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(71) Applicant: HUNTSMAN INTERNATIONAL LLC

[US/US]; 10003 Woodloch Forest Drive, The Woodlands, Texas 77380 (US).

(72) Inventors: VANROY, Bram; Grijpenlaan 18, 3300 Tienen

(BE). GIANNINI, Giacomo; Grijpenlaan 18, 3300 Tienen

(BE). VERBEKE, Hugo; Grijpenlaan 18, 3300 Tienen

(BE). VAN LOOY, Kevin; Grijpenlaan 18, 3300 Tienen

(BE). STERZ, Peter; Land-Au 30, 94469 Deggendorf

(DE). BILLER, Peter; Land-Au 30, 94469 Deggendorf (DE).

(74) Agent: LEE, Alexander; Grijpenlaan 18, 3300 Tienen

(BE).

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(54) Title: A FOAM COMPOSITION FOR PRODUCING A POLYURETHANE-BASED FOAM COMPRISING AN ADDITIVE TO PREVENT OR REDUCE PHENOLIC YELLOWING

(57) Abstract: The present disclosure provides a foam composition for producing a polyurethane-based foam, the foam composition comprising: an isocyanate component; an isocyanate-reactive component; a base catalyst; and an additive, wherein the additive is an ester of a carboxylic acid and the free carboxylic acid of the ester of the carboxylic acid has a pKa¹ of about 0.5 to about 4.0.



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**A FOAM COMPOSITION FOR PRODUCING A POLYURETHANE-BASED FOAM COMPRISING AN
ADDITIVE TO PREVENT OR REDUCE PHENOLIC YELLOWING**

FIELD OF THE INVENTION

[0001] The present disclosure relates to a foam composition for producing a polyurethane-based foam, a method of producing a polyurethane-based foam, a polyurethane-based foam, and the use of an additive in a polyurethane-based foam to prevent or reduce phenolic yellowing of the foam. The present disclosure is particularly relevant to polyurethane-based foams which are susceptible to phenolic yellowing, and the additive in the foam composition and foam is responsible for the prevention or reduction of phenolic yellowing.

BACKGROUND

[0002] Phenolic yellowing is a problem in polyurethane-based foams, especially when the appearance of the foams is important. The term “phenolic yellowing” as used herein generally refers to the yellowing of a foam (typically, an MDI-based foam) due to the presence of oxides of nitrogen (NO_x) or other similar agents that generate nitrophenol and/or quinone species, which tend to be yellow, in the foam. The test to determine the impact of NO_x on yellow-able phenols is referred to as the phenolic yellowing test and is detailed in EN ISO 105-X18 (the “Courtauld test”). The phenolic yellowing test scores range from 1-5, with 5 indicating no phenolic yellowing.

[0003] During the phenolic yellowing test, a sample piece of foam is sandwiched between a test paper which is infused with 2,6-tert butyl-4-nitrophenol (DBNP). When DBNP comes into contact with the foam, the foam will discolour to yellow. It has been found that this might be related to a foam that contains a basic environment. Thus, a foam having a more acidic environment is less prone to phenolic yellowing.

[0004] However, it is not straightforward to make a foam’s environment more acidic to prevent or reduce phenolic yellowing.

[0005] Current methods of reducing phenolic yellowing in polyurethane-based foams include the use of an acid wash after the polyurethane-based foam is made. The acid wash helps to ensure that the foam contains an acidic environment, which reduces phenolic yellowing. However, the issues with using an acid wash after the foam is made are that (i) an extra step in the foam manufacturing process is added which therefore complicates the

manufacturing process, and (ii) during the use of the foam, the acid wash may no longer be sufficient to protect from phenolic yellowing because the acid is depleted or removed e.g. by the rain or washing of the foam. Additionally, during the use of such foam, any defects or scratches during the use of the foam might result in exposure of a non-protected area to phenolic yellowing.

[0006] An acid may be used in the foam composition to obtain the foam, which helps to prevent or reduce phenolic yellowing by ensuring the foam contains an acidic environment. However, the acid being present in the foam composition significantly reduces the reactivity of the foam composition. The reactivity of the foam composition may be improved by adding e.g., an amine catalyst, but this results in even more phenolic yellowing.

[0007] Another method is to use an acid in a release agent, which is added to the mould of the foam. However, the skin cure of the foam is adversely affected by the acid, resulting in more fouling of the mould (i.e., more polyurethane-based foam sticking to the surface of the mould).

[0008] Thus, there is a need for an additive that may be added to the foam composition, or as a release agent, or as separate additive stream (e.g., in a pigment/color tank) which prevents or reduces phenolic yellowing by creating an acidic environment in the foam, without significantly affecting the reactivity of the foam composition and the skin cure of the foam, and without complicating the manufacturing process.

[0009] The present disclosure addresses the problems and needs mentioned above.

SUMMARY

[0010] In a first aspect, there is provided a foam composition for producing a polyurethane-based foam, the foam composition comprising: an isocyanate component; an isocyanate-reactive component; a base catalyst; and an additive, wherein the additive is an ester of a carboxylic acid and the free carboxylic acid of the ester of the carboxylic acid has a pK_a^1 of about 0.5 to about 4.0.

[0011] The use of an ester of a carboxylic acid, wherein the free carboxylic acid has a pK_a^1 of about 0.5 to about 4.0, as an additive in a foam containing water (residual water from the foam composition and/or from the atmosphere) allows for the foam to have an acidic environment. It is thought this is because the ester of the carboxylic acid slowly undergoes hydrolysis to release the free carboxylic acid in the foam, and therefore maintains an acidic environment in the foam due to the low pK_a^1 of the free carboxylic acid.

- [0012] The presence of an ester of the carboxylic acid in the foam composition does not significantly affect the reactivity of foam composition, unlike the presence of a free carboxylic acid, because the ester of the carboxylic acid is generally not reactive towards isocyanates or other components of the foam composition and does not immediately impact the acidity of the foam and thereby the performance of the catalyst(s). Therefore, the additive may be added to the foam composition, meaning that the manufacturing process is not complicated and the skin cure is excellent.
- [0013] In one embodiment, the ester of the carboxylic acid may be an alkyl ester of the carboxylic acid. Preferably, the alkyl group of the alkyl ester of the carboxylic acid is methyl or ethyl.
- [0014] In one embodiment, the free carboxylic acid may be a dicarboxylic acid. Preferably, the free carboxylic acid may be a dicarboxylic acid having 2 to 4 carbon atoms. More preferably, the free carboxylic acid may be malonic acid or oxalic acid.
- [0015] In one embodiment, the ester of the carboxylic acid may be any one selected from dimethyl malonate, diethyl malonate, dimethyl oxalate and diethyl oxalate (DEO). Preferably, the ester of the carboxylic acid is DEO. It has been surprisingly found by the present inventors that DEO is a particularly effective additive for preventing or reducing phenolic yellowing, without noticeably affecting the reactivity of the foam composition.
- [0016] In one embodiment, the free carboxylic acid of the ester of the carboxylic acid may have a pK_a^1 of about 1.0 to about 3.0. It has been surprisingly found by the present inventors that such a pK_a^1 range effectively prevents or reduces phenolic yellowing.
- [0017] In one embodiment, the additive may be present in the foam composition in an amount of less than 5.0 wt% based upon the total weight of the foam composition. Preferably, the additive may be present in the foam composition in an amount of less than 2.0 wt%, based upon the total weight of the foam composition, or less than 1.0 wt%. The low amount of additive therefore minimally interferes with the properties of the foam besides its resistance to phenolic yellowing. Additionally, the minimal dilution effect of the additive allows polyurethane-based foams to be made at very low density without losing foam performance.
- [0018] In one embodiment, the isocyanate-reactive component may comprise a polyether polyol, a polyester polyol, a silica-based polyol (such as dihydroxyl-terminated polydimethylsiloxane, PDMS-diol), or a polydiene polyol (such as polybutadiene polyol). Preferably, the isocyanate-reactive component comprises a polyether polyol. Polyurethane-based foams obtained from polyether polyols are particularly susceptible to phenolic yellowing because the polyol does not contain ester groups which may hydrolyse

to form free acid, unlike polyester polyols which may hydrolyse to form some free acid (e.g., succinic acid, adipic acid, azelaic acid etc.). The hydrolysis of polyester polyols, thereby generating acid and thus improving the phenolic yellowing, is accompanied by a loss in foam strength and performance due to the breakdown of the polymer backbone. In one embodiment, the polyether polyol comprises an ethylene oxide- and/or propylene oxide-based polyether polyol, poly(1,3-propanediol), polytetrahydrofuran (PTMEG or PTHF), or combinations or copolymers thereof. The ethylene oxide- and/or propylene oxide-based polyether polyol may be prepared by adding ethylene oxide and/or propylene oxide to an initiator, optionally wherein the initiator is glycerol.

[0019] In one embodiment, the base catalyst may comprise an amine catalyst. An amine catalyst achieves a good balance between gel/blow reaction via the respective urethane/urea formation.

[0020] In one embodiment, the isocyanate component may comprise an aromatic polyisocyanate, an aliphatic polyisocyanate or combinations thereof. In one embodiment, the isocyanate component comprises a methylene diphenyl diisocyanate (MDI)-based compound. MDI-based foams are prone to aromatic yellowing and therefore the combination of phenolic yellowing and aromatic isocyanate yellowing will result in an overall higher degree of yellowing relative to aliphatic polyisocyanate-based foams. Thus, the additive is particularly useful in foams obtained from an MDI-based isocyanate component.

[0021] In one embodiment, water may be present in the foam composition, preferably in an amount of at least 0.2 wt% based upon the total weight of the foam composition. A small amount of water may be required in the foam composition, and preferably at least 0.2 wt%, to ensure sufficient hydrolysis of the additive in the foam. The foam might contain some residual unreacted water after the foaming reaction from the foam composition.

[0022] In a second aspect, there is provided a method of producing a polyurethane-based foam, comprising: mixing the foam composition described herein to form a reactive mixture, and allowing the reactive mixture to cure to form a polyurethane-based foam.

[0023] In a third aspect, there is provided a polyurethane-based foam obtainable by the method described herein.

[0024] In a fourth aspect, there is provided the use of an additive to prevent or reduce phenolic yellowing in a polyurethane-based foam, wherein the additive is an ester of a carboxylic acid and the free carboxylic acid of the ester of the carboxylic acid has a pK_a^1 of about 0.5 to about 4.0, and wherein the polyurethane-based foam is obtained from a foam composition comprising an isocyanate-reactive component, an isocyanate component, and

a base catalyst. The additive may be added to the foam composition, to a release agent, or to a color package used in e.g., a mould. Preferably, the additive is added to the foam composition so that the entire foam is protected from phenolic yellowing, not just the surface of the foam. Most preferably the additive is added to the isocyanate component, or to a separate color stream, to avoid any hydrolysis or transesterification (which might be caused by the isocyanate-reactive component).

[0025] In a fifth aspect, there is provided a thermoplastic polyurethane composition for producing a non-foamed thermoplastic polyurethane, the composition comprising: an isocyanate component; an isocyanate-reactive component; and an additive, wherein the additive is an ester of a carboxylic acid and the free carboxylic acid of the ester of the carboxylic acid has a pK_a^1 of about 0.5 to about 4.0.

[0026] The foregoing embodiments should not be read to limit or otherwise narrow the scope of any inventive concepts otherwise provided by the present disclosure. While multiple embodiments are disclosed, other embodiments will become apparent to those skilled in the art from the following description. Accordingly, the description is to be regarded as illustrative rather than restrictive.

DETAILED DESCRIPTION

[0027] The present disclosure relates to a foam composition for producing a polyurethane-based foam, the foam composition comprising: an isocyanate component; an isocyanate-reactive component; a base catalyst; and an additive, wherein the additive is an ester of a carboxylic acid and the free carboxylic acid of the ester of the carboxylic acid has a pK_a^1 of about 0.5 to about 4.0. The additive helps to prevent or reduce phenolic yellowing in the polyurethane-based foam.

[0028] The phrase “to prevent or reduce phenolic yellowing” as used herein refers to the prevention of phenolic yellowing in the foam, or a reduction of phenolic yellowing compared to an identical foam without the additive, as tested via EN ISO 105-X18 (the Courtauld test).

[0029] Phenolic yellowing is an undesirable occurrence in polyurethane-based foams, particularly where the appearance of the foams is important, such as in consumer goods or footwear applications. Thus, the present disclosure may preferably be directed to the use of the additive in a polyurethane-based foam in consumer goods or footwear to prevent or reduce phenolic yellowing.

[0030] **[Foam composition]**

[0031] The foam composition comprises an isocyanate component, an isocyanate-reactive component, a base catalyst, and an additive.

[0032] The isocyanate component is not particularly limited, and any isocyanate component known in the art may be used. The isocyanate component may comprise an aliphatic polyisocyanate, an aromatic polyisocyanate, a prepolymer of a polyisocyanate, or a combination thereof. Preferably, the isocyanate component comprises an aromatic diisocyanate compound, more preferably a methylene diphenyl diisocyanate (MDI)-based compound. The isocyanate component may be pure MDI or may be a prepolymer thereof, i.e., a prepolymer made from MDI and a polyol. According to an embodiment, the isocyanate component used in the foam composition may comprise at least 50 weight%, or at least 75 weight%, or at least 80 weight%, or at least 85 weight%, or at least 90 weight%, or at least 95 weight%, or about 100 weight%, of an aromatic diisocyanate, such as MDI (preferably, 4,4'-diphenylmethane diisocyanate) or a prepolymer based upon MDI and a polyol, based upon the total weight of the isocyanate component.

[0033] Examples of aliphatic polyisocyanates suitable for use in the isocyanate component include, but are not limited to, hexamethylene diisocyanate (HDI), tetraalkyl xylene diisocyanate, cyclohexane diisocyanate, 1,12-dodecane diisocyanate, 1,4-tetramethylene diisocyanate, 1,3- and 1,4-cyclohexane diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane (isophorone diisocyanate), 4,4'-, 2,2'- or 2,4'-dicyclohexyl-methane diisocyanate, as well as the corresponding isomer mixtures.

[0034] Examples of aromatic polyisocyanates suitable for use in the isocyanate component include, but are not limited to, m-phenylene diisocyanate, p-phenylene diisocyanate, 4,4'- or 2,4'- or 2,2'-diphenylmethane diisocyanate (MDI), polymethylene polyphenylene diisocyanate (mixtures of MDI and oligomers thereof known in the art as "crude" or polymeric MDI having an isocyanate functionality of greater than 2), 2,4- or 2,6-toluene diisocyanate (TDI), dianisidine diisocyanate, bitolylene diisocyanate, naphthalene-1,4-diisocyanate and diphenylene 4,4'-diisocyanate.

[0035] Prepolymers formed from the reaction of a polyisocyanate (e.g., MDI, modified MDI and/or polymeric-MDI) with a polyol may also be suitable for use in the isocyanate component. The polyol may be a polyether polyol, a polyester polyol, a polycarbonate polyol, a polycaprolactone polyol, other polyol which may be used either individually or in combinations of two or more, or a combination thereof. In addition, the polyol may be a

copolymer of one or more of a polyether polyol, a polyester polyol, a polycarbonate polyol, a polycaprolactone polyol, or other polyol.

[0036] According to an embodiment, the isocyanate component may comprise an isocyanate-terminated prepolymer. The isocyanate-terminated prepolymer may be prepared by reaction of an excessive amount of a polyisocyanate having at least 80 weight%, or at least 85 weight%, or at least 90 weight%, or at least 95 weight%, of MDI (such as 4,4'-MDI) with a suitable difunctional polyol in order to obtain a prepolymer having a desired NCO value. Methods to prepare prepolymers have been described in the art. The relative amounts of polyisocyanate and polyol depend on their equivalent weights and on the desired NCO value and can be determined easily by those skilled in the art. The NCO value of the isocyanate-terminated prepolymer is preferably above 3%, preferably above 5%, more preferably above 8%, and more preferably above 10%. The NCO value of the isocyanate-terminated prepolymer may be from 3% to 40%, or from 5% to 30%, or from 10% to 20%.

[0037] The isocyanate component may be present in the foam composition in an amount that is effective for a given foam composition. The isocyanate component may be present in the foam composition in an amount of from about 5 wt% to about 95 wt%, or from 5 wt% to about 85 wt%, or from 5 wt% to about 75 wt%, or 5 wt% to about 65 wt%, or from 10 wt% to about 60 wt%, or from about 15 wt% to about 50 wt%, or from about 20 wt% to about 50 wt%, based upon the total weight of the foam composition.

[0038] The isocyanate-reactive component is not particularly limited, and any isocyanate-reactive component known in the art may be used. In one embodiment, the isocyanate-reactive component may comprise a polyether polyol, a polyester polyol, a polyether polyester polyol, a polycarbonate polyol, a polycaprolactone polyol, other polyol which may be used either individually or in combinations of two or more, or combinations thereof. Preferably, the isocyanate-reactive component comprises a polyether polyol, such as a PTMEG (polytetramethylene ether glycol, PTHF) polyol or an ethylene oxide- and/or propylene oxide-based polyether polyol.

[0039] The weight-average molecular weight (as measured by gel permeation chromatography when referred to herein) of the polyether polyol, the polyester polyol, the polyether polyester polyol, the polycarbonate polyol, the polycaprolactone polyol or the other polyol in the isocyanate-reactive component may be from about 500 g/mol to about 20000 g/mol, or from about 500 g/mol to about 15000 g/mol, or from about 950 g/mol to about 10000 g/mol, or from about 1000 g/mol to about 7500 g/mol, or from about 1000 g/mol to 7000 g/mol. More specifically, when the isocyanate component contains PTMEG (PTHF), the

weight-average molecular weight of the PTMEG may range from about 500 g/mol to about 5000 g/mol, or from about 1000 g/mol to about 4500 g/mol, or from about 1000 g/mol to about 4000 g/mol, or from about 1500 g/mol to about 3500 g/mol. When the isocyanate component contains polyether polyol made from EO and/or PO, the weight-average molecular weight of the EO and/or PO-based polyether polyol may range from about 500 g/mol to about 10000 g/mol, or from about 500 g/mol to about 9000 g/mol, or from about 750 g/mol to about 8000 g/mol, or from about 1000 g/mol to about 7000 g/mol.

[0040] Examples of polyether polyols include, but are not limited to, polyethylene glycol, polypropylene glycol, polypropylene glycol-ethylene glycol copolymer, polytetramethylene ether glycol, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, and polyether polyols obtained by ring-opening copolymerization of alkylene oxides, such as ethylene oxide and/or propylene oxide and/or butylene oxide, with isocyanate-reactive initiators having functionality from 2 to 8.

[0041] The polyether polyol may be made by the addition of alkylene oxides to initiators, which may contain from 2 to 8 active hydrogen atoms per molecule. In some embodiments, the initiators may include glycols, glycerol, trimethylolpropane, triethanolamine, pentaerythritol, sorbitol, sucrose, ethylenediamine, ethanolamine, diethanolamine, aniline, toluenediamines (e.g., 2,4- and 2,6- toluenediamines), polymethylene polyphenylene polyamines, N-alkylphenylene-diamines, o-chloro-aniline, p-aminoaniline, diaminonaphthalene, or a combination thereof. Suitable alkylene oxides that may be used to form the polyether polyols include ethylene oxide (EO), propylene oxide (PO), butylene oxide, or a combination thereof. In a preferred embodiment, polyol is prepared by using glycerol as the initiator, and EO and PO as the alkylene oxides. Thus, in one embodiment, the ethylene oxide- and/or propylene oxide-based polyether polyol is prepared by adding ethylene oxide and/or propylene oxide to an initiator, optionally wherein the initiator is glycerol.

[0042] When the alkylene oxide used to form the polyether polyol is EO and/or PO, the polyether polyol may comprise PO, EO, or a combination of PO and EO groups or moieties in the polymeric structure. These PO and EO units may be arranged randomly or in block sections throughout the polymeric structure. In some embodiments, the EO content of the polyol may range from 0 to 100% by weight based on the total weight of the polyol. In some embodiments, the PO content of the polyol may range from 100 to 0% by weight based on the total weight of the polyol. In some embodiments, the EO content of a polyol can range from 1% to 99% by weight of the polyol while the PO content can range from 99% to 1% by

weight of the polyol. Often the EO content of a polyol can range from 5% to 80% by weight of the polyol, or from 5% to 30% by weight of the polyol. On the other hand, the PO content can range from 20% to 95% by weight of the polyol, or from 70 to 95% of the polyol. Moreover, in some embodiments, the EO and/or PO units can either be located terminally on the polymeric structure of the polyol or within the interior sections of the polymeric backbone structure of the polyol. Suitable polyether polyols include poly(oxyethylene oxypropylene) diols obtained by the sequential addition of PO and EO to initiators that are known in the art.

[0043] In a preferred embodiment, the isocyanate-reactive component comprises an ethylene oxide-capped polyether polyol, such as Daltocel®F428C available from Huntsman Corporation.

[0044] Examples of polyester polyols include, but are not limited to, those which may be obtained by reacting a diol and a polybasic acid. Examples of diols include ethylene glycol, polyethylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,9-nonanediol and 2-methyl-1,8-octanediol. Examples of polybasic acids include phthalic acid, dimer acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid and sebacic acid.

[0045] Examples of polycarbonate polyols include, but are not limited to, aliphatic polycarbonate diols, for example those based upon alkylene glycols, ether glycols, alicyclic glycols or mixtures thereof. In some embodiments, the alkylene groups for preparing the polycarbonate polyol can comprise from 5 to 10 carbon atoms and can be a straight chain, cycloalkylene or combinations thereof. Non-limiting examples of such alkylene groups include hexylene, octylene, decylene, cyclohexylene and cyclohexyldimethylene. The polycarbonate polyols can be prepared, in non-limiting examples, by reacting the alkylene glycol with a dialkyl carbonate, such as methyl, ethyl, n-propyl or n-butyl carbonate, or diaryl carbonate, such as diphenyl or dinaphthyl carbonate, or by reacting a hydroxy-terminated alkylene diol with phosgene or bischloroformate, in a manner well known to those skilled in the art.

[0046] Polycaprolactone polyols include, but are not limited to, those prepared by condensing caprolactone in the presence of an initiator such as water, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, dipropylene glycol, 1,3-propylene glycol, polyethylene glycol, polypropylene glycol, poly(oxyethylene-oxypropylene)glycols and similar polyalkylene glycols, either blocked or capped containing up to about 40 or more alkyleneoxy units in the molecule, 3-methyl-1,5-pentanediol, cyclohexanediol, 4,4'-

methylene-bis-cyclohexanol, 4,4'-isopropylidene bis-cyclohexanol, xylenediol, 2-(4-hydroxymethylphenyl)ethanol, 1,4-butanediol, glycerol, trimethylolpropane, 1,2,6-hexanetriol, triethanolamine, triisopropanolamine, erythritol, pentaerythritol and N,N,N',N'-tetrakis-(2-hydroxyethyl)ethylene diamine. The caprolactone reacted with the initiator can be caprolactone itself or a substituted caprolactone as described in US Pat. No. 3169945.

[0047] The isocyanate-reactive component may be present in the foam composition in an amount that is effective for a given foam composition. The isocyanate-reactive component may be present in the foam composition in an amount of from about 30 wt% to about 90 wt%, or from about 40 wt% to about 80 wt%, or from about 45 wt% to about 80 wt%, or from about 50 wt% to about 80 wt%, or from about 50 wt% to about 75 wt%, based upon the total weight of the foam composition.

[0048] According to an embodiment, the isocyanate-reactive component (including any polyisocyanate used to prepare any optional prepolymer) may comprise at least 30 weight% of polyether polyol, based upon the total weight of the isocyanate-reactive component (including the polyisocyanates used in the prepolymer), or at least 40 weight%, or at least 50 weight%, or at least 60 weight%, or at least 65 weight%, or at least 70 weight%, or at least 75 weight%, or at least 80 weight%, or at least 85 weight%, or at least 90 weight%, or at least 95 weight%, or 100 weight% of polyether polyol.

[0049] According to an embodiment, the isocyanate-reactive component (including any polyisocyanate used to prepare any optional prepolymer, or optional blowing agent or additive) may contain less than 100 weight% of polyester polyol, based upon the total weight of the isocyanate-reactive component (including the polyisocyanates used in the prepolymer), or less than 90 weight%, or less than 80 weight%, or less than 70 weight%, or less than 60 weight%, or less than 50 weight%, or less than 40 weight%, or less than 30 weight%, or less than 25 weight%, or less than 20 weight%, or less than 15 weight%, or less than 10 weight%, or less than 5 weight%, or less than 3 weight%, or less than 2 weight%, or less than 1 weight%, and preferably essentially free of polyester polyol.

[0050] According to an embodiment, the isocyanate-reactive component (including any polyisocyanate used to prepare any optional prepolymer, or optional blowing agent or additive) may contain less than 100 weight% of polycarbonate polyol, based upon the total weight of the isocyanate-reactive component (including the polyisocyanates used in the prepolymer), or less than 90 weight%, or less than 80 weight%, or less than 70 weight%, or less than 60 weight%, or less than 50 weight%, or less than 40 weight%, or less than 30

weight%, or less than 25 weight%, or less than 20 weight%, or less than 15 weight%, or less than 10 weight%, or less than 5 weight%, or less than 3 weight%, or less than 2 weight%, or less than 1 weight%, and preferably essentially free of polycarbonate polyol.

[0051] According to an embodiment, the isocyanate-reactive component (including any polyisocyanate used to prepare any optional prepolymer, or optional blowing agent or additive) may contain less than 100 weight% of polycaprolactone polyol, based upon the total weight of the isocyanate-reactive component (including the polyisocyanates used in the prepolymer), or less than 90 weight%, or less than 80 weight%, or less than 70 weight%, or less than 60 weight%, or less than 50 weight%, or less than 40 weight%, or less than 30 weight%, or less than 25 weight%, or less than 20 weight%, or less than 15 weight%, or less than 10 weight%, or less than 5 weight%, or less than 3 weight%, or less than 2 weight%, or less than 1 weight%, and preferably essentially free of polycaprolactone polyol.

[0052] According to an embodiment, the isocyanate-reactive component comprises less than 80 wt% of polyester and/or polycarbonate polyol, based upon the total of the isocyanate-reactive component (including the polyisocyanates used to make the prepolymer), or less than 60 wt%, or less than 50 wt%, or less than 40 wt%, or less than 30 wt%, or less than 20 wt%, or less than 10 wt%, or less than 5 wt%, or less than 2 wt%.

[0053] According to an embodiment, the isocyanate-reactive component comprises a polyether polyol having a weight-average molecular weight of at least 500 g/mol, wherein the amount of polyether polyol is at least 30 weight% based upon the total weight of the polyisocyanate compounds having a molecular weight of at least 500 g/mol in the isocyanate-reactive component, or at least 40 weight%, or at least 50 weight%, or at least 60 weight%, or at least 65 weight%, or at least 70 weight%, or at least 75 weight%, or at least 80 weight%, or at least 85 weight%, or at least 90 weight%, or at least 95 weight%, or 100 weight% of polyether polyol, based upon the total weight of the polyisocyanate compounds having a weight-average molecular weight of at least 500 g/mol in the isocyanate-reactive component.

[0054] According to an embodiment, the isocyanate-reactive component (including the polyisocyanates used to prepare any optional prepolymer, or optional blowing agent or additive) may comprise EO- and/or PO-based polyether polyols, wherein the amount of EO- and/or PO-based polyether polyol is at least about 30 weight% based upon the total weight of the isocyanate-reactive component (including the polyisocyanates used in the prepolymer), or at least about 40 weight%, or at least about 50 weight%, or at least about 60 weight%, or at least about 65 weight%, or at least about 70 weight%, or at least about

75 weight%, or at least about 80 weight%, or at least about 85 weight%, or at least about 90 weight%, or 100 weight%.

[0055] According to an embodiment, the isocyanate-reactive component (including the polyisocyanates used to prepare any optional prepolymer, or optional blowing agent or additive) may comprise PTMEG (PTHF), wherein the amount of PTMEG is at least about 30 weight% based upon the total weight of the isocyanate-reactive component (including the polyisocyanates used in the prepolymer), or at least about 40 weight%, or at least about 50 weight%, or at least about 60 weight%, or at least about 65 weight%, or at least about 70 weight%, or at least about 75 weight%, or at least about 80 weight%, or at least about 85 weight%, or at least about 90 weight%, or 100 weight%.

[0056] According to an embodiment, the isocyanate-reactive component may comprise one or more chain extenders each having a weight-average molecular weight of less than about 500 g/mol, or from about 16 g/mol to about 500 g/mol, or from about 16 g/mol to about 250 g/mol. A chain extender is typically a diol compound. The one or more chain extenders is independently selected from water, 1,6-hexanediol, 1,4-butanediol, monoethylene glycol, diethylene glycol, triethyleneglycol, tetraethyleneglycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1,3-propanediol, 1,3-butanediol, 1,5-pentanediol, polycaprolactone diol, 2-methyl-1,3-propanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, hydroquinone bis (2-hydroxyethyl) ether (HQEE), 1,3-Bis (2-hydroxyethyl) resorcinol (HER), ethanolamine, methyldiethanolamine and/or phenyldiethanolamine, or any combinations thereof. Preferably the one or more chain extenders is selected from water, 1,6 hexanediol, 1,4-butanediol and ethylene glycol. Water and 1,4-butanediol are preferred. The combined use of water and 1,4-butanediol is preferred.

[0057] In one embodiment, the amount of the chain extender present in the foam composition may be from about 0.1 to about 20 weight%, or from about 0.5 to about 12 weight%, or from about 0.5 to about 5 weight%, based on the total weight of the isocyanate-reactive component in the foam composition.

[0058] Polyurethane-based foams obtained from polyether polyols are more likely to suffer from phenolic yellowing than polyurethane-based foams obtained from e.g., polyester polyols, because polyester polyols contain an ester group which may be hydrolysed to form a carboxylic acid. The presence or use of the additive is therefore particularly suited to polyurethane-based foams obtained from polyether polyols. The additive is however still

useful at preventing or reducing phenolic yellowing in polyurethane-based foams obtained from polyester polyols.

[0059] The base catalyst is not particularly limited, and any base catalyst known in the art may be used. The purpose of the base catalyst is to achieve a good balance between gel/blow reaction via the respective urethane/urea formation. Preferably, the base catalyst comprises an amine catalyst, and more preferably is DABCO (TEDA, triethylenediamine). The base catalyst may be present in the foam composition in an amount of from about 0.001 wt% to about 2 wt%, or from about 0.1 wt% to about 1 wt%, or from about 0.1 wt% to about 0.5 wt%, based upon the total weight of the foam composition. Representative amine catalysts include, but are not limited to, bis-(2-dimethylaminoethyl)ether (JEFFCAT® ZF-20 catalyst), N,N,N'-trimethyl-N'-hydroxyethylbisaminoethylether (JEFFCAT® ZF-10 catalyst), N-(3-dimethylaminopropyl)-N,N-diisopropanolamine (JEFFCAT® DPA catalyst), N,N-dimethylethanolamine (JEFFCAT® DMEA catalyst), triethylene diamine (JEFFCAT® TEDA catalyst), blends of N,N-dimethylethanolamine ethylene diamine (such as JEFFCAT® TD-20 catalyst), N,N-dimethylcyclohexylamine (JEFFCAT® DMCHA catalyst), benzyldimethylamine (JEFFCAT® BDMA catalyst), pentamethyldiethylenetriamine (JEFFCAT® PMDETA catalyst), N,N,N',N'',N''- pentamethyldipropylene triamine (JEFFCAT® ZR-40 catalyst), N,N-bis(3- dimethylaminopropyl)-N-isopropanolamine (JEFFCAT® ZR-50 catalyst), N'-(3- (dimethylamino)propyl -N,N-dimethyl -1,3 -propanediamine (JEFFCAT® Z-130 catalyst), 2-(2-dimethylaminoethoxy)ethanol (JEFFCAT® ZR-70 catalyst), N,N,N-trimethylaminoethyl-ethanolamine (JEFFCAT® Z-110 catalyst), N-ethylmorpholine (JEFFCAT® NEM catalyst), N-methylmorpholine (JEFFCAT® NMM catalyst), 4-methoxyethylmorpholine, N,N'dimethylpiperazine (JEFFCAT® DMP catalyst), 2,2'-dimorpholinodiethylether (JEFFCAT® DMDEE catalyst), 1,3,5-tris(3-(dimethylamino)propyl)-hexahydro-s-triazine (JEFFCAT® TR-90 catalyst), 1- propanamine, 3-(2-(dimethylamino)ethoxy), substituted imidazoles such as 1,2-dimethylimidazol and 1-methyl-2-hydroxyethylimidazole, N,N'-dimethylpiperazines or bis-substituted piperazines such aminoethylpiperazine, N,N',N'-trimethyl aminoethylpiperazine or bis-(N-methyl piperazine)urea, N-methylpyrrolidines and substituted methylpyrrolidines such as 2-aminoethyl-N-methylpyrrolidine or bis-(N- methylpyrrolidine)ethyl urea, 3-dimethylaminopropylamine, N,N,N'',N''- tetramethyldipropylene triamine, tetramethylguanidine, 1,2-bis-diisopropanol. Other examples of amine catalysts include N-alkylmorpholines, such as N-methylmorpholine, N-ethylmorpholine, N-butylmorpholine and dimorpholinodiethylether, N,N'- dimethylaminoethanol, N,N-dimethylamino ethoxy

ethanol, bis-(dimethylaminopropyl)-amino-2-propanol, bis-(dimethylamino)-2-propanol, bis-(N,N-dimethylamino)ethyl ether; N,N,N'-trimethyl-N'-hydroxyethyl-bis-(aminoethyl)ether, N,N-dimethyl amino ethyl-N'-methyl amino ethanol, tetramethyliminobispropylamine, Polycat SA1/10, Polycat SA2 LE, Polycat SA 4, Polycat SA 5 from Evonik and Toyocat' DB 30, Toyocat DB 40, Toyocat DB 60 from Tosoh, N-methylimidazole, 1,2-dimethylimidazole, N-methylmorpholine, N-ethylmorpholine, triethylamine, N,N'-dimethylpiperazine, 1,3,5-tris(dimethylaminopropyl)hexahydrotriazine, 2,4,6-tris(dimethylaminomethyl)phenol, N-methyl dicyclohexylamine, pentamethyl dipropylene triamine, N-methyl-N'-(2-dimethylamino)-ethyl-piperazine, tributylamine, pentamethyl diethylene triamine, hexamethyltriethylene tetramine, heptamethyltetraethylenepentamine, dimethylaminocyclohexylamine, pentamethyldipropylene-triamine, triethanolamine, dimethylethanolamine, bis(dimethylaminoethyl)ether, tris(3-dimethylamino)propyl amine, Jeffcat DPA, Jeffcat Z130, Dabco NE300, Dabco NE1091 and Dabco NE1550. Additionally, metal catalysts can be used in the present invention. Suitable metal catalysts include, but are not limited to, organometallic compounds such as those comprising at least one transition metal. The transition metal may be selected from Groups IVB, VB, VIIB, VIIB and VIIB of the Periodic Table of the Elements. In some embodiments, the metal catalyst comprises an organometallic compound comprising one or more metals selected from the group consisting of metals of Group VIIB of the Periodic Table of the Elements, such as iron, tin, bismuth, zinc. In some embodiments, the organometallic compound comprises one or more chelating ligands. Non-limiting examples of such chelating ligands include, but are not limited to, acetylacetone, alkyl or aryl acetoacetate, gluconate, cyclopentadienyl, or combinations thereof. The catalyst or catalyst package may consist of different combinations of catalysts, including but not limited to combinations of multiple amine catalysts, combinations of multiple metal catalyst or combinations of amine and metal catalysts.

[0060] Typically, more base catalyst is required in a foam composition comprising an EO- and/or PO-based polyether polyol relative to a PTMEG polyether polyol in order to achieve the desired reactivity. When more catalyst is present in the foam composition, phenolic yellowing is a greater issue. Therefore, phenolic yellowing may be a particular problem when the isocyanate-reactive component is an ethylene oxide- and/or propylene oxide-based polyether polyol.

- [0061] Water may be present in the foam composition, preferably in an amount of at least about 0.05 wt%, or at least about 0.1 wt%, or at least about 0.2 wt%, based upon the total weight of the foam composition. Water may be present in the foam composition in an amount of from about 0.05 wt% to about 2.5 wt%, or from about 0.1 wt% to about 2 wt%, or from about 0.2 wt% to about 2 wt%, based upon the total weight of the foam composition. Water may be present in the foam composition and thus residual water may be left over in the foam once the foam is produced. The residual water hydrolyses the ester of the carboxylic acid to produce an acidic environment in the foam, which prevents or reduces phenolic yellowing. The residual water may be supplemented by water in the atmosphere or the humidity, or the water which hydrolyses the additive may be fully derived from the atmosphere such that no water is added to the foam composition.
- [0062] According to an embodiment, the foam composition may comprise a blowing agent composition, which may comprise at least 20 wt%, or at least 40 wt%, or at least 60 wt%, or at least 80 wt%, or at least 90 wt% water, based upon the total weight of all the blowing agents used in the blowing agent composition.
- [0063] According to an embodiment, the blowing agent composition may comprise a physical blowing agent. Suitable physical blowing agents may be selected from CO₂, N₂, isobutene, methylformate, dimethyl ether, methylene chloride, acetone, t-butanol, argon, krypton, xenon, chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), hydrochlorofluoro carbons (HCFCs), hydrofluoroolefins (HFOs), Hydrochlorofluoro olefins (HCFOs), and hydrocarbons such as pentane, isopentane and cyclopentane and mixtures thereof. According to preferred embodiments, the physical blowing agents are selected from at least CO₂ and/or N₂.
- [0064] According to preferred embodiments, the physical blowing agents may be selected from HFO blowing agents and/or HCFO blowing agents and/or hydrocarbons such as cyclopentane. HFO blowing agents may be selected from 3,3,3-trifluoropropene, 1,2,3,3,3-pentafluoropropene, cis- and/or trans-1,3,3,3-tetrafluoropropene and/or 2,3,3,3-tetrafluoropropene, and/or 1,1,1,4,4,4-hexafluorobut-2-ene, and/or 1-chloro-3,3,3-trifluoropropene, and/or 2-chloro-3,3,3-trifluoropropene and mixtures thereof. Preferred examples of commercially available suitable HFO blowing gases are Honeywell HFO-1234ze (Honeywell's trade name for trans - 1,3,3,3-tetrafluoropropene) or Opteon® 1100 (Chemours' trade name for cis-1,1,1,4,4,4-hexafluorobut-2-ene, CF₃CH=CHCF₃). A preferred example of a commercially available suitable HCFO blowing gas is Honeywell Solstice® 1233zd (Honeywell's trade name for trans-1-chloro-3,3,3-trifluoropropene,

$\text{CHCl}=\text{CHCF}_3$) or Forane® 1233zd (Arkema's trade name for trans-1-chloro-3,3,3-trifluoropropene, $\text{CHCl}=\text{CHCF}_3$).

[0065] According to embodiments, the amount of blowing agents used in the foam composition can vary based on, for example, the intended use and application of the foam product and the desired foam stiffness and density.

[0066] According to embodiments, the amount of water and/or further blowing agents used in the foam composition is from about 0.1 to about 25 parts by weight, more preferably from about 0.25 to about 15 pbw per hundred weight parts isocyanate-reactive component, in order to produce a low density flexible foam having a density of 500 kg/m^3 or less, e.g. a low density foam having densities in the range $50\text{-}500 \text{ kg/m}^3$.

[0067] The foam composition may comprise a surfactant, such as a silicone-based surfactant. The surfactant may be present in an amount of from about 0 wt% to about 5 wt%, depending on the requirements of the particular foam composition. Examples of suitable commercially available surfactants include, but are not limited to Tegostab B8494, Tegostab B8905, Tegostab B8993, Tegostab B8948, Tegostab B8017, Tegostab B8930, Tegostab B8950, Tegostab B8960, Vorasurf DC193, Vorasurf 5382, Niox L1500, Niox L1550, Niox L1542, Niox UAX 7061, Niox UAX 6897, Niox UAX 6639, Niox UAX 7061, Tegostab B8466 and Tegostab B8416.

[0068] The foam composition may be separated into two parts: an isocyanate part and isocyanate-reactive part, which may be kept separately to avoid a reaction between the two parts. The isocyanate part may comprise the isocyanate component and the additive. The isocyanate-reactive part may comprise the isocyanate-reactive component, the base catalyst and, if present, water or a suitable blowing agent. The "foam composition" as used herein therefore refers to two separate parts (isocyanate part and isocyanate-reactive part) or a composition in which the two parts are mixed.

[0069] According to an embodiment, the isocyanate index of the foam composition is in the range 40 to 125, or 60 to 125, or 65 to 120, or 70 to 120, or 75 to 120, or 80 to 120, or 85 to 120, or 88 to 120, or 90 to 120, or 90 to 110, or 92 to 110, or 95 to 110, or 95 to 105, or 98 to 105, or 98 to 102.

[0070] As used herein, the "isocyanate index" or "NCO index" or "index" is the ratio of NCO-equivalents to the sum of equivalents of isocyanate-reactive hydrogen atoms present in a formulation, given as a percentage:

$$\frac{[\text{NCO}] \times 100}{[\text{active hydrogen}]} \quad (\%)$$

In other words, the NCO-index expresses the percentage of isocyanate actually used in a formulation with respect to the amount of isocyanate theoretically required for reacting with the amount of isocyanate-reactive hydrogen used in a formulation. The expression "isocyanate-reactive hydrogen" as used herein for the purpose of calculating the isocyanate index refers to the total of active hydrogen atoms in hydroxyl and amine groups present in the reactive compositions; this means that for the purpose of calculating the isocyanate index at the actual polymerisation process one hydroxyl group is considered to comprise one reactive hydrogen, one primary amine group is considered to comprise one reactive hydrogen and one water molecule is considered to comprise two active hydrogens.

[0071] According to an embodiment, the isocyanate component has an NCO value in the range 3 to 50, or 5 to 33.56, or 8 to 30, or 10 to 26, or 13 to 23. The "NCO value" or "isocyanate value" as used herein is the weight percentage of reactive isocyanate (NCO) groups in an isocyanate, modified isocyanate or isocyanate prepolymer compound.

[0072] According to an embodiment, the hardblock content of the foam composition is from about 12 to about 65 %, or from about 12 % to about 50 %, or from about 12 % to about 40 %, or from about 14 % to about 35 %, or from about 14 % to about 30 %, or from about 14 % to about 27 %, or from about 15 % to about 25 %, or from about 17 % to about 22 %.

[0073] According to an embodiment, the hardblock content of the foam composition is from about 15 % to about 65 %, or from about 17 % to about 65 %, or from about 20 % to about 65 %, or from about 25 % to about 65 %, or from about 30 % to about 65 %, or from about 35 % to about 65 %, or from about 40 % to about 65 %.

[0074] The term "hardblock" used herein refers to 100 times the ratio of the amount (in parts by weight, pbw) of polyisocyanate + isocyanate-reactive compounds having a weight-average molecular weight of less than about 500 g/mol (wherein isocyanate-reactive compounds having a molecular weight of more than 500 g/mol incorporated in the polyisocyanates are not taken into account) over the amount (in pbw) of all polyisocyanate + all isocyanate-reactive compounds used. The hardblock content is expressed in %.

[0075] The foam composition may further comprise solid polymer particles such as styrene-based polymer particles. Examples of styrene polymer particles include so-called "SAN" particles of styrene-acrylonitrile. Alternatively small amounts of polymer polyols may be added as an additional polyol in the isocyanate-reactive component. An example of a commercially available polymer polyol is HYPERLITE® Polyol 1639 which is a polyether polyol modified with a styrene-acrylonitrile polymer (SAN) with a solid content of approximately 41 wt% (also referred to as polymer polyol).

[0076] The foam composition may further comprise one or more conventional auxiliaries, such as organo-metallic compounds (for e.g., organic salts of transition metals such as titanium, iron, nickel), post-transition metals (for e.g., zinc, tin, and bismuth), alkali metals (for e.g., lithium, sodium, and potassium), alkaline earth metals (for e.g., magnesium and calcium), silicates and fumed silicate or combinations thereof, surfactants, silane adhesion promoters, antioxidants, waxes, colorants, flame retardants, microbial inhibitors, fillers, viscosity reducers, carbon black, titanium dioxide, and metal flake infra-red opacifiers, inert and insoluble fluorinated compounds, and perfluorinated cell-size reducing compounds, calcium carbonate fillers, glass fibers and/or ground up foam waste reinforcing agents, zinc stearate, butylated hydroxy toluene antioxidants, dyestuffs and pigments.

[0077] When present, these additional auxiliaries may be used in an amount of about 0.01-15% by weight, or about 0.1-10% by weight, or about 0.5-5% by weight, based on the total weight of the foam composition. These ranges may apply separately to each additional auxiliary present in the foam composition or to the total of all additional auxiliaries present.

[0078] According to embodiments, the foam composition may comprise fillers such as wood chips, wood dust, wood flakes, wooden plates; paper and cardboard, both shredded or layered; sand, vermiculite, clay, cement and other silicates; ground rubber, ground thermoplastics, ground thermoset materials; honeycombs of any material, like cardboard, aluminium, wood and plastics; metal particles and plates; cork in particulate form or in layers; natural fibers, like flax, hemp and sisal fibers; synthetic fibers, like polyamide, polyolefin, polyaramide, polyester and carbon fibers; mineral fibers, like glass fibers and rock wool fibers; mineral fillers like BaSO_4 and CaCO_3 ; nanoparticles, like clays, inorganic oxides and carbons; glass beads, ground glass, hollow glass beads; expanded or expandable beads; untreated or treated waste, like milled, chopped, crushed or ground waste and in particular fly ash; woven and non-woven textiles; and combinations of two or more of these materials.

[0079] **[Additive]**

[0080] The additive is added to the foam composition, and more preferably to the isocyanate part used to obtain the foam, to ensure the whole foam is protected against phenolic yellowing. The additive is preferably not reactive, or substantially not reactive, towards the isocyanate part and/or the isocyanate-reactive part of the foam composition.

[0081] The additive may be present in the foam composition in an amount that is effective for a given foam composition. The additive may be present in the foam composition in an amount of less than about 5.0 wt%, or less than about 4.0 wt%, or less than about 3.0 wt%, or less than about 2.0 wt% based upon the total weight of the foam composition. The

additive may be present in the foam composition in an amount of between about 0.05 wt% and about 5.0 wt%, or between about 0.05 wt% and about 4.0 wt%, or between about 0.05 wt% and about 3.0 wt%, or between about 0.05 wt% and about 2.0 wt%, or between about 0.05 wt% and about 1.0 wt%, or between about 0.05 wt% and about 0.5 wt%, or between about 0.1 wt% and about 0.5 wt%, or between about 0.2 wt% and about 0.5 wt%.

[0082] According to embodiments, the additive is present in the foam composition in an amount that is in correspondence with the amount of base/catalyst/amine. The additive is present in the foam composition in an amount where the ratio of ester groups (from the additive) to amino groups (from the catalyst and possibly other components of the foam composition) is from about 0.1 to about 20, more preferably from about 0.1 to about 10, more preferably from about 0.1 to about 5, more preferably from about 0.2 to about 5, more preferably from about 0.5 to about 5, more preferably from about 0.5 to about 4, more preferably from about 0.5 to about 3, or more preferably from about 0.5 to about 2. According to some embodiments, the additive is present in the foam composition in an amount where the ratio of ester groups (from the additive) to amino groups (from the catalyst and possibly other components of the foam composition) is from about 0.1 to about 20, more preferably from about 0.1 to about 10, more preferably from about 0.5 to about 10, more preferably from about 0.8 to about 10, more preferably from about 1.0 to about 10, more preferably from about 1.1 to about 10, more preferably from about 1.3 to about 10, or most preferably from about 1.5 to about 10.

[0083] The additive is an ester of a carboxylic acid (or made from an anhydride). The ester of the carboxylic acid may be commercially available or may be synthesised e.g., through an esterification reaction between a free carboxylic acid and an alcohol compound such as a mono-ol, a diol, a triol, or even higher functional alcohols. Alternatively, the ester may be formed by the reaction of an anhydride with an alcohol compound such as a mono-ol, a diol, a triol, or even higher functional alcohols. The synthesis of esters of carboxylic acids has been intensively studied for decades and the skilled person would be capable of synthesising the desired esters of carboxylic acids (e.g., via the carboxylic acid route and/or via the anhydride route).

[0084] The free carboxylic acid of the ester of the carboxylic acid has a pKa^1 of about 0.5 to about 4.0, or from about 1.0 to about 3.0, or from about 1.0 to about 2.8, or from about 1.0 to about 2.6, or from about 1.0 to about 2.4, or from about 1.0 to about 2.2, or from about 1.0 to about 2.0, or from about 1.0 to about 1.8, or from about 1.0 to about 1.6, or from about 1.0 to about 1.5. If any anhydride is used in the synthesis procedure, the

corresponding carboxylic acid of the anhydride is used to determine if the pK_a^1 of about 0.5 to about 4.0 (or the alternative ranges) is used. The “free carboxylic acid” refers to the acidic form of the carboxylic acid (or anhydride), e.g., before an esterification reaction. As used herein, the pK_a is measured at 25°C. As used herein, the “ pK_a^1 ” refers to the first dissociation of the carboxylic acid, and pK_a^2 refers to the second dissociation of the carboxylic acid and is relevant for dicarboxylic acids.

- [0085] Examples of a carboxylic acid or anhydride having a pK_a^1 of about 0.5 to about 4.0, thereby useful to make the ester additive according to the invention, include, but are not limited to, oxalic acid (ethanedioic acid), maleic acid (cis-butenedioic acid), malonic acid (propanedioic acid), trans-butenedioic acid, 2-methylpropanedioic acid, 2-hydroxy-benzoic acid, 2-phenylbenzoic acid, hydroxyethanoic acid, 2-methyl-benzoic acid, formic acid, carbonic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, 2-chlorobutanoic acid, 3-chlorobutanoic acid, bromoacetic acid, 2-butyric acid, 2-chloropropanoic acid, 3-chloropropanoic acid, glycine, fluoroacetic acid, difluoroacetic acid, 2-nitrobenzoic acid, fumaric acid, acetylenedicarboxylic acid, muconic acid, glutamic acid, alanine, valine, leucine, isoleucine, methionine, proline, phenylalanine, tryptophan, asparagine, glutamine, serine, threonine, tyrosine, cysteine, aspartic acid, glutamic acid, lysine, arginine, and histidine.
- [0086] Preferably, the free carboxylic acid (or anhydride) is free of halogens. This will avoid the formation of very strong acids or the formation/loss of halogenated byproducts during the lifetime or recycling of the material. Preferably, the free carboxylic acid (or anhydride) is free of aromatic rings. This will avoid the formation of aromatic byproducts during the lifetime or recycling of the material which can contribute to discoloration.
- [0087] Preferably, the free carboxylic acid (or anhydride) is free of other isocyanate reactive groups besides the carboxylic acid group(s). This will avoid any interference with the material reactivity and/or crosslinking behaviour of the material.
- [0088] Preferably, the free carboxylic acid is a dicarboxylic acid, and more preferably the free carboxylic acid is a dicarboxylic acid having 2 to 4 carbon atoms. The free carboxylic acid may be any one selected from oxalic acid, malonic acid, maleic acid and fumaric acid. In a preferred embodiment, the free carboxylic acid is malonic acid or oxalic acid, and more preferably oxalic acid.
- [0089] The ester additive can be made by the esterification reaction using a carboxylic acid and a hydroxyl group containing material. Preferably the additive, in its pure form, does not contain any isocyanate-reactive groups as such (except for impurities). Preferably the

additive can be considered as a type of plasticizer or diluent in the matrix. Most preferably the additive does not take part in the foam reaction.

[0090] The ester additive can be made by the esterification reaction using a carboxylic acid and a hydroxyl group containing material. According to some embodiments, the carboxylic acid has more than 1 carboxylic acid functional group per molecule. According to some embodiments, the carboxylic acid has more than 2 carboxylic acid functional group per molecule. According to some embodiments, the hydroxyl containing molecule has more than 1 hydroxyl functional group per molecule. According to some embodiments, the hydroxyl containing molecule has more than 2 hydroxyl functional group per molecule.

[0091] Preferably, the ester of the carboxylic acid is an alkyl ester of the carboxylic acid. The alkyl group of the alkyl ester may be a hydrocarbon chain (consisting of H and C only) which does not contain any functional groups such as hydroxyl groups. The hydrocarbon chain may contain 1 to 10 carbon atoms, and the alkyl group may be a C1-C10 alkyl group. Preferably, the alkyl group is any one selected from methyl, ethyl, n- or i-propyl and n-, i- or tert-butyl, and more preferably the alkyl group is methyl or ethyl.

[0092] The alkyl group may be derived from the alcohol compound used to form the ester. The alcohol compound may be any one selected from methanol, ethanol, n- or i-propanol and n-, i- or tert-butanol.

[0093] In a particularly preferred embodiment, the ester of the carboxylic acid is any one selected from dimethyl malonate, diethyl malonate, dimethyl oxalate and diethyl oxalate (DEO). Preferably, the ester of the carboxylic acid is diethyl oxalate (DEO).

[0094] According to an embodiment, the additive may have a weight-average molecular weight of about 50 to about 200 g/mol, or from about 70 to about 200 g/mol, or from about 90 to about 200 g/mol, or from about 110 to about 200 g/mol, or from about 120 to about 200 g/mol, or from about 130 to about 200 g/mol, or from about 130 to about 160 g/mol, or from about 140 to about 150 g/mol.

[0095] According to an embodiment, the half-life times of hydrolysis of the additive at 25°C using a buffered solution of nominal pH 7.0 is less than 10 days, or less than 5 days, or less than 3 days, or less than 2 days, or less than 1.5 days, or less than 1.2 days, or less than 1 day, or less than 12 hours (according to ECHA hydrolysis methods).

[0096] According to an embodiment, the boiling point of the additive is higher than 50°C to avoid that it evaporates during the use, and more preferably higher than 70°C, more preferably higher than 90°C, more preferably higher than 110°C, more preferably higher than 130°C, more preferably higher than 150°C, and most preferably higher than 170°C.

[0097] According to an embodiment, the boiling point of the carboxylic acid used to make the additive is higher than 50°C to avoid that it evaporates during the use, and more preferably higher than 70°C, more preferably higher than 90°C, more preferably higher than 110°C, more preferably higher than 130°C, more preferably higher than 150°C, and most preferably higher than 170°C.

[0098] More than one additive to prevent or reduce phenolic yellowing may be used in the present disclosure. That is, more than one ester of a carboxylic acid may be added to the foam composition. Preferably, only one additive is used in the present disclosure.

[0099] **[Method of producing a polyurethane-based foam]**

[0100] The method of producing a polyurethane-based foam comprises: mixing the foam composition to form a reactive mixture, and allowing the reactive mixture to cure to form a polyurethane-based foam.

[0101] That is, the foam is formed by mixing the two parts of the foam composition (isocyanate part and isocyanate-reactive part), or by mixing of the foam composition. Foams are made using any mixing device (such as a lab mixer, machine mixing head, static mixing or impingement mixing) where the reactive components are mixed and then allowed to foam. Typically, but optionally, the foaming occurs in a mould (e.g., a footwear mould) after the reaction of the components, which typically takes seconds to minutes (or hours in more extreme cases). The foam can be handled and used once foaming has occurred (e.g., after demoulding).

[0102] All reactants in the foam composition can be reacted at once or can be reacted in a sequential manner. The various components used in the manufacture of the compositions of the invention can be added in any order. The process can be selected from a bulk process, either batch or continuous process including cast process.

[0103] The isocyanate component and isocyanate reactive component (and any other relevant components in the foam composition) may be mixed in an amount such that the isocyanate index is as desired.

[0104] According to embodiments, the polyurethane-based foam may be made at a density of about 30 to about 900 kg/m³ (according to ISO 845). More preferably the polyurethane-based foam is made at a density of about 30 to about 700 kg/m³, or about 30 to about 500 kg/m³, or about 30 to about 350 kg/m³, or about 30 to about 250 kg/m³, or about 30 to about 200 kg/m³.

[0105] According to embodiments, the polyurethane-based foam may be made at a density of about 30 to about 900 kg/m³ (according to ISO 845). More preferably the polyurethane-

based foam is made at a density of about 30 to about 500 kg/m³, or about 100 to about 500 kg/m³, or about 150 to about 500 kg/m³, or about 200 to about 500 kg/m³, or about 200 to about 400 kg/m³.

[0106] **[Polyurethane-based foam]**

[0107] The polyurethane-based foam is obtainable, or obtained, by the method described herein.

The use of the additive in the polyurethane-based foam helps to achieve a phenolic yellowing test result rating of 3 or more out of 5, when tested via EN ISO 105-X18 (the Courtauld test). In one embodiment, the polyurethane-based foam has a phenolic yellowing test result of 4 or more out of 5.

[0108] In an embodiment, the polyurethane-based foam may be used in: footwear, shoe soles, and midsoles; orthopaedic products; artificial leather; mattresses; foam seals and gaskets; elastomeric wheels and tires; automotive suspension and seating; general upholstery applications and floor covering; bicycle saddles; lightweight synthetic fibers; general and sports clothing and apparel; seating and furniture foam; grips and handles; and microcellular foam applications.

[0109] **[Use of the additive to prevent or reduce phenolic yellowing in a polyurethane-based foam]**

[0110] There is provided a use of the additive to prevent or reduce phenolic yellowing in a polyurethane-based foam, wherein the additive is an ester of a carboxylic acid and the free carboxylic acid of the ester of the carboxylic acid has a pK_a¹ of about 0.5 to about 4.0, and wherein the polyurethane-based foam is obtained from a foam composition comprising an isocyanate-reactive component, an isocyanate component, and a base catalyst.

[0111] The additive may be added to the foam composition, added to the release agent e.g., when a mould is used in foaming, or added to the foam via any other practicable method such as via a color paste. The foam composition is otherwise identical to the description above.

[0112] The additive is also identical to the additive described above.

[0113] **[Thermoplastic polyurethane composition]**

[0114] The additive described herein may also be used in a thermoplastic polyurethane (TPU) composition, wherein a TPU composition is reacted to form a non-foamed TPU. The thermoplastic polyurethane composition for producing the thermoplastic polyurethane comprises: an isocyanate component; isocyanate-reactive component; and an additive, wherein the additive is an ester of a carboxylic acid and the free carboxylic acid of the ester of the carboxylic acid has a pK_a¹ of about 0.5 to about 4.0.

[0115] The additive may be added to any TPU composition known in the art in order to reduce phenolic yellowing of the TPU. The additive is applicable to TPU compositions because TPU also undergoes phenolic yellowing, particularly when basic compounds are used in its preparation. The isocyanate component, isocyanate-reactive component and additive may be as described above with reference to the polyurethane-based foam, as long as the TPU produced has thermoplastic characteristics. Such characteristic is the ability to melt, solidify, remelt and solidify, without any significant change in the composition and properties of the TPU.

[0116] **[Non-limiting embodiments]**

[0117] In an embodiment of the present disclosure, there is provided a foam composition for producing a polyurethane-based foam, the foam composition comprising: an isocyanate component comprising an aromatic diisocyanate or a prepolymer thereof; an isocyanate-reactive component comprising a polyether polyol; a base catalyst; and an additive, wherein the additive is an ester of a carboxylic acid and the free carboxylic acid of the ester of the carboxylic acid has a pK_a^1 of about 1.0 to about 3.0.

[0118] In an embodiment of the present disclosure, there is provided a foam composition for producing a polyurethane-based foam, the foam composition comprising: an isocyanate component comprising an aromatic diisocyanate or a prepolymer thereof; an isocyanate-reactive component which is an ethylene oxide- and/or propylene oxide-based polyether polyol; a base catalyst; and an additive selected from dimethyl malonate, diethyl malonate, dimethyl oxalate or diethyl oxalate (DEO).

[0119] In an embodiment of the present disclosure, there is provided a foam composition for producing a polyurethane-based foam, the foam composition comprising: an isocyanate component comprising an aromatic diisocyanate or a prepolymer thereof; an isocyanate-reactive component which is an ethylene oxide- and/or propylene oxide-based polyether polyol; a base catalyst; and an additive which is diethyl oxalate (DEO).

[0120] In an embodiment of the present disclosure, there is provided a use of an additive to prevent or reduce phenolic yellowing in a polyurethane-based foam, wherein the additive is an ester of a carboxylic acid and the free carboxylic acid of the ester of the carboxylic acid has a pK_a^1 of about 1.0 to about 3.0, and wherein the polyurethane-based foam is obtained from a foam composition comprising: an isocyanate-reactive component comprising a polyether polyol; an isocyanate component comprising an aromatic diisocyanate or a prepolymer thereof; and a base catalyst.

[0121] In an embodiment of the present disclosure, there is provided a use of an additive to prevent or reduce phenolic yellowing in a polyurethane-based foam, wherein the additive is any one selected from dimethyl malonate, diethyl malonate, dimethyl oxalate and diethyl oxalate (DEO), and wherein the polyurethane-based foam is obtained from a foam composition comprising: an isocyanate-reactive component comprising a polyether polyol; an isocyanate component comprising an aromatic diisocyanate or prepolymer thereof; and a base catalyst.

[0122] In an embodiment of the present disclosure, there is provided a use of an additive in a polyurethane-based foam in footwear to prevent or reduce phenolic yellowing, wherein the additive is diethyl oxalate (DEO), and wherein the polyurethane-based foam is obtained from a foam composition comprising: an isocyanate-reactive component comprising a polyether polyol; an isocyanate component comprising an aromatic diisocyanate or a prepolymer thereof; and a base catalyst.

[0123] **[Examples]**

[0124] The present disclosure will be described in more detail with reference to the Examples.

The present disclosure is not limited to the following Examples.

[0125] Chemicals used:

Daltocel® F 428 C	an ethyleneoxide-capped polyether polyol available from Huntsman (OH value 26-30 mg KOH/g).
Polymeg® 2000	Polytetramethylene ether glycol (PTMEG) produced by polymerizing tetrahydrofuran available from LyondellBasell (OH value of 56 mg KOH/g)
Dabco® Solid (TEDA)	Catalyst: Dabco crystalline, 100% solid triethylene diamine (1,4-diazabicyclo[2.2.2]octane) from Evonik
BDO	Chain extender: 1,4-butanediol obtained from Sigma Aldrich
Water	Blowing agent: Distilled water
Dabco 25s	25% triethylene diamine (1,4-diazabicyclo[2.2.2]octane) dissolved in 1,4-butanediol, polyurethane catalyst obtained from Evonik
VORASURF® DC 193	General-purpose silicone surfactant from DOW
DEO	Diethyl oxalate, additive obtained from Sigma-Aldrich
Isocyanate 1	Suprasec® 2445 from Huntsman. Polyether-modified MDI prepolymer with an NCOv = 16%
Isocyanate 2	Isocyanate prepolymer based on Suprasec® MPR with Polymeg® 2000 with an NCOv = 16%

[0126] The foam samples are made according to the practical knowledge of those skilled in the art.

This is done by varying the mixing ratio of the polyol blend and isocyanate blend and determining which mixing ratio provides the strongest foam after a given time (e.g., 70 seconds) using an indentation drop test. In some cases, the reactivity of the foam system was too slow, and alternatively an index of 100 was used (see Tables below). In some cases, the exact same index was used between the comparative example and the example according to the invention, to ensure the observed differences in phenolic yellowing do not originate from differences in the foam formulation. In all cases the calculated system index is determined and provided in the Table, and information is provided. The cream time and end of rise time was monitored as the time where the mixture starts to foam and the time the foam reaches its highest point respectively. Both free rise density (according to ISO 845) and moulded density (according to ISO 1183-1) are determined by ISO methods.

[0127] The formulation of the examples is split into two separate blends, called the “isocyanate blend” or “ISO blend” (referring to the isocyanate component) and the “isocyanate reactive blend” or “polyol blend” (referring to the isocyanate-reactive component). The isocyanate reactive blend (as shown in the examples) refers to all other ingredients besides the isocyanate and thus may contain polyols, crosslinkers, chain extenders, catalysts and surfactants (but could also contain other ingredients as described in certain embodiments). When the additive according to the invention was used, it was blended into the prepolymer (e.g., 0.71w% or 0.86w% or 1.42 w% or 1.72w% depending on the formulation) before loading it on the machine.

[0128] The foam samples (free rise & moulded) are made using a 2K PU casting Green machine with a DVM2408 mixing head. The “isocyanate blend” and “isocyanate reactive blend” were kept at the temperatures indicated in the Tables by the machine before the casting was done. A slab mould was treated with the water-based release agent Kezal 710/161 (obtained from Kezal) and the release carrier (water) was allowed to evaporate, before the polyurethane material was casted into the mould which was maintained at 50°C. The screw speed of the mixing head was set at 6000 rpm, and an output of 40-60 g/s was used. Foam sample slabs (20x15x1 cm) were made with an overpack of about two (moulded density ~ 2x free rise density). The samples were not post-cured (at elevated temperature), and were tested 2-5 days after the preparation of the foam.

[0129] All foam samples are subjected to the Courtauld phenolic yellowing test (EN ISO 105-X18). The test specimens are cut out from the foam slab to obtain a small strip of 10 cm by 2 cm. Then the foam piece is split into two in the height (1cm) direction to obtain the final test

specimen (10x2x0.5 cm). Each test specimen is placed in between a paper which is impregnated with 2,6-tert butyl-4-nitrophenol and placed between glass plates, as is also done for a reference test specimen. The glass plates are stacked and wrapped using BHI free film. The whole stack is pressed together using a clamping device to ensure proper contact of the impregnated paper with the test specimens. The device is placed in an oven at 50°C for 16h. After the test, the test specimens are left to cool and the reference test specimen is checked to ensure it properly yellowed. The test specimens are scored against the original foam piece (not subjected to the test; we used the other half of the split foam sample) using a grayscale to determine the intensity of discoloration versus the reference (grayscale 5 = no discoloration; 1 = high discoloration). The following scores can be obtained: 1, 1/2, 2, 2/3, 3, 3/4, 4, 4/5, 5. Typical requirement for apparel applications is a score of 4, 4/5 or 5. For the ease of comparison, the improvement points between the comparative example (CE) and example according to the invention (E) are also provided.

[0130] Table 1: Examples EO/PO polyether system

System		CE-1	E-1	CE-2	E-2	CE-3	E-3	CE-4	E-4	CE-5	E-5	E-6
Polyol blend	Daltocel F 428 C	75.54	75.54	75.14	75.12	61.01	61.01	53.35	53.35	54.93	54.91	53.02
	TEDA	0.31	0.31	0.30	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Water	0.46	0.46	1.22	1.22	0.39	0.39	0.92	0.92	0.95	0.95	0.91
	VORASURF® DC 193	0.19	0.19	0.19	0.19	0.16	0.16	0.14	0.14	0.15	0.15	0.14
	BDO	0.00	0.00	0.00	0.00	3.16	3.16	2.76	2.76	2.13	2.13	2.06
	Dabco 25s	0.00	0.00	0.00	0.00	1.05	1.05	0.92	0.92	1.90	1.89	1.83
ISO blend	Isocyanate 1	23.50	23.30	23.15	22.97	34.22	33.92	41.90	41.54	39.94	39.62	41.31
	DEO	0.00	0.20	0.00	0.20	0.00	0.29	0.00	0.36	0.00	0.34	0.72
Processing	Total system	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	Index (calc)	100.0	99.2	50.6*	50.3	79.8*	79.2*	77.1*	76.5*	71.4*	70.9	76.6*
	Iso T [°C]	30	30	30	30	30	30	30	30	30	30	30
	Polyol T [°C]	32	32	32	32	32	32	32	32	32	32	32
Reactivity - foaming	Cream time [s]	13	14	6.5	7	9.5	13	8	9	5.5	5	5
	End of rise [s]	330	360	120	110	115	140	100	110	60	62	70
	Free rise density [kg/m3]	215	183	138	139	240	248	108	108	117	117	108
	Moulded density [kg/m3]	400	400	250	250	400	400	250	250	250	250	250
	Min. demould time [s]	> 600	> 600	180	180	330	360	360	360	430	400	360
Performance	Phenolic yellowing score	2	3/4	3	4	3	4	2	4/5	2	3/4	4/5
	improvement points by additive		1.5		1		1		2.5		1.5	2.5
	* = system is processed at the index that can be found by the indenter optimum											

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[0131] The experimental data shown in Table 1 clearly shows the improved phenolic yellowing score for the EO/PO-based foams made according to the invention. In all examples in Table 1, the phenolic yellowing score has improved by at least 1 point, and in some cases even by 2.5 points. The data also clearly shows that the additive works for different amounts of water used (examples set 1 and 2), different amounts of chain extender used (examples set 1 and 3, and examples set 2 and 4), and different amounts of catalyst used (examples set 4 and 5). The data also clearly shows that the concentration of the additive can be varied to obtain a desired phenolic yellowing score (example E-5 and E-6). The additive according to the invention is especially useful for systems with a high water level and high catalyst level (example sets 4 and 5). (Note: example set 1, as described in the text above, refers to the set of samples CE-1 and E-1).

[0132] The experimental data in Table 1 also clearly shows that the additive according to the invention has no/minimal impact on the foam reactivity (similar cream time, end of rise time, minimum demould time) and the foam density (free rise density).

[0133] Table 2: Examples Polymeg® polyether system

System		CE-7	E-7	CE-8	E-8	CE-9	E-9	CE-10	E-10	CE-11	E-11	E-12
Polyol blend	Polymeg® 2000	74.06	74.09	66.38	66.83	55.53	55.29	51.01	50.57	49.43	49.10	49.15
	TEDA	0.30	0.30	0.27	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Water	0.45	0.45	1.08	1.08	0.36	0.36	0.88	0.87	0.85	0.85	0.85
	VORASURF® DC 193	0.19	0.19	0.17	0.17	0.15	0.15	0.14	0.14	0.13	0.13	0.13
	BDO	0.00	0.00	0.00	0.00	2.87	2.86	2.64	2.62	1.92	1.91	1.91
	Dabco 25s	0.00	0.00	0.00	0.00	0.96	0.95	0.88	0.87	1.71	1.69	1.70
ISO blend	Isocyanate 2	25.00	24.80	32.11	31.42	40.13	40.10	44.45	44.61	45.96	45.99	45.61
	DEO	0.00	0.18	0.00	0.22	0.00	0.29	0.00	0.32	0.00	0.33	0.66
Processing	Total system	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	Index (calc)	76.6*	76.0	65.7*	63.9*	87.1*	87.4*	76.2*	77.1*	81.3*	81.9*	81.1*
	Iso T [°C]	40	40	40	40	40	40	40	40	40	40	40
	Polyol T [°C]	49	49	49	49	49	49	49	49	49	49	49
Reactivity - foaming	Cream time [s]	9.5	8	5.5	6	8	8	6	6.5	3	3	3
	End of rise [s]	150	125	42	42	110	120	41	40	25	24	25
	Free rise density [kg/m3]	280	264	182	193	203	200	146	147	130	141	139
	Moulded density [kg/m3]	500	500	300	300	400	400	300	300	250	250	250
	Min. demould time [s]	555	600	330	300	480	480	435	435	300	270	270
Performance	Phenolic yellowing score	3	4/5	3/4	4/5	3	4/5	3	5	2/3	4/5	5
	improvement points by additive		1.5		1		1.5		2		2	2.5
	* = system is processed at the index that can be found by the indenter optimum											

- [0134] The experimental data shown in Table 2 clearly shows the improved phenolic yellowing score for the foams made according to the invention. In all examples in Table 2, the phenolic yellowing score has improved by at least 1 point, and in some cases even by 2.5 points. The data also clearly shows that the additive works for different amounts of water used (examples set 7 and 8), different amounts of chain extender used (examples set 7 and 9, and examples set 8 and 10), and different amounts of catalyst used (examples set 10 and 11). The data also clearly shows that the concentration of the additive can be varied to obtain a desired phenolic yellowing score (example E-11 and E-12). The additive according to the invention is especially useful for systems with a high water level and high catalyst level (example sets 10 and 11).
- [0135] The experimental data in Table 2 also clearly shows that the additive according to the invention has no/minimal impact on the foam reactivity (similar cream time, end of rise time, minimum demould time) and the foam density (free rise density).
- [0136] As an additional experiment, the additive (DEO) was added at a 5 weight% loading to solvent-based release agent TM VP 1495/10 (from Rika Chemie GmbH). In this case a solvent based release agent is required (instead of the water-based release agent Kezal 710/161 used in the other tests) to ensure the additive (DEO) does not hydrolyse readily in the release. The foam of composition CE-11 was made using a mould treated with the release agent TM VP 1495/10 containing 5 weight% DEO. Surprisingly the foam had an improved phenolic yellowing score of 3 (instead of 2/3). The foam made using this approach shows identical foam reactivity and skin cure, thus demonstrating the effective phenolic yellowing improvement without affecting the reactivity.
- [0137] In a comparable experiment, the foam of composition CE-11 was made using a mould treated with a modified version of the water-based release agent Kezal 710/161 (modified to contain 5w% citric acid). The foam made with this approach showed a significant reduction in skin cure and was not able to be demoulded properly (skin patches remained in the mould, when demoulded after 5 minutes). This demonstrates that the use of an acid in the release agent is not recommended as it significantly impacts the foam reactivity and skin cure.
- [0138] As an additional experiment, the additive (DEO) was added at a 15 weight% loading to a REPI white UV 10513 color paste. This modified color paste was used in a basic lab experiment (using a hand mixer) at a 3 weight% loading to prepare composition CE-11 as a free rise density foam. A piece of the foam was then tested according to the Courtauld phenolic yellowing test (EN ISO 105-X18), resulting in a phenolic yellowing score of 4/5. A

similar experiment using only the standard (non-modified) REPI white UV 10513 color paste to prepare composition CE-11 only resulted in a phenolic yellowing score of 3. This additional experiment shows that the additive according to the invention can also be used in color pastes to improve the phenolic yellowing of polyurethane foams.

[0139] All ranges described herein are exemplary in nature and include any and all values in between. The terms “substantially”, “approximately” and “about” used herein are interchangeable and refer to a measurement that includes the stated measurement and any measurements reasonably close to the stated measurement. Measurements that are reasonably close to the stated measurement deviate from the stated measurement by a reasonably small amount as understood and readily ascertained by individuals having ordinary skill in the relevant art. Such deviations may be attributable to measurement error, differences in measurement and/or manufacturing equipment calibrations, human error in reading and/or setting measurements, minor adjustments made to optimize performance and/or structural parameters in view of differences in measurement associated with other components, particular implementation scenarios, imprecise adjustment and/or manipulation of objects by a person or machine. In the event it is determined that individuals having ordinary skill in the relevant art would not readily ascertain values for such reasonably small differences, the terms “about” and “approximately” can be understood to mean plus or minus 10% of the stated value.

[0140] Throughout the description and claims, the terms take the meanings explicitly defined herein, unless the context clearly dictates otherwise.

[0141] The phrases “in one embodiment”, “in an embodiment” and “in some embodiments” etc. as used herein do not necessarily refer to the same embodiment(s), though they may. Furthermore, the phrases “in another embodiment” and “in some other embodiments” as used herein do not necessarily refer to a different embodiment, though they may. All embodiments of the present disclosure are intended to be combinable.

[0142] The terms “comprises” and “comprising” mean to include but not limited to, such that further features may be present. The terms may also mean to consist of or consist essentially of.

[0143] All references and test methods cited herein are incorporated by reference in their entireties.

-END-

CLAIMS

1. A foam composition for producing a polyurethane-based foam, the foam composition comprising:
 - an isocyanate component;
 - an isocyanate-reactive component;
 - a base catalyst; and
 - an additive, wherein the additive is an ester of a carboxylic acid and the free carboxylic acid of the ester of the carboxylic acid has a pK_a^1 of about 0.5 to about 4.0.
2. A foam composition according to Claim 1, wherein the ester of the carboxylic acid is an alkyl ester of the carboxylic acid, preferably wherein the alkyl group of the alkyl ester of the carboxylic acid is methyl or ethyl.
3. A foam composition according to Claim 1 or Claim 2, wherein the free carboxylic acid is a dicarboxylic acid, preferably wherein the free carboxylic acid is a dicarboxylic acid having 2 to 4 carbon atoms, and more preferably wherein the free carboxylic acid is malonic acid or oxalic acid.
4. A foam composition according to any preceding claim, wherein the ester of the carboxylic acid is any one selected from dimethyl malonate, diethyl malonate, dimethyl oxalate and diethyl oxalate (DEO), preferably wherein the ester of the carboxylic acid is DEO.
5. A foam composition according to any preceding claim, wherein the free carboxylic acid of the ester of the carboxylic acid has a pK_a^1 of about 1.0 to about 3.0.
6. A foam composition according to any preceding claim, wherein the additive is present in the foam composition in an amount of less than about 2.0 wt%, based upon the total weight of the foam composition.
7. A foam composition according to any preceding claim, wherein the isocyanate-reactive component comprises a polyether polyol or a polyester polyol, preferably wherein the isocyanate-reactive component comprises a polyether polyol.
8. A foam composition according to Claim 7, wherein the isocyanate-reactive component comprises an ethylene oxide- and/or propylene oxide-based polyether polyol, optionally wherein the ethylene oxide- and/or propylene oxide-based polyether polyol is prepared by adding ethylene oxide and/or propylene oxide to an initiator, optionally wherein the initiator is glycerol.
9. A foam composition according to any preceding claim, wherein the isocyanate-reactive component comprises less than 50 wt% of polyester polyol and/or polycarbonate polyol, based upon the total weight of the isocyanate-reactive component.

10. A foam composition according to any preceding claim, wherein the base catalyst comprises an amine catalyst.
11. A foam composition according to any preceding claim, wherein the isocyanate component comprises a methylene diphenyl diisocyanate (MDI)-based compound.
12. A foam composition according to any preceding claim, wherein water is present in the foam composition, preferably in an amount of at least about 0.2 wt%, based upon the total weight of the foam composition.
13. A method of producing a polyurethane-based foam, comprising: mixing the foam composition as defined in any of Claims 1-12 to form a reactive mixture, and allowing the reactive mixture to cure to form a polyurethane-based foam.
14. A polyurethane-based foam obtainable by the method as defined in Claim 13.
15. Use of an additive to prevent or reduce phenolic yellowing in a polyurethane-based foam, wherein the additive is an ester of a carboxylic acid and the free carboxylic acid of the ester of the carboxylic acid has a pK_a^1 of about 0.5 to about 4.0, and wherein the polyurethane-based foam is obtained from a foam composition comprising an isocyanate-reactive component, an isocyanate component and a base catalyst.
16. Use according to Claim 15, wherein the additive is added to the foam composition, or a non-water-based release agent for a mould in which the polyurethane-based foam is prepared, or a color paste for the polyurethane-based foam.
17. A thermoplastic polyurethane composition for producing a non-foamed thermoplastic polyurethane, the composition comprising: an isocyanate component; isocyanate-reactive component; and an additive, wherein the additive is an ester of a carboxylic acid and the free carboxylic acid of the ester of the carboxylic acid has a pK_a^1 of about 0.5 to about 4.0.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/086037

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	C08G18/32	C08G18/34	C08G18/48	C08G18/66	C08G18/76
ADD.					
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED					
Minimum documentation searched (classification system followed by classification symbols) C08G					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched					
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages				Relevant to claim No.
X	CN 110 283 352 A (JIAHUA CHEMICAL TECH DEVELOPMENT SHANGHAI CO LTD) 27 September 2019 (2019-09-27)				1-14,17
A	claim 1				15,16

X	CN 111 518 252 A (SHANGHAI FUJIA FINE CHEMICAL CO LTD) 11 August 2020 (2020-08-11)				1-14,17
A	claim 1				15,16

X	US 4 997 858 A (JOURQUIN LUCIEN [BE] ET AL) 5 March 1991 (1991-03-05)				1-14,17
A	claim 1				15,16

X	US 10 696 777 B2 (EVONIK OPERATIONS GMBH [DE]) 30 June 2020 (2020-06-30)				1-14,17
A	claim 3				15,16

-/-					
☒ Further documents are listed in the continuation of Box C.					
☒ See patent family annex.					
* Special categories of cited documents :					
"A" document defining the general state of the art which is not considered to be of particular relevance			"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention		
"E" earlier application or patent but published on or after the international filing date			"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone		
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)			"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art		
"O" document referring to an oral disclosure, use, exhibition or other means			"&" document member of the same patent family		
"P" document published prior to the international filing date but later than the priority date claimed					
Date of the actual completion of the international search 14 March 2025			Date of mailing of the international search report 27/03/2025		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Bergmeier, Martin		

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/086037

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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