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(54) **Title**: HIGHLY THERMALLY AND HYDROLYTICALLY RESISTANT POLYCARBONATE POLYOL

(57) **Abstract**: The present invention relates to highly thermally and hydrolytically resistant polycarbonate polyols and their use for the production of thermoplastic polyurethanes and polyurethane dispersions.

Highly thermally and hydrolytically resistant polycarbonate polyol

The present invention relates to highly thermally and hydrolytically resistant polycarbonate polyols and their use for the production of polyurethane dispersions and thermoplastic elastomers.

Polycarbonate polyols prepared from aliphatic polyalcohols, mainly from α,ω-alkane diols, for example 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol etc., are sold as polyols which can be used for the preparation of polyurethanes, for example thermoplastic polyurethanes, fibers, polyurethane foams, polyurethane dispersions for coatings, adhesives, binders for leather and textile applications as well as sealants, building up flexible segments which have excellent resistance to thermal aging, hydrolysis, light and oxidative degradation. This resistance is due to the fact that carbonate linkages in the polymer chain exhibit extremely high chemical stability.

Thermoplastic polyurethanes in particular are used for injection molding applications and, accordingly, have to withstand high temperatures and hydrolysis during service lifetime. Polyurethane dispersions as well as coatings, adhesives, sealants as well as artificial textiles and leather made of such dispersions have to withstand hydrolysis upon storage and during the service lifetime.

EP-A 1 288 241 describes special aliphatic polycarbonate polyols which are manufactured with the aid of especially pure α,ω-pentane and/or -hexane diols having very high content of primary hydroxyl groups. These polycarbonate polyols are, according to the teaching of EP-A 1 288 241, advantageous for thermoplastic polyurethanes. The content of the primary hydroxyl groups of these aliphatic polycarbonate polyols is determined from the thermally cleaved organic substances which are obtained in a vacuum upon thermal treatment of a polycarbonate polyol specimen at 160 to 200°C and subsequently analyzed by chromatography for secondary group containing alcohols. The amount of cleaved organic substances corresponds to approximately 10% of the whole terminal alcohol groups, thus demonstrating the insufficient thermal stability of polycarbonate polyols in the temperature range of 160 to 200°C. Such polycarbonate polyols cannot therefore be used for polyurethanes having excellent thermal stability.

Thus, there was a need to provide novel polycarbonate polyol(s) having a very low level of special admixtures (below referred to as mixtures of polycarbonate polyols or mixture), which can be used for the preparation of thermoplastic polyurethane elastomers and polyurethane dispersions that show excellent resistance to high temperatures, light and oxidative degradation as well as resistance to hydrolysis.

Consequently, one object of the presently claimed is to provide novel mixtures of polycarbonate polyols which can be used for the preparation of polyurethanes in general and thermoplastic polyurethanes and polyurethane dispersions in particular that show excellent resistance to high temperatures, light and oxidative degradation as well as resistance to hydrolysis.

The object was met by the provision of a mixture comprising polycarbonate polyol having a decomposition temperature of > 180 °C at 1 mbar which contains altogether a low amount of amines (R_3N, R represents, independent of each other, H or a C_1 to C_{30} alkyl group) and/or ammonium ions (R_4N^+, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group), alkali metal atoms and/or ions, earth alkali metal atoms and/or ions, metals and/or ions of the 13th through 15th Group of the Periodic Table of the Elements (i.e. metals from Boron, Carbon and Nitrogen Group), and transition metal atoms and/or ions of the 4th through 12th Group of the Periodic Table of the Elements in relation to the total weight of the polycarbonate polyol and the pH value of the 10 wt.% slurry of this mixture in water lies in the range from 5.0 to 8.0.

In one aspect the present invention is directed to a mixture comprising at least one polycarbonate polyol having a decomposition temperature of > 180 °C at 1 mbar comprising recurring units each independently represented by the following formula (1),

-O-R-O-C(=O)- (1),

wherein R represents substituted or unsubstituted, linear or branched, alkylene having 2 to 30 carbon atoms or substituted or unsubstituted arylalkylene having 6 to 30 carbon atoms or substituted or unsubstituted heteroarylalkylene having 6 to 30 carbon atoms or substituted or unsubstituted cyclylalkylene having 6 to 30 carbon atoms or substituted or unsubstituted heterocyclylalkylene having 6 to 30 carbon atoms,

and

terminal hydroxyl groups,

whereby the sum of the weight contents of amines (R_3N, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group) and/or ammonium ions (R_4N^+, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group), metal atoms and/or metal ions and/or metal compounds comprising metal in the respective oxidation state selected from the group consisting of Li, Li^+, Na, Na^+, K, K^+, Ca, Ca^{2+}, Sr, Sr^{2+}, Mg, Mg^{2+}, Ba, Ba^{2+}, Al, Al^{3+}, Ga, Ga^{3+}, In, In^{3+}, Tl, Tl^+, Ge, Ge^{2+}, Ge^{4+}, Sn, Sn^{4+}, Pb, Pb^{2+}, Pb^{4+}, Sb, Sb^{3+}, Sb^{5+}, Bi, Bi^{3+}, Ti, Ti^{3+}, Ti^{4+}, Zr, Zr^{4+}, Hf, Hf^{4+}, V, V^{2+}, V^{3+}, V^{4+}, V^{5+}, Nb, Nb^{3+}, Nb^{5+}, Ta, Ta^{3+}, Ta^{5+}, Cr, Cr^{2+}, Cr^{3+}, Cr^{6+}, Mo, Mo^{4+}, Mo^{6+}, W, W^{3+}, W^{4+}, W^{6+}, Mn, Mn^{2+}, Mn^{3+}, Mn^{4+}, Mn^{7+}, Re, Re^{3+}, Re^{4+}, Re^{6+}, Re^{7+}, Fe, Fe^{2+}, Fe^{3+}, Co, Co^{2+}, Co^{3+}, Ni, Ni^{2+}, Ru, Ru^{2+}, Ru^{3+}, Rh, Rh^{3+}, Pd, Pd^{2+}, Os, Os^{4+}, Ir, Ir^{3+}, Ir^{4+}, Pt, Pt^{2+}, Pt^{4+}, Cu, Cu^+, Cu^{2+}, Ag, Ag^+, Au, Au^+, Au^{3+}, Zn, Zn^{2+}, Cd, Cd^{2+}, Hg, Hg^+ and Hg^{2+} is in the range of 0,1 to 20 ppm in relation to the total weight of the

polycarbonate polyol and the pH-value of a 10 wt.% slurry of this mixture in water lies in the range from 5.0 to 8.0.

The content of metal atoms, metal ions and metal compounds is, for example, quantitatively or semi-quantitatively determined by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) using, for example, a Spectroflame P instrument (Spectro, Germany). Any other quantitative analysis capable of determining very low amounts of metals may, of course, be used.

The pH of the polycarbonate polyol comprising mixture is measured at a 10 wt.% slurry of the mixture comprising polycarbonate polyol which was obtained by vigorous agitation of the mixture with deionized water at room or at elevated temperature of up to 95 °C for 30 minutes under an inert atmosphere, cooling the slurry down to room temperature, if necessary, and making the pH measurement of the aqueous phase at room temperature.

The decomposition temperature is defined as the temperature at which the weight of a measured, dried sample of polycarbonate polyol which is free of volatile organic compounds decreases by at least 0.1 wt.-%, that is, the weight of the sample becomes less than 99.9 wt.-% during heating under reduced pressure for at least 4 hours, assuming the weight of the measured, dried sample which is free of volatile organic compounds at the start of measurement to be 100 wt.-%.

Preferably the polycarbonate polyol has a decomposition temperature of > 200 °C at a pressure of 1 mbar. More preferably the polycarbonate polyol has a decomposition temperature of > 210 °C at a pressure of 1 mbar.

Even more preferably, the polycarbonate polyol has a decomposition temperature of >180°C at a pressure of 0.1 mbar. Particularly preferably, the polycarbonate polyol has a decomposition temperature of >200°C at a pressure of 0.1 mbar.

Alkylene group R of formula (1) is derived from a hydrocarbon chain, preferably alkylene chain of a diol, as a constituent of the polycarbonate polyol according to the present invention. The hydrocarbon chain is a multivalent, preferably divalent saturated hydrocarbon chain having 2 to 30 carbon atoms, preferably 3 to 16 carbon atoms, more preferably 4 to 12 carbon atoms. Alkylene groups may be linear or branched. Preferred branched alkylene groups have one or two branches, preferably one branch. Alkylene groups may furthermore contain incorporated cycloaliphatic or cycloaromatic groups.

Alkylene groups including C_{2-30} alkylene, C_{3-16} alkylene and C_{4-12} alkylene may each be unsubstituted or substituted with 1, 2, 3, 4 or 5 substituent(s) selected from the group consisting of -

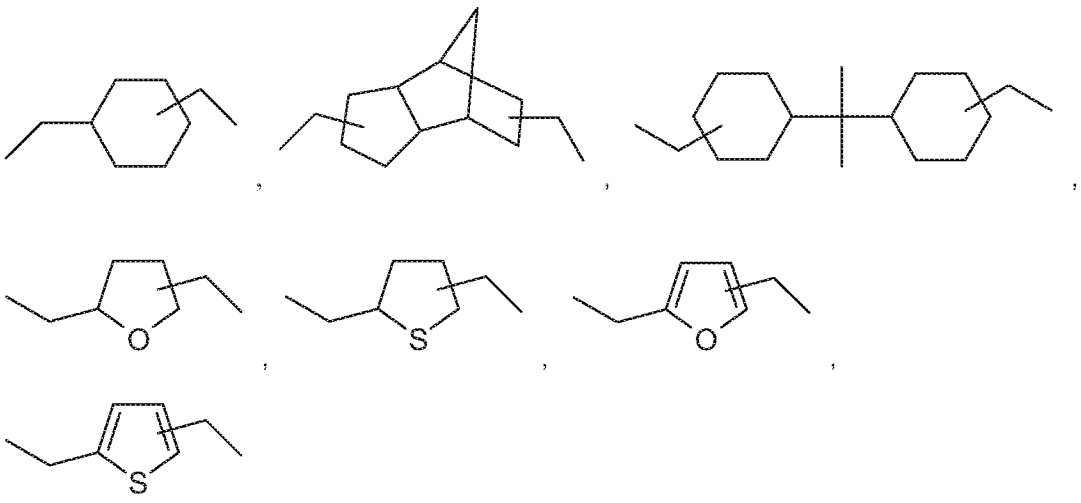
O-C_{1-18}-alkyl, -S-C_{1-18}-alkyl, -F, Cl, Br, I, -CN, -CF_3, -OCF_3, -SCF_3, -OH, -SH, - SO_3H, C_{6-30}–aryl and C_{6-30}-arylalkyl.

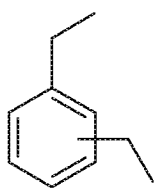
Alkylene groups including C_{2-30} alkylene, C_{3-16} alkylene and C_{4-12} alkylene may be unsubstituted or substituted with 1, 2, 3, 4 or 5 substituent(s) preferably selected from the group consisting of -F, Cl, Br, I, -CN, -CF_3, -OCF_3, -SCF_3, -OH, -SH, - SO_3H, -O-CH_3, -O-C_2H_5, -O-C_3H_7, -O-C_4H_9, -O-C_5H_{11}, -O-C_6H_{13} and -O-R, wherein R represents C_7-C_{30} alkyl groups, C_6-C_{30} aryl groups, C_6-C_{30} arylalkyl groups, -S-CH_3, -S-C_2H_5, -S-C_3H_7, -S-C_4H_9, -S-C_5H_{11}, -S-C_6H_{13} and -S-R, wherein R represents C7-C30 alkyl groups, C_6-C_{30} aryl groups, C_6-C_{30} arylalkyl groups.

Suitable alkylene groups, preferably C_{3-16}-alkylene groups, include -$(CH_2)_3$-, -$(CH_2)_4$-,-$(CH_2)_5$-, -$(CH_2)_6$-, -$(CH_2)_7$-, -$(CH_2)_8$-, -$(CH_2)_9$-, -$(CH_2)_{10}$-, -$(CH_2)_{11}$-, -$(CH_2)_{12}$-, -$(CH_2)_{13}$-, -$(CH_2)_{14}$-, -$(CH_2)_{15}$-, -$(CH_2)_{16}$- .

Alkylene group R in formula (1) represents preferably linear or branched alkylene having 3 to 16 carbon atoms. More preferably R represents linear or branched alkylene having 4 to 12 carbon atoms. Particularly preferred are -$(CH_2)_4$-, -$(CH_2)_5$-, -$(CH_2)_2$-$(CHCH_3)$-$(CH_2)_2$-, and/or -$(CH_2)_6$-.

Suitable arylalkylene, heteroarylalkylene, cyclylalkylene and heterocyclylalkylene groups include those isomers according to formulae (2) as depicted below:





(2)

"Cyclyl" means a non-aromatic mono-or multicyclic ring system comprising about 3 to about 12 carbon atoms, preferably about 5 to about 10 carbon atoms. Preferred cycloalkyl rings contain about 5 to about 7 ring atoms. The cycloalkyl can be optionally substituted with one or more "ring system substituents" which may be the same or different, and are as defined herein. Non-limiting examples of suitable monocyclic cycloalkyls include cyclopropyl, cyclopentyl, cyclohexyl, cycloheptyl and the like. Non-limiting examples of suitable multicyclic cycloalkyls include 1-decalinyl, norbornyl, adamantyl and the like, as well as partially saturated species such as, for example, indanyl, tetrahydronaphthyl and the like.

"Aryl" means an aromatic monocyclic or multicyclic ring system comprising about 6 to about 14 carbon atoms, preferably about 6 to about 10 carbon atoms. The aryl group can be optionally substituted with one or more "ring system substituents" which may be the same or different, and are as defined herein. Non-limiting examples of suitable aryl groups include phenyl and naphthyl.

"Aralkyl" means an aryl group, as defined above, that is bound to an alkyl group.

"Heteroaryl" means an aromatic monocyclic or multicyclic ring system comprising about 5 to about 14 ring atoms, preferably about 5 to about 10 ring atoms, in which one or more of the ring atoms is an element other than carbon, for example oxygen or sulfur, alone or in combination. Preferred heteroaryls contain about 5 to about 6 ring atoms. The "heteroaryl" can be optionally substituted by one or more "ring system substituents" which may be the same or different, and are as defined herein. The prefix oxa or thia before the heteroaryl root name means that at least an oxygen or sulfur atom respectively, is present as a ring atom. "Heteroaryl" may also include a heteroaryl as defined above fused to an aryl as defined above. Non-limiting examples of suitable heteroaryls include furanyl, thienyl, benzofuranyl, benzothienyl.

"Heterocyclyl" means a non-aromatic saturated monocyclic or multicyclic ring system comprising about 3 to about 10 ring atoms, preferably about 5 to about 10 ring atoms, in which one or more of the atoms in the ring system is an element other than carbon, for example oxygen or sulfur, alone or in combination. There are no adjacent oxygen and/or sulfur atoms present in the ring system. Preferred heterocyclyls contain about 5 to about 6 ring atoms. The prefix oxa or thia before the heterocyclyl root name means that at least a nitrogen, oxygen or sulfur atom respectively is present as a ring atom. The heterocyclyl can be optionally substituted by one or more "ring system substituents" which may be the same or different, and are as defined herein. Sulfur atom of the heterocyclyl can be optionally oxidized to the corresponding S-oxide or S,S-dioxide. Non-limiting

examples of suitable monocyclic heterocyclyl rings include 1,4-dioxanyl, tetrahydrofuranyl, tetrahydrothiophenyl, lactone, and the like.

"Heteroarylalkylene" means a heteroaryl group, as defined above, that is bound to an alkylene group or is part of an alkylene group, as defined above, wherein said alkylene group is bound to the rest of the molecule.

"Cyclylalkylene" means a cyclyl group, as defined above, that is bound to an alkylene group or is part of an alkylene group, as defined above, wherein said alkylene group is bound to the rest of the molecule.

"Arylalkylene" means an aryl group, as defined above, that is bound to an alkylene group or is part of an alkylene group, as defined above, wherein said alkylene group is bound to the rest of the molecule.

"Heterocyclylalkylene" means a heterocyclyl group, as defined above, that is bound to an alkylene group or is part of an alkylene group, as defined above, wherein said alkylene group is bound to the rest of the molecule.

"Ring system substituent" means a substituent attached to an aromatic or non-aromatic ring system which, for example, replaces available hydrogen on the ring system. Ring system substituents may be the same or different, each being independently selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, heteroaryl, aralkyl, alkylaryl, heteroaralkyl, heteroarylalkenyl, heteroarylalkynyl, alkylheteroaryl, hydroxy, hydroxyalkyl, alkoxy, aryloxy, aralkoxy, acyl, aroyl, halo, nitro, cyano, carboxy, alkoxycarbonyl, aryloxycarbonyl, aralkoxycarbonyl, alkylsulfonyl, arylsulfonyl, heteroarylsulfonyl, alkylthio, arylthio, heteroarylthio, aralkylthio, heteroaralkylthio, cycloalkyl, heterocyclyl, and $SO_2Y_1Y_2$, wherein Y_1 and Y_2 can be the same or different and are independently selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, and aralkyl. "Ring system substituent" may also mean a single moiety which simultaneously replaces two available hydrogens on two adjacent carbon atoms (one H on each carbon) on a ring system. Examples of such moiety are methylene dioxy, ethylenedioxy, and —$C(CH_3)_2$—.

"Ring system substituent" also includes substituents off of an heterocyclyl ring, wherein said substituents on adjacent carbon atoms, on a carbon atom and an adjacent heteroatom, or on a single carbon atom, together with the carbon atom(s) and/or the combination of the carbon atom and the adjacent heteroatom to which said substituents are attached, form a four to seven-membered cycloalkyl, cycloalkenyl, heterocyclyl, aryl or heteroaryl ring.

Preferably the sum of the weight contents of amines (R_3N, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group) and/or ammonium ions (R_4N^+, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group), metal atoms and/or metal ions and/or metal compounds comprising metal in the respective oxidation state selected from the group consisting of Li, Li^+, Na, Na^+, K, K^+, Ca, Ca^{2+}, Sr, Sr^{2+}, Mg, Mg^{2+}, Ba, Ba^{2+}, Al, Al^{3+}, Ga, Ga^{3+}, In, In^{3+}, Tl, Tl^+, Ge, Ge^{2+}, Ge^{4+}, Sn, Sn^{4+}, Pb, Pb^{2+}, Pb^{4+}, Sb, Sb^{3+}, Sb^{5+}, Bi, Bi^{3+}, Ti, Ti^{3+}, Ti^{4+}, Zr, Zr^{4+}, Hf, Hf^{4+}, V, V^{2+}, V^{3+}, V^{4+}, V^{5+}, Nb, Nb^{3+}, Nb^{5+}, Ta, Ta^{3+}, Ta^{5+}, Cr, Cr^{2+}, Cr^{3+}, Cr^{6+}, Mo, Mo^{4+}, Mo^{6+}, W, W^{3+}, W^{4+}, W^{6+}, Mn, Mn^{2+}, Mn^{3+}, Mn^{4+}, Mn^{7+}, Re, Re^{3+}, Re^{4+}, Re^{6+}, Re^{7+}, Fe, Fe^{2+}, Fe^{3+}, Co, Co^{2+}, Co^{3+}, Ni, Ni^{2+}, Ru, Ru^{2+}, Ru^{3+}, Rh, Rh^{3+}, Pd, Pd^{2+}, Os, Os^{4+}, Ir, Ir^{3+}, Ir^{4+}, Pt, Pt^{2+}, Pt^{4+}, Cu, Cu^+, Cu^{2+}, Ag, Ag^+, Au, Au^+, Au^{3+}, Zn, Zn^{2+}, Cd, Cd^{2+}, Hg, Hg^+ and Hg^{2+} is in the range of 0,1 to 10 ppm in relation to the total weight of the polycarbonate polyol and the pH-value of a 10 wt.% slurry of this mixture in water lies in the range from 5.5 to 7.5.

The polycarbonate polyol is a polyol with an averaged amount of hydroxyl groups per molecule (hydroxy functionality or f_{OH}) ranging from 1.90 to 2.10, preferably 1.93 to 2.07, most preferably 1.95 to 2.05. The polycarbonate polyol comprising the recurring unit according to formula (1) in addition to alkylene groups R may optionally contain 0 to 10 wt.% of at least one polyvalent alcohol such as, for example, 2,2,2-trimethylolpropane, glycerol, pentaerythrithol, dipentaerythritol and their ethoxylated and/or propoxylated analogues, sugar derivatives, branched polyalkylene glycols having a molecular weight from 92 to 1000 g/mol.

The number average molecular weight of the polycarbonate polyol of the present invention is in the range from 300 to 20,000 g/mol, more preferably in the range from 400 to 10,000 g/mol, even more preferably in the range from 500 to 3,000 g/mol as can be determined by GPC (at 25°C, THF solution, according to polystyrene standard), by the estimation of the OH-number (titration methods) and subsequent calculation of the molecular weight, by ^{1}H-NMR spectroscopy (^{1}H nuclear magnetic resonance spectroscopy) by estimating the relation of the hydroxyl and/or adjacent alkylene end groups with the alkylene groups forming the polymer backbone.

The terminal groups of the polycarbonate polyol can conveniently be determined by measuring the hydroxy value of the polycarbonate polyol or analyzing the polycarbonate polyol by ^{1}H-NMR. The hydroxy number of a substance is the amount (mg) of potassium hydroxide (KOH) which corresponds to the molar equivalent hydroxyl groups of the polymer determined by titration techniques, for example by reacting the polymer with acetic anhydride and titration of the acetic acid formed from this reaction by potassium hydroxide solution.

In another aspect the presently claimed invention relates to a process for the production of polycarbonate polyol wherein the polycarbonate polyol can be obtained by subjecting to a polymerization reaction the following components:
(I) at least one compound of general formula HO-R-OH, wherein R is defined as given above; and
(II) at least one carbonate compound;
and
(III) optionally a polyvalent alcohol.

Examples of carbonate compounds (II) above include phosgene, diphosgene, dialkyl carbonates, such as dimethyl carbonate, diethyl carbonate and dibutyl carbonate; alkylene carbonates, such as ethylene carbonate, 1,2-propylene carbonate and trimethylene carbonate; and diaryl carbonates, such as diphenyl carbonate. Among these, dialkyl carbonates, alkylene carbonates and diaryl carbonates are preferred. Even more preferred are dialkyl and alkylene carbonates.

With respect to the amount of the carbonate compound (II), there is no particular limitation. However, preferably the molar ratio of the carbonate compound (II) to the total molar amount of the diol (I) is in the range from 20 : 1 to 1 : 20, more preferably in the range form 10 :1 to 1 : 10.

Non-limiting examples of compounds of general formula HO-R-OH include linear diols, such as ethylene glycol, 1,3-propanediol, 2-Butyl-2-ethylpropan-1,3-diol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecandiol, 1,12-dodecandiol and branched diols, such as 1,2-propanediol, neopentyl glycol, 3-methylpentane-1,5-diol, 2-ethyl-1,6-hexanediol, 2-methyl-1,3-propanediol and 2-methyl-1,8-octanediol, hydrogenated Bisphenol A, isomers of 1,4-cyclohexyldimethanol, tricyclodecyldimethanol isomers according to the formulae (2), and mixtures thereof.

The process for producing the polycarbonate polyol of the present invention comprises at least the steps of
(1) performing a polymerization reaction of the above-mentioned raw materials (I) and optionally (III) with (II), while removing the low molecular by-product formed from (II) from the reaction system, to thereby obtain a polycarbonate prepolymer; and
(2) performing a self-condensation of the above-obtained polycarbonate prepolymer,
to thereby obtain the polycarbonate polyol of the presently claimed invention; and
(3) optionally a purification step.

In the step (1), the compound of general formula HO-R-OH (I) and the carbonate compound (II) are mixed together, and the resultant mixture is subjected to a polymerization reaction, to thereby

obtain a polycarbonate prepolymer.

The main reactions involved in the polymerization reaction are the condensation reaction, namely, the reaction of the compound of general formula HO-R-OH (I) with the carbonate compound (II), upon which the nucleophilic substitution reaction at the carbonate center of the carbonate compound (II) the nucleophilic hydroxyl groups of the compound of general formula HO-R-OH (I) and optionally of the compounds (III) takes place. In the preferred case of dialkyl or alkylene carbonates as compound (II) it is a transesterification reaction which proceeds under formation of the hydroxyl group-containing by-product which is cleaved from the carbonate compound (II). Since the transesterification reaction is an equilibrium reaction, when the hydroxyl group-containing by-product accumulates in the reaction system, the polymerization does not satisfactorily advance. Therefore, it is preferred that the polymerization reaction is performed while removing the low molecular hydroxyl group-containing by-product from the reaction system.

Preferably the polymerization reaction of the step (1) is performed with carbonate compounds different from phosgene or diphosgene in the following manner: a vapor containing the hydroxyl group-containing by-product which is produced during the polymerization reaction, is generated, and the vapor thus generated is condensed to obtain a condensate, and at least a part of the thus obtained condensate is removed from the reaction system. For facilitating the generation of the vapor, it is preferred that the polymerization reaction is performed at sufficiently high temperature or/and under reduced pressure. In some instances, for increasing the efficiency of the removal of the hydroxyl group-containing by-product especially after achieving considerable conversion rates, a method may be adopted in which an inert gas (such as nitrogen, argon, helium, carbon dioxide and a lower hydrocarbon gas) which does not have an adverse effect on the polymerization reaction, is introduced into the reaction system so that the hydroxyl group-containing by-product is removed in a form entrained by the inert gas.

In order to suppress the distillation of the compounds of general formula HO-R-OH (I) and the carbonate compound (II), and in order to efficiently remove the hydroxyl group-containing by-product from the reaction system, it is preferred that the polymerization reaction is performed in a reactor equipped with a fractionating column. When using a fractionating column, the separating capability thereof is important. Hence, a fractionating column is used which generally has a number of theoretical plates of 5 or more, preferably 7 or more.

A fractionating column is used generally in such a form as equipped, at its top, with an appropriate reflux condenser. The reflux condenser is used for condensing the vapor ascending inside of the fractionating column, to form a condensate, and for causing at least a part of the condensate to flow

down inside of the fractioning column, back to the reactor. Use of such a fractionating column is advantageous in that the vapor containing the hydroxyl group-containing by-product (which ascends inside of the fractionating column) and the condensate (which flows down inside of the fractionating column) contact each other in a counter flow, thereby causing the hydroxyl group-containing by-product in the condensate to move into the vapor, and also causing the compounds of general formula HO-R-OH (I) and the carbonate compound (II) in the vapor to move into the condensate, to thereby facilitate the efficient removal of the hydroxyl group-containing by-product from the reaction system.

Preferably the polymerization reaction is performed by using the reactor as mentioned above, while generating a vapor containing the hydroxyl group-containing by-product, and the generated vapor is condensed into a condensate by means of a reflux condenser, followed by removal of a part of the obtained condensate as a distillate from the reaction system while causing the residue of the condensate to flow down inside of the fractioning column, back to the reactor.

In addition, in order to efficiently perform the polymerization reaction, it is important to appropriately control the amount of the vapor (containing the hydroxyl group-containing by-product) which ascends inside of the fractionating column per unit time (i.e., it is important to appropriately control the so-called "throughput"). When the throughput is too small, the rate of removal of the hydroxyl group-containing by-product becomes low and hence the reaction time becomes long. On the other hand, when the throughput is too large, the efficiency of the reaction is decreased, due to, for example, the distillation of the compounds of general formula HO-R-OH (I). Therefore, it is preferred that the throughput is as great as possible, as long as the efficiency of the reaction is not decreased.

The control of the reflux ratio and throughput is performed by appropriately controlling the temperature and pressure for the reaction. The appropriate control of the reflux ratio and throughput is extremely advantageous in that the polymerization reaction can be completed in a relatively short time, thereby improving not only the productivity of the polycarbonate polyol but also the quality thereof.

The reaction temperature in the step (1) is preferably in the range of from 80 to 180 °C, more preferably from 110 to 170 °C.

When the reaction temperature is lower than 80 °C, the rate of the transesterification reaction becomes low and hence the reaction time becomes long.

The pressure for the reaction is preferably in the range of from 0.1 mbar to 15 bar (not included into consideration is the pressure which can by set up by any inert component such as an inert gas).

With respect to the timing of the termination of the polymerization reaction, there is no particular limitation; however, when the polymerization reaction is terminated at an early stage of reaction where the conversion of diol (as described below) is still low, there is a disadvantage in that not only does the yield of the obtained polycarbonate prepolymer become low, but also the reaction time of the step (2) as described below becomes long.

On the other hand, when the polymerization reaction is performed so as to achieve a very high conversion of diol, there is a problem in that, as the reaction proceeds, the compounds of general formula HO-R-OH (I) , the carbonate compound (II) and optionally compounds according the component (III) contained in the reaction mixture in the reactor are consumed and hence the concentrations of the compounds of general formula HO-R-OH (I), the carbonate compound (II) and optionally compounds according the component (III) in the reaction mixture become low, thus decreasing the polymerization rate. As a result, an extremely long period of time is required for achieving a very high conversion of the alcohol adducts.

Therefore, it is generally preferred that the polymerization reaction in the step (1) is terminated when the conversion of diol has reached 50 to 95 %.

In step (2) the polycarbonate prepolymer obtained in the step (1) is subjected to a self-condensation reaction, thereby producing the polycarbonate polyol of the present invention. Since this self-condensation reaction is a transesterification, as the reaction proceeds, the compounds of general formula HO-R-OH (I), carbonate compounds (II) and, optionally, compounds of the component (III) are eliminated from the terminals of the polycarbonate polyol being produced. Since the transesterification reaction is an equilibrium reaction, when the compounds of general formula HO-R-OH (I) and optionally compounds of the component (III) accumulate in the reaction system, the polymerization does not satisfactorily advance. Therefore, it is preferred that the polymerization reaction is performed while removing the compounds of general formula HO-R-OH (I) and optionally compounds of the component (III) from the reaction system.

Generally, the removal of the compounds resulting from the residual leaving groups of the carbonate compound (II), the compounds of general formula HO-R-OH (I) and optionally compounds of the component (III) from the reaction system is performed by evaporation and hence, in the step (2), the polymerization reaction is generally performed under reduced pressure.

Preferably, the contents (reaction mixture) of the reactor are heated under reduced pressure to effect a self-condensation reaction while removing to the outside of the reaction system a vapor being generated which is comprised mainly of the compounds resulting from the residual leaving groups of the carbonate compound (II), compounds of general formula HO-R-OH (I) and optionally compounds of the component (III). Differing from the case of the step (1), in the step (2), for efficiently removing the compounds resulting from the residual leaving groups of the carbonate compound (II), compounds of general formula HO-R-OH (I) and optionally compounds of the component (III) as they are separated from the polycarbonate polyol being produced, it is preferred that the vapor comprised mainly of the compounds resulting from the residual leaving groups of the carbonate compound (II), compounds of general formula HO-R-OH (I) and optionally compounds of the component (III) is directly removed from the reaction system to the outside, without using a fractionating column or the like. In addition, it is possible that, by using a thin film evaporator, the reaction mixture obtained in the step (1) is caused to flow down in the form of a thin film in the evaporator, thereby evaporating off the compounds resulting from the residual leaving groups of the carbonate compound (II), compounds of general formula HO-R-OH (I) and optionally compounds of the component (III) while performing the reaction in the step (2).

In step (2), generally, the reaction mixture obtained in the step (1), as such, namely without being purified, is subjected to a self-condensation reaction. The reaction mixture may contain unreacted compounds of general formula HO-R-OH (I) or unreacted carbonate compound (II) or optionally compounds of the component (III); however, these unreacted substances are removed either in the depressurization operation immediately upon initiation of the reaction in the step (2) or at the early stage of the reaction in the step (2).

In step (2) the reaction temperature is preferably in the range of from 125 °C to 180 °C, more preferably from 130 °C to 170 °C and the step (2) takes place under reduced pressure, that is below 1 bar.

Preferably the pressure for the reaction in the step (2) is generally in the range of from 0.1 mbar to 500 mbar, more preferably in the range of from 0.1 to 100 mbar.

Generally, the polymerization reaction and the self-condensation reaction is performed in the presence of a catalyst. The catalyst can be appropriately selected from compounds capable of catalyzing transesterification reactions. Typical catalysts for the synthesis of polycarbonate polyols can be selected from the group consisting of amines (R_3N, R = wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group) and/or ammonium salts (R_4N^+, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30}

arylalkyl group), alkali metal compounds such as oxides, hydroxides, carbonates, carboxylates, alkoxides, amides, ketonates, aldonates, aldoimides, ketoimides, earth alkali metal compounds such as oxides, hydroxides, carbonates, carboxylates, alkoxides, amides, ketonates, aldonates, aldoimides, ketoimides, various metal compounds of the metals of the 13th through 15th Group of the Periodic Table of the Elements (that is compounds comprising metals chosen from Boron, Carbon and Nitrogen Group), and transition metal compounds comprising metals of the 3rd through 12th Group of the Periodic Table of the Elements. The catalysts can be used as single compounds as well as mixtures and, if convenient, can be generated in situ immediately prior or during polycarbonate condensations reaction according to step (1) and/or (2).

In a particular process set up ketonate compounds of the transition metals of the 3rd Group of the Periodic Table of the Elements are preferred catalysts for the preparation of the polycarbonate polyols starting from the compounds of the general formula (I) HO-R-OH, dialkyl carbonates or/and alkylene carbonates (II) and optional polyalcohols according to component (III). Even more preferred catalysts are ketonates of rare earth metals. Particularly preferable are purified and free of water Y and Yb ketonates, such as Y and Yb acetylacetonates.

The amount of catalyst is preferably in the range of from 1 ppm to 10000 ppm by weight, more preferably 10 ppm to 1000 ppm by weight, based on the total weight of the alcohol containing components (I) and optionally (III) charged into the reactor.

In step (3) of the process of the preparation of the polycarbonate polyols the crude polycarbonate polyol obtained after steps (1) and (2) may need to be purified so that polycarbonate polyol mixtures are obtained with the proviso that the sum of the weight contents of amines (R_3N, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group) and/or ammonium ions (R_4N^+, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group), metal atoms and/or metal ions and/or metal compounds comprising metal in the respective oxidation state selected from the group consisting of Li, Li^+, Na, Na^+, K, K^+, Ca, Ca^{2+}, Sr, Sr^{2+}, Mg, Mg^{2+}, Ba, Ba^{2+}, Al, Al^{3+}, Ga, Ga^{3+}, In, In^{3+}, Tl, Tl^+, Ge, Ge^{2+}, Ge^{4+}, Sn, Sn^{4+}, Pb, Pb^{2+}, Pb^{4+}, Sb, Sb^{3+}, Sb^{5+}, Bi, Bi^{3+}, Ti, Ti^{3+}, Ti^{4+}, Zr, Zr^{4+}, Hf, Hf^{4+}, V, V^{2+}, V^{3+}, V^{4+}, V^{5+}, Nb, Nb^{3+}, Nb^{5+}, Ta, Ta^{3+}, Ta^{5+}, Cr, Cr^{2+}, Cr^{3+}, Cr^{6+}, Mo, Mo^{4+}, Mo^{6+}, W, W^{3+}, W^{4+}, W^{6+}, Mn, Mn^{2+}, Mn^{3+}, Mn^{4+}, Mn^{7+}, Re, Re^{3+}, Re^{4+}, Re^{6+}, Re^{7+}, Fe, Fe^{2+}, Fe^{3+}, Co, Co^{2+}, Co^{3+}, Ni, Ni^{2+}, Ru^{2+}, Ru^{3+}, Rh, Rh^{3+}, Pd, Pd^{2+}, Os, Os^{4+}, Ir, Ir^{3+}, Ir^{4+}, Pt, Pt^{2+}, Pt^{4+}, Cu, Cu^+, Cu^{2+}, Ag, Ag^+, Au, Au^+, Au^{3+}, Zn, Zn^{2+}, Cd, Cd^{2+}, Hg, Hg^+ and Hg^{2+} is in the range of 0.1 to 20 ppm, preferably in the range of 0.1 to 10 ppm, in relation to the total weight of the polycarbonate polyol and the pH-value of a 10 wt.% slurry of this mixture in water lies in the range from 5.0 to 8.0, preferably in the range from 5.5 to 7.5.

This purification step can be done by simple separation of the mixture comprising polycarbonate polyol from the catalyst by filtration, extraction, washing, chromatography, ion exchange and others known to the man skilled in the art.

In another aspect the presently claimed invention is related to the use of a mixture as described above for the preparation of polyurethane polymers (herewith are also ment polyurethane-co-polyurea polymers). Hence, the mixture of the present invention is advantageous for various uses, such as a raw material for thermoplastically formable polyurethanes (such as a thermoplastic elastomers) used for producing various shaped articles (for example, a spandex, which is a polyurethane elastomeric fiber); a component for a coating material or an adhesive; and a polymeric plasticizer.

In another aspect the presently claimed invention is directed to thermoplastic polyurethanes and aqueous polyurethane dispersions (herewith are also meant polyurethane-polyurea copolymers and polyurethane-polyurea dispersions as well) that show excellent resistance to hydrolysis, light and oxidative degradation as well as resistance to high temperatures.

The thermoplastic polyurethanes are obtained from the inventively claimed mixture of at least one polycarbonate polyol of the present invention and at least one polyisocyanate and, optionally, from other difunctional alcohols, difunctional amines, monoalcohol-monoamines, difunctional thiols, water as chain extenders as well as optionally from monofunctional alcohols, monofunctional amines, monofunctional thiols as chain terminating reagents.

Aqueous polyurethane dispersions are obtained from at least one polycarbonate polyol mixture according to the invention,
at least a polyisocyanate,
optionally, at least one hydrophilic compound chosen from the group of difunctional polyethylene oxide alcohols or/and monoalkoxylated, for example but not limited to monomethoxylated, monofunctional polyethylene oxide alcohols with a number average molecular weight of less than 3000 g/mol, such as for example monomethoxypolyethylene glycol 750 (MPEG 750), Desmophen® LB25 (Bayer), difunctional alcohols or/and monofunctional alcohols, carrying ionic or potentially ionic groups, such as for example but not limited to, di(hydroxymethyl)propionic acid, di(hydroxymethyl)butanoic acid, monohydroxypivalic acid, difunctional or/and monofunctional alcohols, carrying sulphonic acid or sulphonate groups, difunctional or/and monofunctional amines (or/and aminoalcohols) carrying ionic or potentially ionic groups, such as for example but not limited to N-(2-aminoethyl)-β-alanine, N-(2-aminoethyl)-2-aminoethane

sulphonic acid, N-(2- or 3-aminopropyl)-2-aminoethane sulphonic acid, difunctional and monofunctional dihydroxyphosphonic acids, difunctional and monofunctional diaminophosphonic acids and the like,
and optionally from other difunctional alcohols, difunctional amines, monoalcohol-monoamines, difunctional thiols, water as chain extenders as well as optionally from monofunctional alcohols, monofunctional amines, monofunctional thiols as chain terminating reagents,
and optionally ionic or/and non-anionic surfactants suitable for dispersing polyurethanes in water.

The weight averaged particle size d50 of such polyurethane dispersions, as can be determined by ultracentrifugation techniques, is typically in the range from 5 to 2000 nm, preferably from 15 to 1000 nm. The particle size distribution can vary from narrow to broad and maybe monomodal, bimodal and polymodal. D50-value means that 50 wt.% of all particles of the dispersions have particle size below this value and the other 50 wt.% of the particles have a particle size above this value. The width of the particle size distribution is defined as U90-value which is the ratio of (d90-d10)/d50. This value typically varies from 0.01 to 100. The smaller this value, the narrower the particle size distribution.

Examples of polyisocyanates used for producing the thermoplastic elastomers of the presently claimed invention include conventional aromatic diisocyanates, such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, a mixture of 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate (TDI), diphenylmethane-4,4'-diisocyanate (MDI), naphthalene-1,5-diisocyanate (NDI), 3,3'-dimethyl-4,4'-biphenylene diisocyanate, crude TDI, hydrogenated TDI (H6TDI), polymethylenepolyphenyl isocyanate, crude MDI, xylylene diisocyanate (XDI) and phenylene diisocyanate; conventional aliphatic diisocyanates, such as 4,4'-methylenebis(cyclohexyl) diisocyanate (hydrogenated MDI), hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI) and cyclohexane diisocyanate (hydrogenated XDI), pentamethylene diisocyanate; and modified products thereof, such as isocyanurate products, carbodiimide products and biuret products.

In order to produce polyurethanes (polyurethane-co-polyurea) of the presently claimed invention, a urethane-forming technique known in the art may be employed. For example, the polycarbonate polyol of the presently claimed invention is reacted with an organic polyisocyanate in the presence or absence of a solvent under atmospheric pressure at a temperature of from room temperature to 200 °C to form polyurethane. Preferred examples of solvents include dimethylformamide, diethylformamide, dimethylacetamide, dimethylsulfoxide, tetrahydrofuran, acetone, methyl ethyl ketone, methyl isobutyl ketone, dioxane, cyclohexanone, benzene, toluene and ethyl cellosolve.

When a chain extender or/and chain terminating agent is optionally used, a chain extender or/and chain terminating agent may be added to the reaction system either before initiating the reaction or during the reaction. In the event of the polyurethane dispersions the process includes a step of dispersing the polyurethane or a polyurethane solution after the optional chain extension or/and chain termination step or during this step. In the event that chain extending reagents bearing potential ionic groups are used to render the polyurethane polymer dispersible in water it is necessary to transform these potentially ionic groups partially or completely into ionic groups by reacting them with suitable bases, such as for example amines, alkali metal hydroxides, alkali metal carbonates and the like. This neutralization step can take place prior to dispersion step or parallel to dispersion step. It is also possible to use external ionic or non-ionic surfactants to make dispersions. The dispersion of polyurethane polymer in water takes place with the aid of high shear forces such as agitation, high speed agitation, high pressure homogenization and other methods known to the man skilled in the art. The optional organic solvent can either remain in the dispersion or be removed by an appropriate method. The removal of the optional organic solvent can take place partially or completely prior to dispersion step, during the dispersion step or after the dispersion step. Also mixtures of different solvents can be used. It is also possible to use radical polymerisable vinylic monomers as solvents and to remove these monomers from the polyurethane dispersion by radical polymerization to form certain amount of polyvinylic dispersion along with polyurethane dispersion. Suitable radical polymerisable vinylic monomers are for example styrene, (meth)acrylic acid esters, vinylalcohol ethers and esters and the like.

Thermoplastic polyurethanes and polyurethane dispersions comprising inventive polycarbonate polyol may contain further additives typical for these products such as thermal and UV-light stabilizers, antioxidants, antimicrobial and antibacterial additives, lubricants, pigments and inorganic fillers, foaming and antifoaming agents, flame retardants and the like.

Thermoplastic polyurethanes and polyurethane dispersions comprising inventive polycarbonate polyols can be advantageously used for injection molding applications and, accordingly, have to withstand high temperatures as well, whereas polyurethane dispersions as well as coatings, adhesives, sealants as well as artificial textiles and leather made of such dispersion have to withstand hydrolysis upon storage and during the service lifetime.

Examples

Starting materials.

Polycarbonate polyol mixture 1: polycarbonate polyol made from 1,6-hexanediol (>99% purity) with the aid of metallic sodium (sodium alkoxide generated in situ) and diethyl carbonate according to the Example 1 of EP-A-1 288 241. This polycarbonate polyol had an OH-value of 110 mg KOH/g and a number averaged molecular weight of ca. 1000 g/mol . The weight contents of amines (R_3N, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group) and/or ammonium ions (R_4N^+, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group), metal atoms and/or metal ions and/or metal compounds comprising metal in the respective oxidation state selected from the group consisting of Li, Li^+, Na, Na^+, K, K^+, Ca, Ca^{2+}, Sr, Sr^{2+}, Mg, Mg^{2+}, Ba, Ba^{2+}, Al, Al^{3+}, Ga, Ga^{3+}, In, In^{3+}, Tl, Tl^+, Ge, Ge^{2+}, Ge^{4+}, Sn, Sn^{4+}, Pb, Pb^{2+}, Pb^{4+}, Sb, Sb^{3+}, Sb^{5+}, Bi, Bi^{3+}, Ti, Ti^{3+}, Ti^{4+}, Zr, Zr^{4+}, Hf, Hf^{4+}, V, V^{2+}, V^{3+}, V^{4+}, V^{5+}, Nb, Nb^{3+}, Nb^{5+}, Ta, Ta^{3+}, Ta^{5+}, Cr, Cr^{2+}, Cr^{3+}, Cr^{6+}, Mo, Mo^{4+}, Mo^{6+}, W, W^{3+}, W^{4+}, W^{6+}, Mn, Mn^{2+}, Mn^{3+}, Mn^{4+} , Mn^{7+}, Re, Re^{3+}, Re^{4+}, Re^{6+}, Re^{7+}, Fe, Fe^{2+}, Fe^{3+}, Co, Co^{2+}, Co^{3+}, Ni, Ni^{2+}, Ru, Ru^{2+}, Ru^{3+}, Rh, Rh^{3+}, Pd, Pd^{2+}, Os, Os^{4+}, Ir, Ir^{3+}, Ir^{4+}, Pt, Pt^{2+}, Pt^{4+}, Cu, Cu^+, Cu^{2+}, Ag, Ag^+, Au, Au^+, Au^{3+}, Zn, Zn^{2+}, Cd, Cd^{2+}, Hg, Hg^+, Hg^{2+} was 49 ppm as was determined by ICP-AES technique. The pH value of an aqueous 10 wt.% slurry was 6.6.

Polycarbonate polyol mixture 2: commercially available polycarbonate polyol Eternacoll® UH 200 made from 1,6-hexanediol (>99% purity) with the aid of a titanium catalyst and dialkyl carbonate from Ube Chemicals Inc.. This polycarbonate polyol had an OH-value of 56 mg KOH/g and a number averaged molecular weight of ca. 2000 g/mol. The weight contents of amines (R_3N, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group) and/or ammonium ions (R_4N^+, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group), metal atoms and/or metal ions and/or metal compounds comprising metal in the respective oxidation state selected from the group consisting of Li, Li^+, Na, Na^+, K, K^+, Ca, Ca^{2+}, Sr, Sr^{2+}, Mg, Mg^{2+}, Ba, Ba^{2+}, Al, Al^{3+}, Ga, Ga^{3+}, In, In^{3+}, Tl, Tl^+, Ge, Ge^{2+}, Ge^{4+}, Sn, Sn^{4+}, Pb, Pb^{2+}, Pb^{4+}, Sb, Sb^{3+}, Sb^{5+}, Bi, Bi^{3+}, Ti, Ti^{3+}, Ti^{4+}, Zr, Zr^{4+}, Hf, Hf^{4+}, V, V^{2+}, V^{3+}, V^{4+}, V^{5+}, Nb, Nb^{3+}, Nb^{5+}, Ta, Ta^{3+}, Ta^{5+}, Cr, Cr^{2+}, Cr^{3+}, Cr^{6+}, Mo, Mo^{4+}, Mo^{6+}, W, W^{3+}, W^{4+}, W^{6+}, Mn, Mn^{2+}, Mn^{3+}, Mn^{4+} , Mn^{7+}, Re, Re^{3+}, Re^{4+}, Re^{6+}, Re^{7+}, Fe, Fe^{2+}, Fe^{3+}, Co, Co^{2+}, Co^{3+}, Ni, Ni^{2+}, Ru^{2+}, Ru^{3+}, Ru3+, Rh, Rh^{3+}, Pd, Pd^{2+}, Os, Os^{4+}, Ir, Ir^{3+}, Ir^{4+}, Pt, Pt^{2+}, Pt^{4+}, Cu, Cu^+, Cu^{2+}, Ag, Ag^+, Au, Au^+, Au^{3+}, Zn, Zn^{2+}, Cd, Cd^{2+}, Hg, Hg^+, Hg^{2+} was 28 ppm as was determined by ICP-AES technique. The pH value of an aqueous 10 wt.% slurry was 5.2.

Polycarbonate polyol mixture 3: polycarbonate polyol made from 1,6-hexanediol (>99% purity) with the aid of a purified ytterbium(III) acetylacetonate as catalyst and dimethyl carbonate purified by distillation mainly according to the Example 1 of EP-A 1 520 869. This polycarbonate polyol had an OH-value of 56 mg KOH/g and a number averaged molecular weight of ca. 2000 g/mol. The weight contents of amines (R_3N, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group) and/or ammonium ions (R_4N^+, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group), metal atoms and/or metal ions and/or metal compounds comprising metal in the respective oxidation state selected from the group consisting of Li, Li^+, Na, Na^+, K, K^+, Ca, Ca^{2+}, Sr, Sr^{2+}, Mg, Mg^{2+}, Ba, Ba^{2+}, Al, Al^{3+}, Ga, Ga^{3+}, In, In^{3+}, Tl, Tl^+, Ge, Ge^{2+}, Ge^{4+}, Sn, Sn^{4+}, Pb, Pb^{2+}, Pb^{4+}, Sb, Sb^{3+}, Sb^{5+}, Bi, Bi^{3+}, Ti, Ti^{3+}, Ti^{4+}, Zr, Zr^{4+}, Hf, Hf^{4+}, V, V^{2+}, V^{3+}, V^{4+}, V^{5+}, Nb, Nb^{3+}, Nb^{5+}, Ta, Ta^{3+}, Ta^{5+}, Cr, Cr^{2+}, Cr^{3+}, Cr^{6+}, Mo, Mo^{4+}, Mo^{6+}, W, W^{3+}, W^{4+}, W^{6+}, Mn, Mn^{2+}, Mn^{3+}, Mn^{4+} , Mn^{7+}, Re, Re^{3+}, Re^{4+}, Re^{6+}, Re^{7+}, Fe, Fe^{2+}, Fe^{3+}, Co, Co^{2+}, Co^{3+}, Ni, Ni^{2+}, Ru, Ru^{2+}, Ru^{3+}, Rh, Rh^{3+}, Pd, Pd^{2+}, Os, Os^{4+}, Ir, Ir^{3+}, Ir^{4+}, Pt, Pt^{2+}, Pt^{4+}, Cu, Cu^+, Cu^{2+}, Ag, Ag^+, Au, Au^+, Au^{3+}, Zn, Zn^{2+}, Cd, Cd^{2+}, Hg, Hg^+, Hg^{2+} was 6 ppm as was determined by ICP-AES technique. The pH value of an aqueous 10 wt.% slurry was 7.1.

Thermal stability of polycarbonate polyol mixtures

Thermal stability of polycarbonate polyol mixtures was determined according to the following general procedure: a sample of the polycarbonate polyol mixture in an amount of 100 g to 500 g was placed in a round bottomed flask equipped with a mechanical agitator and connected to a vacuum trap cooled down to -78°C with dry ice-acetone bath. The polycarbonate polyol mixture was heated at a temperature of at least 180°C for at least 2 hours at a maximum pressure of 1 mbar. Thermally cleaved fractions were collected in the vacuum trap, weighed and analyzed by gas chromatography. The results of the thermal stability tests are summarized in Table 1.

Table 1. Results of thermal stability test of polycarbonate polyol mixtures.

Example	Polycarbonate-Polyol Mixture No.	Amount (g)/ Temperature (°C) / Pressure (mbar) / duration (h)	Amount trapped by cooling with "dry ice" (g)	Comment
inventive	3	500/180 /1 /8	0.006	cleaved amount corresponds to 0.001% of the initial sample; >70 % of the cleaved substances is 5-hexene-1-ol
inventive	3	200/180 /0.1 /3	0.045	cleaved amount corresponds to 0.02% of the initial sample; >70 % of the cleaved substances is 5-hexene-1-ol
inventive	3 (another batch)	200/180/0.5/8	<0.001	not even a trace amount for GC-analysis could be collected
inventive	3 (the same batch as above)	200/205/0.02/8	1) 0.170 of which 2) 0.152 was H_2O, i.e. residual of 0.018	cleaved amount corresponds to 0.01% of the initial sample; >70 % of the cleaved substances is 5-hexene-1-ol
comparative	1	200/180/0.1/6	2.0	cleaved amount corresponds to 1.0% of the initial sample; >70 % of the cleaved substances is 5-hexene-1-ol
comparative	2	200/180 /0.1 /2	0.545	cleaved amount corresponds to 0.27% of the initial sample; >70 % of the cleaved substances is 5-hexene-1-ol

From the results shown in Table 1 it is clear that only in the event of the specific polycarbonate polyol mixtures having weight contents of amines (R_3N, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group) and/or ammonium ions (R_4N^+, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group), metal atoms and/or metal ions and/or metal compounds comprising metal in the respective oxidation state selected from the group consisting of Li, Li^+, Na, Na^+, K, K^+, Ca, Ca^{2+}, Sr, Sr^{2+}, Mg, Mg^{2+}, Ba, Ba^{2+}, Al, Al^{3+}, Ga, Ga^{3+}, In, In^{3+}, Tl, Tl^+, Ge, Ge^{2+}, Ge^{4+}, Sn, Sn^{4+}, Pb, Pb^{2+}, Pb^{4+}, Sb, Sb^{3+}, Sb^{5+}, Bi, Bi^{3+}, Ti, Ti^{3+}, Ti^{4+}, Zr, Zr^{4+}, Hf, Hf^{4+}, V, V^{2+}, V^{3+}, V^{4+}, V^{5+}, Nb, Nb^{3+}, Nb^{5+}, Ta, Ta^{3+}, Ta^{5+}, Cr, Cr^{2+}, Cr^{3+}, Cr^{6+}, Mo, Mo^{4+}, Mo^{6+}, W, W^{3+}, W^{4+}, W^{6+}, Mn, Mn^{2+}, Mn^{3+}, Mn^{4+} , Mn^{7+}, Re, Re^{3+}, Re^{4+}, Re^{6+}, Re^{7+}, Fe, Fe^{2+}, Fe^{3+}, Co, Co^{2+}, Co^{3+}, Ni, Ni^{2+}, Ru, Ru^{2+}, Ru^{3+}, Rh, Rh^{3+}, Pd, Pd^{2+}, Os, Os^{4+}, Ir, Ir^{3+}, Ir^{4+}, Pt, Pt^{2+}, Pt^{4+}, Cu, Cu^+, Cu^{2+}, Ag, Ag^+, Au, Au^+, Au^{3+}, Zn, Zn^{2+}, Cd, Cd^{2+}, Hg, Hg^+, Hg^{2+} of lower than 20 ppm and a pH value of a 10 wt.% aqueous slurry in the range of 5.0 to 8.0 it is possible to achieve an excellent thermal stability of the polycarbonate polyol. The amount of the cleaved organic substances in the case of comparative polycarbonate polyols is much higher even under less severe thermal conditions.

Hydrolysis stability of polycarbonate polyol mixtures

Hydrolysis stability of polycarbonate polyol mixtures was determined according to the following general procedure:
a sample of the polycarbonate polyol mixture in an amount of 10 g and 500 g H_2O were held together at 100°C and intensive agitation for 2h. After that the organic sample was separated from aqueous phase and was analyzed by Gel Permeation Chromatography againt polystyrene standard in THF at room temperature. The GPC results of the polycarbonate mixtures 2 and 3 were compared with the initial data prior hydrolysis test. GPC diagrams are shown in Fig. 1 and Fig. 2. While the polycarbonate polyol mixture according to this invention did not change at all the molecular weight of the polycarbonate polyol mixture of the state of the art (mixture 2) dropped down significantly.

Patent Claims

1. A mixture comprising at least one polycarbonate polyol having a decomposition temperature of > 180°C at 1 mbar comprising recurring units each independently represented by the following formula (1),

-O-R-O-C(=O)- (1),

wherein R represents substituted or unsubstituted, linear or branched alkylene having 2 to 30 carbon atoms or substituted or unsubstituted arylalkylene having 6 to 30 carbon atoms or substituted or unsubstituted heteroarylalkylene having 6 to 30 carbon atoms or substituted or unsubstituted cyclylalkylene having 6 to 30 carbon atoms or substituted or unsubstituted heterocyclylalkylene having 6 to 30 carbon atoms,

and

terminal hydroxyl groups,

whereby the sum of weight contents of amines (R_3N, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group) and/or ammonium ions (R_4N^+, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group), metal atoms and/or metal ions and/or metal compounds comprising metal in the respective oxidation state selected from the group consisting of Li, Li^+, Na, Na^+, K, K^+, Ca, Ca^{2+}, Sr, Sr^{2+}, Mg, Mg^{2+}, Ba, Ba^{2+}, Al, Al^{3+}, Ga, Ga^{3+}, In, In^{3+}, Tl, Tl^+, Ge, Ge^{2+}, Ge^{4+}, Sn, Sn^{4+}, Pb, Pb^{2+}, Pb^{4+}, Sb, Sb^{3+}, Sb^{5+}, Bi, Bi^{3+}, Ti, Ti^{3+}, Ti^{4+}, Zr, Zr^{4+}, Hf, Hf^{4+}, V, V^{2+}, V^{3+}, V^{4+}, V^{5+}, Nb, Nb^{3+}, Nb^{5+}, Ta, Ta^{3+}, Ta^{5+}, Cr, Cr^{2+}, Cr^{3+}, Cr^{6+}, Mo, Mo^{4+}, Mo^{6+}, W, W^{3+}, W^{4+}, W^{6+}, Mn, Mn^{2+}, Mn^{3+}, Mn^{4+} , Mn^{7+}, Re, Re^{3+}, Re^{4+}, Re^{6+}, Re^{7+}, Fe, Fe^{2+}, Fe^{3+}, Co, Co^{2+}, Co^{3+}, Ni, Ni^{2+}, Ru, Ru^{2+}, Ru^{3+}, Rh, Rh^{3+}, Pd, Pd^{2+}, Os, Os^{4+}, Ir, Ir^{3+}, Ir^{4+}, Pt, Pt^{2+}, Pt^{4+}, Cu, Cu^+, Cu^{2+}, Ag, Ag^+, Au, Au^+, Au^{3+}, Zn, Zn^{2+}, Cd, Cd^{2+}, Hg, Hg^+ and Hg^{2+} is in the range of 0.1 to 20 ppm in relation to the total weight of the polycarbonate polyol and the pH-value of a 10 wt.% slurry of this mixture in water lies in the range from 5.0 to 8.0.

2. The mixture according to claim 1, wherein the polycarbonate polyol has a decomposition temperature of > 200 °C at 1 mbar.

3. A mixture comprising at least one polycarbonate polyol having a decomposition temperature of > 180°C at 0.1 mbar comprising recurring units each independently represented by the following formula (1),

-O-R-O-C(=O)- (1),

wherein R represents substituted or unsubstituted, linear or branched alkylene having 2 to 30 carbon atoms or substituted or unsubstituted arylalkylene having 6 to 30 carbon atoms

or substituted or unsubstituted heteroarylalkylene having 6 to 30 carbon atoms or substituted or unsubstituted cyclylalkylene having 6 to 30 carbon atoms or substituted or unsubstituted heterocyclylalkylene having 6 to 30 carbon atoms,
and
terminal hydroxyl groups,
whereby the sum of weight contents of amines (R_3N, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group) and/or ammonium ions (R_4N^+, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group), metal atoms and/or metal ions and/or metal compounds comprising metal in the respective oxidation state selected from the group consisting of Li, Li^+, Na, Na^+, K, K^+, Ca, Ca^{2+}, Sr, Sr^{2+}, Mg, Mg^{2+}, Ba, Ba^{2+}, Al, Al^{3+}, Ga, Ga^{3+}, In, In^{3+}, Tl, Tl^+, Ge, Ge^{2+}, Ge^{4+}, Sn, Sn^{4+}, Pb, Pb^{2+}, Pb^{4+}, Sb, Sb^{3+}, Sb^{5+}, Bi, Bi^{3+}, Ti, Ti^{3+}, Ti^{4+}, Zr, Zr^{4+}, Hf, Hf^{4+}, V, V^{2+}, V^{3+}, V^{4+}, V^{5+}, Nb, Nb^{3+}, Nb^{5+}, Ta, Ta^{3+}, Ta^{5+}, Cr, Cr^{2+}, Cr^{3+}, Cr^{6+}, Mo, Mo^{4+}, Mo^{6+}, W, W^{3+}, W^{4+}, W^{6+}, Mn, Mn^{2+}, Mn^{3+}, Mn^{4+} , Mn^{7+}, Re, Re^{3+}, Re^{4+}, Re^{6+}, Re^{7+}, Fe, Fe^{2+}, Fe^{3+}, Co, Co^{2+}, Co^{3+}, Ni, Ni^{2+}, Ru, Ru^{2+}, Ru^{3+}, Rh, Rh^{3+}, Pd, Pd^{2+}, Os, Os^{4+}, Ir, Ir^{3+}, Ir^{4+}, Pt, Pt^{2+}, Pt^{4+}, Cu, Cu^+, Cu^{2+}, Ag, Ag^+, Au, Au^+, Au^{3+}, Zn, Zn^{2+}, Cd, Cd^{2+}, Hg, Hg^+ and Hg^{2+} is in the range of 0.1 to 20 ppm in relation to the total weight of the polycarbonate polyol and the pH-value of a 10 wt.% slurry of this mixture in water lies in the range from 5.0 to 8.0.

4. The mixture according to claim 3, wherein the polycarbonate polyol has a decomposition temperature of > 200 °C at 0.1 mbar.

5. The mixture according to claim 1 or 3, wherein R represents unsubstituted, linear or branched alkylene having 3 to 16 carbon atoms.

6. The mixture according to claim 1, 3 or 5, wherein R represents $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_2-(CHCH_3)-(CH_2)_2-$, and/or $-(CH_2)_6-$.

7. The mixture according to claim 1 or 3, wherein metal atoms and/or metal ions and/or metal compounds comprising metal in the respective oxidation state are selected from the group consisting of Li, Li^+, Na, Na^+, K, K^+, Ca, Ca^{2+}, Mg, Mg^{2+}, Al, Al^{3+}, Ti, Ti^{3+}, Ti^{4+}, Sn, Sn^{4+}, Pb, Pb^{4+}, Sb, Sb^{3+}, Sb^{5+}, Bi and Bi^{3+}.

8. The mixture according to claim 1 or 3, wherein the sum of the weight contents of amines (R_3N, wherein R represents, independent of each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group) and/or ammonium ions (R_4N^+, wherein R represents, independent of

each other, H or a C_1 to C_{30} alkyl group or a C_6 to C_{30} arylalkyl group), metal atoms and/or metal ions and/or metal compounds comprising metal in the respective oxidation state selected from the group consisting of Li, Li^+, Na, Na^+, K, K^+, Ca, Ca^{2+}, Sr, Sr^{2+}, Mg, Mg^{2+}, Ba, Ba^{2+}, Al, Al^{3+}, Ga, Ga^{3+}, In, In^{3+}, Tl, Tl^+, Ge, Ge^{2+}, Ge^{4+}, Sn, Sn^{4+}, Pb, Pb^{2+}, Pb^{4+}, Sb, Sb^{3+}, Sb^{5+}, Bi, Bi^{3+}, Ti, Ti^{3+}, Ti^{4+}, Zr, Zr^{4+}, Hf, Hf^{4+}, V, V^{2+}, V^{3+}, V^{4+}, V^{5+}, Nb, Nb^{3+}, Nb^{5+}, Ta, Ta^{3+}, Ta^{5+}, Cr, Cr^{2+}, Cr^{3+}, Cr^{6+}, Mo, Mo^{4+}, Mo^{6+}, W, W^{3+}, W^{4+}, W^{6+}, Mn, Mn^{2+}, Mn^{3+}, Mn^{4+} , Mn^{7+}, Re, Re^{3+}, Re^{4+}, Re^{6+}, Re^{7+}, Fe, Fe^{2+}, Fe^{3+}, Co, Co^{2+}, Co^{3+}, Ni, Ni^{2+}, Ru, Ru^{2+}, Ru^{3+}, Rh, Rh^{3+}, Pd, Pd^{2+}, Os, Os^{4+}, Ir, Ir^{3+}, Ir^{4+}, Pt, Pt^{2+}, Pt^{4+}, Cu, Cu^+, Cu^{2+}, Ag, Ag^+, Au, Au^+, Au^{3+}, Zn, Zn^{2+}, Cd, Cd^{2+}, Hg, Hg^+ and Hg^{2+} is in the range of 0.1 to 10 ppm in relation to the total weight of the polycarbonate polyol.

9. The mixture according to one or more of claims 1 to 8, wherein the sum of contents of metal ions and metal atoms selected from the group consisting of Li, Li^+, Na, Na^+, K, K^+, Ca, Ca^{2+}, Mg, Mg^{2+}, Al, Al^{3+}, Ti, Ti^{3+}, Ti^{4+}, Sn, Sn^{4+}, Pb, Pb^{4+}, Sb, Sb^{3+}, Sb^{5+}, Bi and $Bi^{3+}$is in the range of 0.1 to 10 ppm in relation to the total weight of the polycarbonate polyol.

10. The mixture according to claim 1 or 3, wherein the pH-value lies in the range from 5.5 to 7.5 .

11. The process of preparation of polycarbonate polyols according to one or more of claims 1 to 10 by subjecting to a polymerization reaction the following components:
(I) at least one compound of general formula HO-R-OH, wherein R represents substituted or unsubstituted, linear or branched alkylene having 2 to 30 carbon atoms or substituted or unsubstituted arylalkylene having 6 to 30 carbon atoms or substituted or unsubstituted heteroarylalkylene having 6 to 30 carbon atoms or substituted or unsubstituted cyclylalkylene having 6 to 30 carbon atoms or substituted or unsubstituted heterocyclylalkylene having 6 to 30 carbon atoms; and
(II) at least one carbonate compound;
and
(III) optionally a polyvalent alcohol.
.

12. Use of a mixture according to one or more of claims 1 to 10 for the preparation of polyurethane polymers.

13. Use according to claim 11, wherein the polyurethane polymer is used for the preparation of polyurethane dispersions.

14. Thermoplastic polyurethane obtained from a mixture according to one or more of claims 1 to 10 and at least a polyisocyanate.

Fig. 1

Comparative example. Hydrolysis stability test for polycarbonate polyol mixture 2.

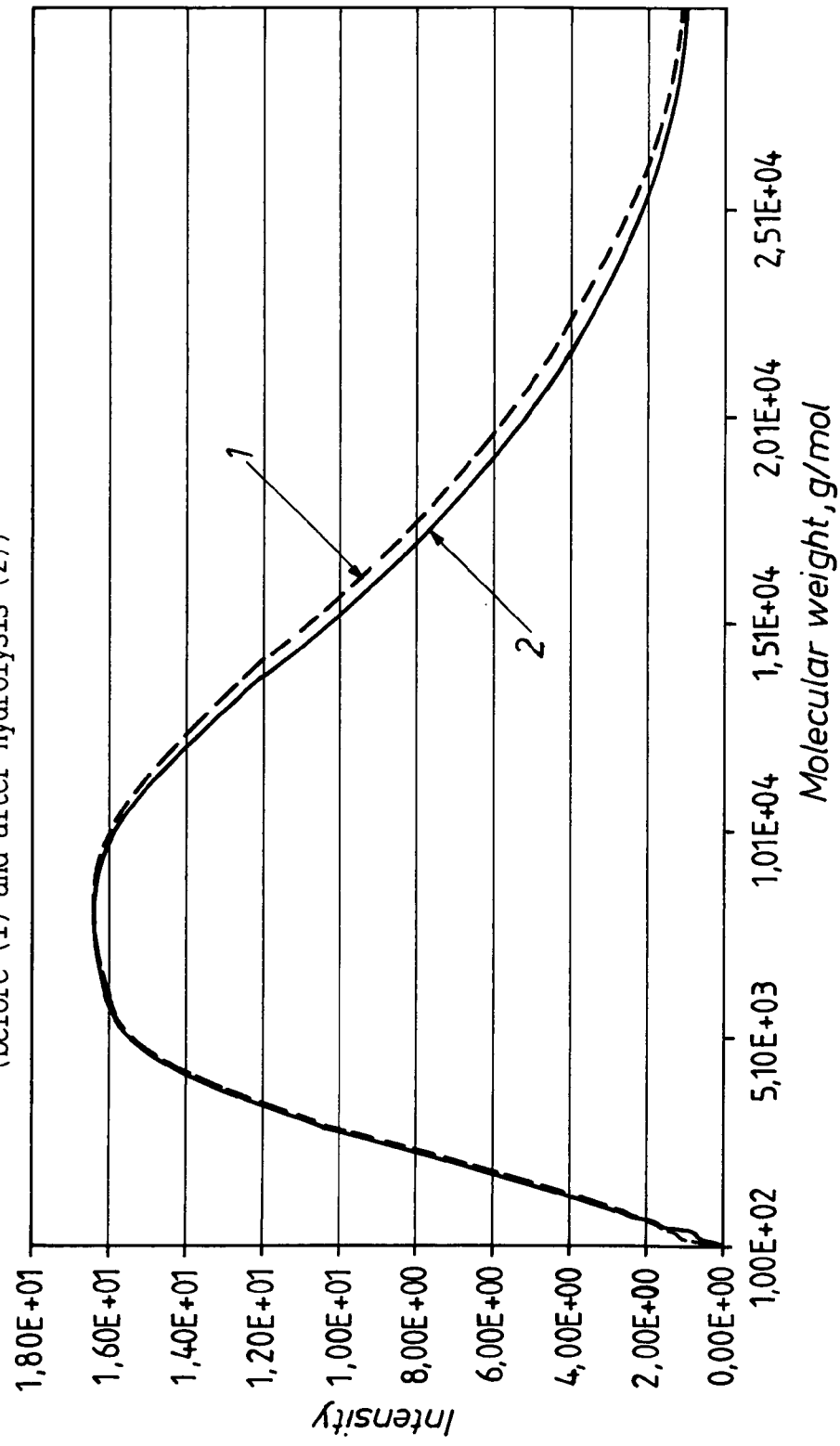


Fig. 2

Inventive example. Hydrolysis stability test for polycarbonate polyol mixture 3.