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(54) Title: POLYURETHANE ELASTOMER

(57) Abstract: Disclosed is a novel polyurethane elastomer obtained by reacting at the least a di, tri or polyisocyanate, a polycarbonate diol of a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, an alkoxyated 2-alkyl-1,3-propanediol and/or an alkoxyated 2,2-dialkyl-1,3-propanediol and/or at least one polycarbonate diol comprising units from two or more said 1,3-propanediols, and a di, tri or polyalcohol.

POLYURETHANE ELASTOMER

The present invention relates to a polyurethane elastomer obtained by reacting at the least a minimum of three basic compounds, said compounds being a di, tri or polyisocyanate, a polycarbonate diol of a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, an alkoxyated 2-alkyl-1,3-propanediol and/or an alkoxyated 2,2-dialkyl-1,3-propanediol, and a di, tri or polyalcohol.

The properties of polyurethane elastomers are primarily determined by the chemical composition although the properties also depend on the processing methods used for production. Variation of the basic starting materials yields elastomeric products which to a large extent are characterised by a segmented, hard and soft, block structure formed by the primary chain. The hard segments are formed by the reaction of a di, tri or polyisocyanate with a di, tri or polyhydric compound. The di, tri or polyhydric compounds used in polyurethane elastomers today are mainly polyester and polyether based. The advantages with polyester based over polyethers based are structural strength, oil, solvent and oxygen resistance and the advantages with polyether based are hydrolytic resistance and low temperature flexibility. The melting temperature of the hard segment and the amount of this segment determines the dimensional thermal stability of a polyurethane elastomer. Interchain interactions (hydrogen bonds mostly) of the hard segments contribute to the high tensile strength, elongation, tear strength and set values obtained. The soft segments result from a long chain di, tri or polyalcohol and the mobility of these segments are responsible for the reversible elastomeric properties. The low temperature flexibility, solvent and UV resistance are largely controlled by the long flexible soft segments in the polyurethane elastomer. Various types of di, tri and polyalcohols have been used and/or evaluated in order to tailor the properties of elastomers. Said di, tri and polyalcohols have molecular weights usually in the range of 600-2500. Di, tri or polyalcohols typically used for polyurethane elastomers have a linear structure and two reactive hydroxyl groups. The morphology (secondary and tertiary structures) of a polyurethane elastomer is dependent on the length and chemical structure of said segments. The exceptional properties of polyurethane elastomers are due to the two or polyphase structure.

There is a pronounced need for speciality polyhydric compounds, such as polycarbonate and polycaprolactone diols, triols and polyols with, compared to polyester diols, triols and polyols, improved UV, chemical, hydrolytic, oxygen and thermal resistance, but with retained mechanical properties. Polycarbonate diols, typically polyester polycarbonate diols, have been shown to have excellent UV, chemical, hydrolytic and oxygen resistance with mechanical properties comparable to those obtained with polyester diols. Polyester polycarbonate diols are in polyurethane elastomers used to a larger extent in areas wherein produced articles are used

in applications wherein hydrolytic stability and resistance to micro-organisms are crucial, such as in outdoor tubes and pipes, sport and leisure applications, rollers for printers and paper machines.

Polycarbonate diols and polyurethanes prepared using polycarbonate diols are disclosed in for instance

- US 5,656,713 teaching thermoformable polyurethanes prepared by the reaction of an aliphatic or cycloaliphatic polyisocyanate, a polyester, polycarbonate and/or polyester carbonate diol having a molecular weight of 2000-5000 and one or more diols having a molecular weight of 90-530,
- EP 0 321 288 teaching a polyurethane-urea spandex having soft segments derived from poly(pentane-1,5-carbonate)diol, poly(hexane-1,6-carbonate)diol, copolymers thereof or mixtures thereof, and
- US 4,463,141 teaching polyether carbonate diols obtained from poly(tetramethylene ether)glycol and a dialkyl carbonate, which diols are useful in preparing polyurethane,

The present invention quite unexpectedly provides a polyurethane elastomer with improved properties over prior art elastomers. The polyurethane elastomer of the present invention is obtained by reacting at the least a di, tri or polyisocyanate, a polycarbonate diol of a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, an alkoxyated 2-alkyl-1,3-propanediol, an alkoxyated 2,2-dialkyl-1,3-propanediol and/or a polycarbonate diol comprising units from two or more said 1,3-propanediols, and a di, tri or polyalcohol. Di, tri and polyalcohol are herein to be understood as linear or branched, aliphatic, cycloaliphatic or aromatic di, tri and polyhydric alcohols and dimers, trimers and polymers comprising units from one or more di, tri or polyhydric alcohols and/or one or more alkylene oxides. Alkyl in said 1,3-propanediols is preferably linear or branched saturated aliphatic alkanyl having 1-8 carbon atoms and alkoxyated is likewise preferably ethoxyated, propoxyated and/or butoxyated having 1-20 alkoxy units.

Said polycarbonate diol is most preferably at least one polycarbonate diol of 2-methyl-1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol and/or is at least one polycarbonate diol comprising units from two or more said 1,3-propanediols. Said polycarbonate diol has in preferred embodiments a molecular weight of 500-5000, such as 500-2500 and can suitably be obtained from for example one or more of said 1,3-propanediols and a carbon dioxide source, such as dimethyl carbonate, diethyl carbonate and/or urea.

The di, tri or polyisocyanate is in preferred embodiments an aliphatic, cycloaliphatic and/or aromatic di, tri or polyisocyanate, such as hexamethylene diisocyanate 2,4-toluene

diisocyanate, 2,6-toluene diisocyanate, tetramethylxylylene diisocyanate, 1,6-hexane diisocyanate, trimethylhexane diisocyanate, 1,12-dodecane diisocyanate, cyclohexane diisocyanate, diphenylmethane diisocyanate, isophorone diisocyanate and/or nonane triisocyanate.

Said di, tri or polyalcohol as defined above is preferably at least one 1, ω -diol, 2-alkyl-1,3-propanediol, 2,2-dialkyl-1,3-propanediol, 2-alkyl-2-hydroxyalkyl-1,3-propanediol and/or 2,2-di(hydroxyalkyl)-1,3-propanediol and/or at least one dimer, trimer or polymer of a said di, tri or polyalcohol and/or a reaction product between at least one alkylene oxide, such as ethylene oxide, propylene oxide, 1,3-butylene oxide, 2,4-butylene oxide, cyclohexene oxide, butadiene monoxide and/or phenylethylene oxide, and at least one 1, ω -diol, 2-alkyl-1,3-propanediol, 2,2-dialkyl-1,3-propanediol, 2-alkyl-2-hydroxyalkyl-1,3-propanediol and/or 2,2-di(hydroxyalkyl)-1,3-propanediol and/or at least one dimer, trimer or polymer of a said di, tri or polyalcohol. The preferred di, tri and polyalcohols can suitably be exemplified by 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,6-cyclohexanedimethanol, 5,5-dihydroxymethyl-1,3-dioxane, 2-methyl-1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, dimethylolpropane, 1,1-dimethylolcyclohexane, glycerol, trimethylolethane, trimethylolpropane, diglycerol, ditrimethylolethane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, anhydroenneaheptitol, sorbitol, mannitol and ethoxylated and/or propoxylated glycerol, trimethylolethane, trimethylolpropane, diglycerol, ditrimethylolethane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, anhydroenneaheptitol, sorbitol and/or mannitol.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilise the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever. In the following, Example 1 refer to preparation of a prepolymer inside the scope of the present invention, which prepolymer is used in Examples 2-4 for preparation of embodiments of the present elastomer. Example 5 refer to preparation of a prepolymer outside the scope of the present invention, which prepolymer is used in Examples 6 and 7 for preparation of reference elastomers. The elastomers obtained in Examples 2-4, 6 and 7 are evaluated in Examples 8-10. Example 11 refers to preparation of a prepolymer inside the scope of the present invention and Examples 12-15 refer to preparation of reference prepolymers outside the scope of the present invention. The prepolymers of Examples 11-15 are used in Example 16 for preparation of embodiment and reference elastomers, which elastomers are evaluated in Examples 17, 18 and 19. The result of evaluations of embodiment and reference elastomers are given in Tables 1-6.

Example 1

287.30 g of a 2-butyl-2-ethyl-1,3-propanediol polycarbonate diol having a molecular weight of 1000 (Oxymer™ B112, Perstorp Specialty Chemicals AB, Sweden) was charged in a reaction vessel equipped with a thermometer, an agitator, a vacuum device, a heating device and a cooling device, and under stirring heated to 70°C. The polycarbonate diol was degassed for 10 min. and 112.70 g of isophorone diisocyanate was drop wise during 1 hour charged to the reaction vessel. Initially a few drops of dibutyltin dilaurate were as catalyst added. The reaction temperature was after said one hour raised to 120°C and the reaction was allowed to continue for a further 2 hours, whereafter obtained prepolymer was degassed, cooled and recovered.

A colourless waxy substance having the following characteristics was obtained:

Glass transition temperature (T _g), °C	0
Molecular weight (M _n)	1603
Isocyanate content, %	5.33

Example 2

30 g of the prepolymer obtained in Example 1 was heated to 120°C and degassed to remove all air. A stoichiometric amount of 1,4-butandiol was now added to the prepolymer for reaction with available free isocyanate groups. Obtained polyurethane elastomer was subsequently cured at 122°C for 24 hours.

Example 3

30 g of the prepolymer obtained in Example 1 was heated to 120°C and degassed to remove all air. A stoichiometric amount of a mixture of 1,4-butandiol and trimethylolpropane (1:1 by weight) was now added to the prepolymer for reaction with available free isocyanate groups. Obtained polyurethane elastomer was subsequently cured at 122°C for 24 hours.

Example 4

30 g of the prepolymer obtained in Example 1 was heated to 120°C and degassed to remove all air. A stoichiometric amount of an polyethoxylated trimethylolpropane, having an average of 3 ethylene oxide units per molecule (Polyol 3610™, Perstorp Specialty Chemicals AB, Sweden), was now added to the prepolymer for reaction with available free isocyanate groups. Obtained polyurethane elastomer was subsequently cured at 122°C for 24 hours.

Example 5 (Reference)

Example 1 was repeated with the difference that ethylene glycol adipate, having a molecular weight of 1000, was used instead of said 2-butyl-2-ethyl-1,3-propanediol polycarbonate diol.

Example 6 (Reference)

Examples 2 was repeated with the difference that the prepolymer of Example 5 was used instead of the prepolymer of Example 1.

Example 7 (Reference)

Examples 3 was repeated with the difference that the prepolymer of Example 5 was used instead of the prepolymer of Example 1.

Example 8

Chemical resistance of the elastomers prepared in Examples 2-4 and 5-7 (Reference) were evaluated with the "spot test" or "watch glass" method. Chemicals used were acetone, hydraulic pump oil, 50% aq. sulphuric acid and 50% aq. sodium hydroxide. Damages such as swelling, discolouration and/or cracking, were visually evaluated after 12, 24, 36, 48 and 60 hours and graded on a scale 0-3, wherein 0 = no visible damages, 1 = slightly visible damages, 2 = distinctly visible damages and 3 = heavy damages. The result is given i Table 1 below.

Example 9

Shore durometer hardness test were performed on the elastomers prepared in Examples 2-4 and 5-7 (Reference). Elastomers according to the present invention (Examples 2-4) were all harder than corresponding polyester based elastomers (references). The shore A values are given in Table 2 below.

Example 10

Thermal properties, glass transition temperature (T_g), of the elastomers prepared in Examples 2-4 and 5-7 (Reference) were measured with DSC at 10°C/min. Elastomers according to the present invention (Examples 2-4) all exhibited a higher T_g than corresponding polyester based elastomers (references). The T_g values are given in Table 3 below.

Example 11

181.99 g of 1,6-hexamethylene diisocyanate together with a few drops of dibutyltin dilaurate as catalyst was charged in a reaction vessel equipped with a thermometer, an agitator, a vacuum device, a heating device, a cooling device and nitrogen purge and heated to 60°C. The temperature was thereafter raised to 70°C and a drop-wise charging of 542.01 g 2-butyl-2-ethyl-1,3-propanediol polycarbonate having a molecular weight of 1000 (Oxymer™ B112, Perstorp Specialty Chemicals AB, Sweden) commenced. The reaction temperature was, after one hour when all polycarbonate diol was charged, raised to 80°C and the reaction was allowed to continue for a further 2 hours. Obtained prepolymer was finally degassed, recovered and cooled.

A colourless waxy substance having the following characteristics was obtained:

Glass transition temperature (T _g), °C	-22
Molecular weight (M _n)	2200
Isocyanate content, %	5.0

Example 12 (Reference)

Example 11 was repeated with the difference that 1,6-hexanediol polycarbonate (Desmophen™ XP 2586, Bayer MaterialScience, Germany) was used instead of said 2-butyl-2-ethyl-1,3-propanediol polycarbonate diol.

Example 13 (Reference)

Example 11 was repeated with the difference that an adipic acid-ethylene glycol copolymer (Fomrez™ 22-112, Crompton Uniroyal Chemical, Great Britain) was used instead of said 2-butyl-2-ethyl-1,3-propanediol polycarbonate diol.

Example 14 (Reference)

Example 11 was repeated with the difference that a poly(tetramethylene ether) glycol (Terathane™ 1000, Invista, USA) was used instead of said 2-butyl-2-ethyl-1,3-propanediol polycarbonate diol.

Example 15 (Reference)

Example 11 was repeated with the difference that a linear polyester caprolactone (Capa™ 2101A, Solvay, Belgium) was used instead of said 2-butyl-2-ethyl-1,3-propanediol polycarbonate diol.

Example 16

180 g of the prepolymer obtained in Example 11 was heated to 90°C and degassed to remove all air. A stoichiometric amount of an 1,4-butanediol was now added to the prepolymer for reaction with available free isocyanate groups. The reaction mixture was degassed a second time before poured into a mould. Obtained polyurethane elastomer was subsequently cured at 120°C for 24 hours. The moulded product was thereafter removed from the mould and post cured for one week at 23°C and 50 % relative humidity.

Reference materials were in the same way prepared from the prepolymers obtained in reference Examples 12-15.

Obtained polyurethane elastomers had following measurement: 245x160x4 mm.

Example 17

Three different samples, from each elastomer obtained in Example 16, were cut out (Cutting Die Type ISO 37-2) for tensile testing. The hardness of the samples was measured with a Shore A Durometer and the result is given in Table 4 below.

Example 18

Three samples, from each elastomer obtained in Example 16, were cut out (Cutting Die Type ISO 37-2) for hydrolysis resistance testing. The specimens were aged for 14 days at 70°C and 95 % relative humidity in a climate chamber. The hardness of the samples was measured with a Shore A Durometer after the testing and compared to the original values as given in Table 4.

The result in percent of said original values are given in Table 5 below.

Example 19

Three samples, from each elastomer obtained in Example 16, were cut out (Cutting Die Type ISO 37-2) for weather resistance testing. The weather resistance was simulated with

accelerated QUV testing according to the following scheme: QUV-A: 4h UV at 60°C, 4h condensation at 50°C, total run time 1000 hours. The retained mechanical properties were determined with a shore A Durometer and tensile testing machine and compared to the original values as given in Table 4.

None of the samples cut out from the elastomer obtained in Example 14 Ref. withstood the QUV and could accordingly not be subsequently tested. Only sample cut out from the elastomer obtained in Example 15 and only two sample cut out from the elastomer obtained in Example 13 Ref. could be tested after the weathering.

The result in percent of said original values are given in Table 6 below.

Table 1

Elastomer acc. Ex. 2	Exposure (hours)				
	12	24	36	48	60
Acetone	1	3	3	3	3
Hydraulic pump oil	0	0	0	0	0
Sulphuric acid 50%	0	0	0	1	1
Sodium hydroxide 50%	0	0	0	0	0

Elastomer acc. Ex. 3	Exposure (hours)				
	12	24	36	48	60
Acetone	2	3	3	3	3
Hydraulic pump oil	0	0	0	0	0
Sulphuric acid 50%	0	0	0	1	1
Sodium hydroxide 50%	0	0	0	0	0

Elastomer acc. Ex. 4	Exposure (hours)				
	12	24	36	48	60
Acetone	0	2	3	3	3
Hydraulic pump oil	0	0	0	0	0
Sulphuric acid 50%	0	0	0	0	0
Sodium hydroxide 50%	0	0	0	0	0

Elastomer acc. Ex. 5 (Ref.)	Exposure (hours)				
	12	24	36	48	60
Acetone	1	3	3	3	3
Hydraulic pump oil	0	0	0	0	0
Sulphuric acid 50%	1	2	3	3	3
Sodium hydroxide 50%	0	0	1	2	2

Elastomer acc. Ex. 6 (Ref.)	Exposure (hours)				
	12	24	36	48	60
Acetone	1	3	3	3	3
Hydraulic pump oil	0	0	0	0	0
Sulphuric acid 50%	1	2	3	3	3
Sodium hydroxide 50%	0	0	2	2	2

Elastomer acc. Ex. 7 (Ref.)	Exposure (hours)				
	12	24	36	48	60
Acetone	1	3	3	3	3
Hydraulic pump oil	0	0	0	0	0
Sulphuric acid 50%	1	2	3	3	3
Sodium hydroxide 50%	0	0	2	2	3

Table 2

Sample	Shore A
Elastomer acc. to Example 2	56 ± 9
Elastomer acc. to Example 3	91 ± 3
Elastomer acc. to Example 4	91 ± 5
Elastomer acc. to Example 5 (Reference)	46 ± 6
Elastomer acc. to Example 6 (Reference)	61 ± 1
Elastomer acc. to Example 7 (Reference)	62 ± 5

Table 3

Sample	Tg, °C
Elastomer acc. to Example 2	14
Elastomer acc. to Example 3	16

Elastomer acc. to Example 4	15
Elastomer acc. to Example 5 (Reference)	-20
Elastomer acc. to Example 6 (Reference)	-18
Elastomer acc. to Example 7 (Reference)	-23

Table 4

Elastomer according to Example	Hardness shore A	E-modulus MPa	Stress at 10% strain, %	Max stress MPa	Elongation %
11	52 ± 4	1.5 ± 0.1	0.1 ± 0.0	3.3 ± 0.8	600 ± 60
12 (Ref.)	91 ± 1	38 ± 2	2.6 ± 0.2	27 ± 2	800 ± 40
13 (Ref.)	93 ± 1	43 ± 1	2.3 ± 0.0	27 ± 7	1300 ± 300
14 (Ref.)	92 ± 1	46 ± 1	2.7 ± 0.1	14 ± 2	800 ± 150
15 (Ref.)	94 ± 0	49 ± 1	2.8 ± 0.1	16 ± 1	800 ± 90

Table 5

Elastomer according to Example	Hardness %	E-modulus %	Max stress %	Elongation %	Weight %
11	-8.8	5.8	-33	29	-5.4
12 (Ref.)	-5.9	5	29	33	0.8
13 (Ref.)	-1.5	-42	-80	-95	2.3
14 (Ref.)	-1.3	-25	12	20	1.2
15 (Ref.)	-1.6	-23	-18	5	1.4

Table 6

Elastomer according to Example	Hardness %	E-modulus %	Max stress %	Elongation %	Weight %
11	-16.9	7.5	-75.6	-74.3	-7.4
12 (Ref.)	-5.6	-37.0	-78.0	-70.0	-0.5
13 (Ref.)	-10.0	-65.0	-94.0	-98.0	-0.3
14 (Ref.)	---	----	---	---	---
15 (Ref.)	-12.0	-69.0	-98.0	-98.0	-0.1

CLAIMS

1. A polyurethane elastomer obtained by reacting at the least a di, tri or polyisocyanate, a polycarbonate diol and a di, tri or polyalcohol characterised in, that said polycarbonate diol is at least one polycarbonate diol of a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, an alkoxyated 2-alkyl-1,3-propanediol and/or an alkoxyated 2,2-dialkyl-1,3-propanediol and/or is at least one polycarbonate diol comprising units from two or more said 1,3-propanediols, wherein alkyl is a linear or branched aliphatic alkanyl having 1-8 carbon atoms and alkoxyated is ethoxyated, propoxyated and/or butoxyated having 1-20 alkoxy units.
2. A polyurethane elastomer according to Claim 1 characterised in, that said polycarbonate diol is at least one polycarbonate diol of 2-methyl-1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol and/or is at least one polycarbonate diol comprising units from two or more said 1,3-propanediols.
3. A polyurethane elastomer according to Claim 1 or 2 characterised in, that said polycarbonate diol is obtained from one or more of said 1,3-propanediols and a carbon dioxide source, such as dimethyl carbonate, diethyl carbonate and/or urea.
4. A polyurethane elastomer according to any of the Claims 1-3 characterised in, that said polycarbonate diol has a molecular weight of 500-5000, such as 500-2500.
5. A polyurethane elastomer according to any of the Claims 1-4 characterised in, that said di or polyisocyanate is an aliphatic, cycloaliphatic and/or aromatic di, tri or polyisocyanate
6. A polyurethane elastomer according to any of the Claims 1-5 characterised in, that said di or polyisocyanate is hexamethylene diisocyanate, 2,4-toluenediisocyanate, 2,6-toluenediisocyanate, tetramethylxylylene diisocyanate, 1,6-hexanediisocyanate, trimethylhexanediisocyanate, 1,12-dodecanediisocyanate, cyclohexanediisocyanate, diphenylmethanediisocyanate, isophoronediisocyanate and/or nonane triisocyanate.
7. A polyurethane elastomer according to any of the Claims 1-6 characterised in, that said di, tri or polyalcohol is at least one 1, ω -diol, 2-alkyl-1,3-propanediol, 2,2-dialkyl-1,3-propanediol, 2-alkyl-2-hydroxyalkyl-1,3-propanediol and/or 2,2-di(hydroxyalkyl)-1,3-propanediol and/or at least one dimer, trimer or polymer of a said di, tri or polyalcohol.

8. A polyurethane elastomer according to any of the Claims 1-6 characterised in, that said di, tri or polyalcohol is a reaction product between at least one alkylene oxide and at least one 1, ω -diol, 2-alkyl-1,3-propanediol, 2,2-dialkyl-1,3-propanediol, 2-alkyl-2-hydroxyalkyl-1,3-propanediol and/or 2,2-di(hydroxyalkyl)-1,3-propanediol and/or at least one dimer, trimer or polymer of a said di, tri or polyalcohol.
9. A polyurethane elastomer according to Claim 8 characterised in, that said alkylene oxide is ethylene oxide, propylene oxide, 1,3-butylene oxide, 2,4-butylene oxide, cyclohexene oxide, butadiene monoxide and/or phenylethylene oxide.
10. A polyurethane elastomer according to any of the Claims 1-6 characterised in, that said di, tri or polyalcohol is 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,6-cyclohexanedimethanol, 5,5-dihydroxymethyl-1,3-dioxane, 2-methyl-1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, dimethylolpropane, 1,1-dimethylolcyclohexane, glycerol, trimethylolethane, trimethylolpropane, diglycerol, ditrimethylolethane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, anhydroenneaheptitol, sorbitol and/or mannitol.
11. A polyurethane elastomer according to any of the Claims 1-6 characterised in, that said di, tri or polyalcohol is an ethoxylated and/or a propoxylated glycerol, trimethylolethane, trimethylolpropane, diglycerol, ditrimethylolethane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, anhydroenneaheptitol, sorbitol and/or mannitol.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE2006/001145

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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)

IPC: C08G

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

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5284928 A (MÜNZMAY ET AL), 8 February 1994 (08.02.1994), see example 1 and 2 --	1-11
A	US 20040131863 A1 (BELLIVEAU, BRIAN PETER ET AL), 8 July 2004 (08.07.2004), see claims 19 and 20 --	1-11
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A	US 20020009599 A1 (WELCH, CLETUS N. ET AL), 24 January 2002 (24.01.2002), see claim 1 --	1-11

 Further documents are listed in the continuation of Box C. See patent family annex.

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INTERNATIONAL SEARCH REPORT

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PCT/SE2006/001145

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5993972 A (REICH, MURRAYH ET AL), 30 November 1999 (30.11.1999), see example 84 -- -----	1-11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2006/001145

International patent classification (IPC)

C08G 18/44 (2006.01)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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