUPRASEC 2085	312.00	312.00	312.00	312.00
Index (%)	250.00	250.00	250.00	250.00
Reaction profile				
CT (sec)	10.00	11.00	10.00	10.00
ST (sec)	42.00	40.00	42.00	40.00
Density (kg/m ³)	32.00	31.00	32.50	33.00
Thermal conductivity (mW/m K)				
initially	24.00	23.60	24.30	23.60
1 week	27.10	26.50	27.50	26.50
3 weeks	29.00	28.60	28.40	28.40
5 weeks	28.30	27.70	28.60	28.30
Compression Strength (kPa)				
parallel to rise	241.00	270.00	269.00	309.00
perpendicular to rise	74.50	79.90	91.40	96.10
Isotropic 33 kg/m ³	116.70	132.00	134.00	142.00
Limited O ₂ index (%)	25.6	26.2	26.2	26.2
Kleinbrenner				
Ext. time (sec)	15.00	15.00	15.00	15.00
Flame Height (cm)	11.00	11.00	12.00	11.00
NBS Smoke				
mass loss (%)	49.00	44.00	44.00	43.00
optical density	71.00	63.00	57.00	71.00

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CLAIMS

1. Process for preparing a poly(alkylene polyaromatic dicarboxylate)ester based polyester polyol comprising the steps of a) depolymerising poly(alkylene polyaromatic dicarboxylate) in the presence of a glycol and b) transesterifying the obtained product by addition of polycarboxylic acids, anhydrides or esters and polyhydric alcohols.

and polymerizing

cl 1

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2. Process according to claim 1 wherein the poly(alkylene polyaromatic dicarboxylate) is poly(ethylene 2,6-naphthalate).

cl 2

3. Process according to claim 2 wherein the poly(ethylene 2,6-naphthalate) comes from a production waste stream or post-consumer waste.

cl 3

4. Process according to any one of the preceding claims wherein the glycol used in step a) is diethyleneglycol.

cl 4

5. Process according to any one of the preceding claims wherein step a) is carried out in the presence of tetra-N-butyltitanate as catalyst.

cl 5

6. Process according to any one of the preceding claims wherein the polyester polyol has an average functionality of 1.5 to 8, a hydroxyl number of 200 to 550 mg KOH/g and a molecular weight of 200 to 3000.

cl 6

7. Polyester polyol obtainable by the process as defined in any one of the preceding claims.

cl 7

8. Process for preparing rigid polyurethane or urethane-modified polyisocyanurate foams by reacting an organic polyisocyanate with a polyfunctional isocyanate-reactive composition in the presence of a blowing agent characterized in that the polyfunctional isocyanate-reactive composition comprises a polyester polyol as defined in claim 7.

cl 8

9. Process according to claim 8 wherein said polyester polyol constitutes 60 to 100 % by weight of total isocyanate-reactive compounds.

cl 9