Adhesive prepared by reacting an organic polyisocyanate with a compound containing isocyanate-reactive hydrogen atoms in the presence of a trimerisation catalyst. The organic polyisocyanate comprises at least a first chain extender.
POLYISOCYANATE-BASED ADHESIVE

The present invention relates to adhesive compositions and adhesives based on polyisocyanate, to polyisocyanate-based adhesive formulations and to reactive mixtures for preparing such adhesives.

Adhesives based on compounds containing more than one isocyanate group per molecule and on compounds containing more than one hydroxyl group per molecule, so-called polyurethane adhesives or polyisocyanate-based adhesives, are used in many application areas due to their outstanding properties, their simple and economical processing and their high strength. One of these application areas is flexible packaging were a laminated film or sheet, produced using an adhesive, is used.

However for some applications the crosslink density of standard polyurethane adhesives is too low, preventing the material to be used in severe climatically conditions. For example car body adhesives should have high heat and salt water resistance.

For other applications, such as flexible food packaging, the cure rate of polyurethane adhesives is very slow, requiring prolonged storage of the final laminate so as to reduce the amount of migratable aromatic amines below the legally required limit.

For adhesives in general, a good and permanent bond to the substrate or substrates to which it is provided, is sought. Adhesives applied may fail according to at least two failure modes. According to a first failure mode, the adhesion between the adhesive and the substrate surface to which the adhesive adheres, is broken. This failure mode is also referred to as "adhesive failure" or "adhesion failure". According to a second failure mode, the adhesive itself is broken under stress provided to the adhesive, e.g. by mutually displacing the two substrate surfaces which are held together by the adhesive. This failure mode is also referred to as "cohesion failure".

For both cohesion and adhesion failure, the maximum stress, which the adhesive can resist, is indicative for the strength of the bond provided by the adhesive. The higher the maximum stress the adhesive can resist, the stronger the bond and the better cohesion or adhesion failure can be avoided.
It is an object of the invention to provide a strong adhesive, suitable to resist to an increased maximum stresses. It is a further object of the present invention to provide an adhesive or adhesive composition based on polyisocyanates experiencing one or more of the disadvantages mentioned above to a less extent, or even not experiencing one or more of the disadvantages mentioned above.

Some adhesives according to embodiments of the present invention provide bonds suitable to be used in more severe climatically conditions, such as at elevated temperature or in salty conditions, e.g. car body adhesives subjected to high heat and/or salt water.

Some adhesives according to embodiments of the present invention provide bonds suitable to be used in as flexible food packaging, due to a reduced migration of aromatic amines, i.e. a migration rate below the legally required limit.

According to a first aspect of the present invention, a polyisocyanate based adhesive is provided, which adhesive is prepared by reacting an organic polyisocyanate with a compound containing isocyanate-reactive hydrogen atoms in the presence of a trimerisation catalyst.

The presence of a trimerisation catalyst has the effect that the polyisocyanate-based adhesive according to the present invention can become a polyisocyanurate-based adhesive.

Some embodiments of the polyisocyanate-based adhesives according to the present invention have the benefit of extremely fast cure and therefore fast handling strength.

Furthermore, some embodiments of the polyisocyanate-based adhesives according to the present invention have an extremely high crosslink density (compared to presently known polyurethane-based adhesives), which increases the strength of the bond as well as the resistance against unfavorable media and creep. The increased strength also results in a higher maximum stress the adhesive can resist before cohesion or adhesion failure occurs.

Some embodiments of the polyisocyanate-based adhesives according to the present invention achieve a faster reduction presence and/or migration of aromatic amine in the cured film, which is extremely valuable when the adhesive is used in food and medical related applications.
Organic polyisocyanates may be aromatic or aliphatic organic polyisocyanates.

The organic polyisocyanate used in the present invention may comprise any number of polyisocyanates, including but not limited to, toluene diisocyanates (TDI), diphenylmethane diisocyanate (MDI) - type isocyanates, and prepolymers of these isocyanates. Preferably the polyisocyanate may have at least two aromatic rings in its structure, and is a liquid product. Polymeric isocyanates having a functionality greater than 2 are preferred.

The functionality of an organic polyisocyanate, as such or as polymeric or prepolymeric polyisocyanates, refers to the average number of isocyanate groups per molecule, averaged over a statistically relevant number of molecules present in the organic polyisocyanate.

In case diphenylmethane diisocyanate (also known as methylene diphenyl diisocyanate, and referred to as MDI) is used to provide an adhesive according to the present invention, the diphenylmethane diisocyanate (MDI) used in the present invention can be in the form of its 2,4', 2,2'- and 4,4'-isomers and mixtures thereof, the mixtures of diphenylmethane diisocyanates (MDI) and oligomers thereof known in the art as "crude" or polymeric MDI (polymethylene polyphenylene polyisocyanates) having an isocyanate functionality of greater than 2, or any of their derivatives having a urethane, isocyanurate, allophonate, biuret, uretonimine, uretdione and/or iminoxadiazinedione groups and mixtures of the same.

Examples of other suitable organic polyisocyanates are toluene diisocyanate (also known as toluene diisocyanate, and referred to as TDI), such as 2,4 TDI and 2,6 TDI in any suitable isomer mixture, hexamethylene diisocyanate (HMDI or HDI), isophorone diisocyanate (IPDI), butylene diisocyanate, trimethylhexamethylene diisocyanate, di(isocyanatocyclohexyl)methane, e.g. 4,4' diisocyanatodicyclohexylmethane (Hi₂MDI), isocyanatomethyl-1,8-octane diisocyanate and tetramethylxylene diisocyanate (TMXDI), 1,5-naphtalenediisocyanate (NDI), p-phenylenediisocyanate (PPDI), 1,4-cyclohaxanediisocyanate (CDI), toldiene diisocyanate (TODI), any suitable mixture of these organic polyisocyanates, and any suitable mixture of one or more of these organic polyisocyanates with MDI in the
form of its 2,4', 2,2'- and 4,4'-isomers and mixtures thereof, the mixtures of diphenylmethane diisocyanates (MDI) and oligomers thereof.

Preferred organic polyisocyanates used for the present invention are polymeric or prepolymeric organic polyisocyanates, such a quasi-prepolymers, semi-prepolymers or full prepolymer, which may be obtained by reacting polyisocyanates, e.g. organic polyisocyanates as set out above, and preferably MDI-based organic polyisocyanates, with compounds containing isocyanate-reactive hydrogen atoms. Polymeric organic polyisocyanates are to be understood as polyisocyanate compounds having an isocyanate value less than 6.5%. Full Prepomers based on organic polyisocyanates are to be understood as polyisocyanate compounds having an isocyanate value ranging between 6.5% and 12%. Semi-prepolymers are to be understood as polyisocyanate compounds having an isocyanate value ranging between 12 and 22%. Quasi-prepolymers are to be understood as polyisocyanate compounds having an isocyanate value ranging between 22 and 28%. It is understood that also other polyisocyanates, having isocyanate values more than 28% can be used. The isocyanate content, isocyanate value or NCO-value, mean the ratio, expressed in percentages, of the molar mass of the isocyanate groups in the isocyanate or polyisocyanate component over the total molar mass of the isocyanate or polyisocyanate component.

Examples of compounds containing isocyanate-reactive hydrogen atoms suitable to provide applicable polymeric or prepolymeric polyisocyanates include alcohols, glycols or even relatively high molecular weight polyether polyols and polyester polyols, mercaptans, carboxylic acids such as polybasic acids, amines, urea and amides. Particularly suitable polymeric or prepolymeric polyisocyanates are reaction products of polyisocyanates with monohydric or polyhydric alcohols.

The polymeric or prepolymeric polyisocyanates are prepared by conventional methods, e.g. by reacting polyhydroxyl compounds which have a molecular weight of from 400 to 5000, in particular mono- or polyhydroxyl polyethers, optionally mixed with polyhydric alcohols which have a molecular weight below 400, with excess quantities of polyisocyanates, for example aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic polyisocyanates.

Given as examples of the polyether polyols are polyethylene glycol, polypropylene glycol, polypropylene glycol-ethylene glycol copolymer, polytetramethylene glycol,
polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, and polyether polyols obtained by ring-opening copolymerisation of alkylene oxides, such as ethylene oxide and/or propylene oxide, with isocyanate-reactive initiators of functionality 2 to 8. The functionality of the isocyanate-reactive initiators is to be understood as the number of isocyanate-reactive hydrogen atoms per molecule initiator. Polyester diols obtained by reacting a polyhydric alcohol and a polybasic acid are given as examples of the polyester polyols. As examples of the polyhydric alcohol, ethylene glycol, polyethylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,9-nonanediol, 2-methyl-1,8-octanediol, and the like can be given. As examples of the polybasic acid, phthalic acid, dimer acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, sebacic acid, and the like can be given. Preferred polyols to be used in the polymeric or prepolymeric polyisocyanates are polyols which improves the miscibility of the polyol with the organic polyisocyanate, e.g. by using polyols comprising a high ethyleneoxyde content. The term miscibility is to be understood as being able to mix without separation into two or more phases. It is understood that components are to be miscible within the applicable ratio.

In a particularly preferred embodiment of the invention, polymeric or prepolymeric polyisocyanates may be used as polyisocyanate component having an average functionality of 2 to 2.9, preferably 2.0 to 2.5, a maximum viscosity of 6000 mPa s, and an isocyanate content (or NCO-value) of 6 to 30 wt%, preferably 10 to 26 wt%. The viscosity is measured using a Brookfield viscosity meter (model DVII) with spindle 21 at a temperature of 25 degrees C.

The second component in the present adhesive formulation is an isocyanate-reactive compound. As an example, any of the above mentioned compounds containing isocyanate-reactive hydrogen atoms suitable to provide applicable prepolymerms can be used.

The best adhesive performance is obtained when both components, the polyisocyanate and the isocyanate-reactive compound, are easily miscible with each other. In this respect good miscibility means a clear solution after good mixing. Again, the term miscibility is to be
understood as being able to mix without separation into two or more phases. It is
understood that components are to be miscible within the applicable ratio.

According to some embodiments of the present invention, at least one of the compound
containing isocyanate-reactive hydrogen atoms and the organic polyisocyanate, may
comprise at least one, and optionally more than one, softblocks. It has been observed that
the softblock content of the adhesive has an influence on the adhesive performance.
Polyisocyanate based adhesives according to the present invention may have a softblock
content between 20 and 70 % by weight, more preferably between 40 and 60 wt%. It was
found that adhesives according to the present invention having a softblock content in the
range of 20% to 70%, in particular in the range of 40% to 60%, show a reduces aromatic
amine release.
Softblock content is defined as the wt% of isocyanate-reactive compounds present as such
and/or if applicable present in the prepolymer, that have a molecular weight (also referred
to as MW) above 500. The weight percent is expressed relative to the weight of the whole
formation of the adhesive.
Hence either a prepolymer may be used which has itself a softblok content, e.g. a fairly
high softblock content and/or an amount, e.g. a high amount of an isocyanate-reactive
compound having a MW larger than 500 may be used.

The softblocks may thus be provided by the compound containing isocyanate-reactive
hydrogen atoms, and/or if applicable, compounds containing isocyanate-reactive hydrogen
atoms used to provide the polyisocyanate prepolymer, in case the organic polyisocyanate
is a polyisocyanate prepolymer.
The softblocks may be provided completely by the compound containing isocyanate-reactive
hydrogen atoms being a component of the adhesive formulation. The softblocks may be
provided completely by the compounds containing isocyanate-reactive hydrogen atoms
used to provide the polyisocyanate prepolymer. The softblocks may be provided partially
by the compound containing isocyanate-reactive hydrogen atoms being component of the
adhesive formulation, and partially by the compounds containing isocyanate-reactive
hydrogen atoms used to provide the polyisocyanate prepolymer. Preferably, at least 50%
of the softblock content, this is at least half of the total mass provided by the soft block
content, is provided by the component of the adhesive formulation, which component
provides the isocyanate-reactive hydrogen atoms to the adhesive formulation.
Optionally, the adhesive formulation may be such that an isocyanate index in the range of 125 to 500 is provided, more preferred in the range of 125 to 300. The isocyanate index is the ratio (expressed in percentage) of the actually used amount of isocyanate groups in the adhesive, over the theoretically needed amount of isocyanate for a complete reaction with the isocyanate-reactive hydrogen atoms in the formulation. Tuning the isocyanate index may influence, i.e. reduce the release of aromatic amines, and increases the maximum stress the adhesive can resist.

The third component of the present adhesive formulation is a catalyst that promotes the trimerisation of isocyanates of the organic polyisocyanate being part of the adhesive. As trimerisation catalyst all of such known catalysts as tetraalkylammonium hydroxides (e.g. tetramethylammonium hydroxide, tetraethylammonium hydroxide and tetrabutylammonium hydroxide), organic weak acid salts (e.g. tetramethylammonium acetate, tetraethylammonium acetate and tetrabutylammonium acetate), trialkylhydroxyalkylammonium hydroxides (e.g. trimethylhydroxypropylammonium hydroxide, trimethylhydroxyethylammonium hydroxide, triethylhydroxypropylammonium hydroxide and triethylhydroxyethylammonium hydroxide), organic weak acid salts (e.g. trimethylhydroxypropylammonium acetate, trimethylhydroxyethylammonium acetate, triethylhydroxypropylammonium acetate and triethylhydroxyethylammonium acetate), tertiary amines (e.g. triethylamine, triethylenediamine, 1,5-diaza-bicyclo[4.3.0]nonene-5,1,8-diazabicyclo[5.4.0]undecene-7 and 2,4,6-tris(dimethylaminomethyl)phenol), metal salts of alkylcarboxylic acids (e.g. acetic acid, caproic acid, caprylic acid, octyl acid, myristic acid and naphthenic acid), and the like, and combinations of two or more of such catalysts may be used. According to preferred embodiments of the present invention, a trimerisation catalyst or catalysts from the group of alkali metal salts of carboxylic acids, such as potassium acetate or potassium 2-ethylhexanoate, may be selected.

The amount of the trimerisation catalyst used may be in the range of e.g. 0.01%wt to 0.1%wt, preferably between 0.02 and 1 wt% based on the whole formulation, more preferably between 0.02 and 0.50 wt%, such as in the range of 0.1 to 0.2 wt%.
Preferably the catalyst may be dissolved in the isocyanate-reactive compound to achieve storage stability.

According to the present invention, at least one, but optionally more than one chain extender is used to provide the adhesive according to the present invention. At least one of the organic polyisocyanate and the compound containing isocyanate-reactive hydrogen atoms comprises this first chain extender. Optionally both the organic polyisocyanate and the compound containing isocyanate-reactive hydrogen atoms may comprise one or more chain extenders, optionally they may comprise the same chain extender. A polyisocyanate prepolymer comprising a chain extender is preferred and may comprise 0.5%wt to 15%wt of chain extender, optionally being present in a range of 4%wt to 11%wt.

The isocyanate-reactive chain extenders may be selected from amines, amino-alcohols and polyols; preferably polyols are used. Further, the chain extenders may be aromatic, cycloaliphatic, araliphatic and aliphatic; preferably, aliphatic ones are used. The chain extenders have a molecular weight of less than 500 and preferably in the range of 50 to 500. Most preferred are aliphatic diols having a molecular weight of 62 to 500, such as ethylene glycol, 1,3-propanediol, 2-methyl-1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-propanediol, 1,3-butanediol, 2,3-butanediol, 1,3-pentanediol, 1,2-hexanediol, 3-methylpentane-1,5-diol, 2,2-dimethyl-1,3-propanediol, 2 ethyl-1,3-hexanediol, diethylene glycol (DEG), dipropylene glycol (DPG) and tripropylene glycol (TPG), and propoxylated and/or ethoxylated products thereof.

The hydroxyl value may be in the range of 225 to 2000, more preferred in the range of 225 to 1600, such as in the range of 700 to 1200, and may have a hydroxyl functionality of e.g. 2.

Suitable diaminechaine extenders are e.g. l-methyl-3,5-diethyl-2,4- or 2,6-diaminobenzene (also known as diethyltoluene diamine or DETDA); 1,3,5-triethyl-2,6-diaminobenzene; 3,5,3’,5’-tetraethyl-4,4’-diaminodiphenylmethane; di(methylthio)-toluene diamines including 3,5-di(methylthio)-2,4 and 2,6-toluene diamine; N,N’-bis(t-butyl)ethylene diamine; 4,4’-methylenebis(2-isopropyl-6-methylaniline); 4,4’-methylenebis(2,6-diisopropylaniline); aceto amino trimethyl cyclohexane methanamine (commercially available as JEFFLINK 754); isophorone diamine; Clearlink 1000 (available from UOP);
4,4'-methylene-bis(3-chloro-2,6,diethylaniline) (commercially available as LONZACURE M-CDEA).

The compositions of adhesives according to the present invention may include other optional components such as additives typically used in adhesive compositions, e.g., wetting agents, dispersing aids, thickeners, surfactants, pigments, mineral fillers, adhesion promoters (such as compounds containing silanyl groups), defoaming agents and antimicrobial agents.

According to a second aspect of the present invention, a reaction mixture for preparing a polyisocyanate-based adhesive is provided. The reaction mixture comprises an organic polyisocyanate, a compound containing isocyanate-reactive hydrogen atoms and a trimerisation catalyst.

A reaction mixture according to the second aspect of the present invention may be suitable to provide an adhesive according to the first aspect of the present invention.

The elements of the reaction mixture, i.e. the organic polyisocyanates, the compounds containing isocyanate-reactive hydrogen atoms and the trimerisation catalysts may be similar, even identical, as corresponding elements set out for the polyisocyanate-based adhesive according to the first aspect of the present invention.

The polyisocyanate is preferably a polymeric or prepolymeric polyisocyanate.

According to the present invention, at least one, but optionally more than one chain extender is used to provide the reaction mixture according to the present invention. At least one of the organic polyisocyanate and the compound containing isocyanate-reactive hydrogen atoms comprises this first chain extender. Optionally both the organic polyisocyanate and the compound containing isocyanate-reactive hydrogen atoms may comprise one or more chain extenders, optionally they may comprise the same chain extender. A polyisocyanate prepolymer comprising a chain extender is preferred and may comprise 0.5%wt to 15%wt of chain extender, optionally being present in a range of 4%wt to 11%wt.

The isocyanate-reactive chain extenders may be selected from amines, amino-alcohols and polyols; preferably polyols are used. Further, the chain extenders may be aromatic,
cycloaliphatic, araliphatic and aliphatic; preferably, aliphatic ones are used. The chain extenders have a molecular weight of less than 500 and preferably in the range of 50 to 500. Most preferred are aliphatic diols having a molecular weight of 62 to 500, such as ethylene glycol, 1,3-propanediol, 2-methyl-1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-propanediol, 1,3-butane-diol, 2,3-butanediol, 1,3-pentanediol, 1,2-hexanediol, 3-methylpentane-1,5-diol, 2,2-dimethyl-1,3-propanediol, 2 ethyl-1,3-hexanediol, diethylene glycol (DEG), dipropylene glycol (DPG) and tripropylene glycol (TPG), and propoxylated and/or ethoxylated products thereof.

The hydroxyl value may be in the range of 225 to 2000, more preferred in the range of 225 to 1600, such as in the range of 700 to 1200, and may have a hydroxyl functionality of e.g. 2.

Suitable diaminechain extenders are e.g. 1-methyl-3,5-diethyl-2,4- or 2,6-diaminobenzene (also known as diethyltoluene diamine or DETDA); 1,3,5-triethyl-2,6-diaminobenzene; 3,5,3′,5′-tetraethyl-4,4′-diaminodiphenylmethane; di(methylthio)-toluene diamines including 3,5-di(methylthio)-2,4 and 2,6-toluene diamine; N,N'-bis(t-butyl)ethylene diamine; 4,4′-methylenebis(2-isopropyl-6-methylaniline); 4,4′-methylenebis(2,6-diisopropylaniline); aceto amino trimethyl cyclohexane methanamine (commercially available as JEFFLINK 754); isophorone diamine; Clearlink 1000 (available from UOP); 4,4′-methylene-bis(3-chloro-2,6-diethylaniline) (commercially available as LONZACURE M-CDEA).

A reaction mixture according to the present invention may have a softblock content between 20 and 70 % by weight, more preferably between 40 and 60 wt%.

Softblock content is defined as the wt% of isocyanate-reactive compounds present as such and if applicable present in the prepolymer, that have a molecular weight (also referred to as MW) above 500. The weight percent is expressed relative to the weight of the whole formulation of the reaction mixture.

Hence either a prepolymer may be used which has itself a softblock content, e.g. a fairly high softblock content and/or an amount, e.g. a high amount of an isocyanate-reactive compound having a MW larger than 500 may be used.

The softblocks may thus be provided by the compound containing isocyanate-reactive hydrogen atoms, and/or if applicable, compounds containing isocyanate-reactive hydrogen
atoms used to provide the polyisocyanate prepolymers, in case the organic polyisocyanate is a polyisocyanate prepolymer.

The softblocks may be provided completely by the compound containing isocyanate-reactive hydrogen atoms being a component of the reaction mixture. The softblocks may be provided completely by the compounds containing isocyanate-reactive hydrogen atoms used to provide the polyisocyanate prepolymers. The softblocks may be provided partially by the compound containing isocyanate-reactive hydrogen atoms being component of the reaction mixture, and partially by the compounds containing isocyanate-reactive hydrogen atoms used to provide the polyisocyanate prepolymers. Preferably, at least 50% of the softblock content, this is at least half of the total mass provided by the soft block content, is provided by the component of the reaction mixture, which component provides the isocyanate-reactive hydrogen atoms to the reaction mixture.

Optionally, the reaction mixture may be such that an isocyanate index in the range of 130 to 500 is provided, more preferred in the range of 125 to 500 is provided, more preferred in the range of 125 to 300.

The isocyanate index is the ratio (expressed in percentage) of the actually used amount of isocyanate groups in the reaction mixture, over the theoretically needed amount of isocyanate for a complete reaction with the isocyanate-reactive hydrogen atoms in the formulation of the reaction mixture. Tuning the isocyanate index may influence, i.e. reduce the release of aromatic amines, and increases the maximum stress applicable to the adhesive obtained using this reaction mixture.

According to a third aspect of the present invention, the polyisocyanate based adhesive according to the first aspect of the present invention is used to produce a structural adhesive.

According to a fourth aspect of the present invention, the polyisocyanate based adhesive according to the first aspect of the present invention is used to produce a laminated film.

The organic polyisocyanate, the isocyanate-reactive compound, i.e. compounds containing isocyanate-reactive hydrogen atoms, and the trimerisation catalyst are compounded and the reaction mixture is used to provide an adhesive, e.g. an adhesive layer of a laminated structure comprising a supporting structure, a second substrate layer and, an adhesive layer binding the
supporting layer to the second substrate layer. The provision of the adhesive layer can be provided, by, for example, coating the reaction mixture on a supporting structure, e.g. a film.

As an applicator of an adhesive according to the present invention there can be mentioned known applicators such as airless spray machine, air spray machine, immersion, roll coater, brush and the like.

The conditions used for curing an adhesive layer, after coating the reaction mixture on a supporting structure, e.g. a film and providing a second substrate layer during the lamination using an adhesive according to the invention, are preferably 20 to 150°C, particularly preferred 60 to 100°C. In producing a laminated structure, e.g. a laminated film, by using the present adhesive, the film used as supporting structure and/or second substrate layer, is not critical. As the film, there can be mentioned a film of polyester type such as polyethylene terephthalate or the like; a film of polyolefin type such as polyethylene, polypropylene or the like; a film of polyamide type such as nylon or the like; a metal foil such as aluminum foil, copper foil or the like; an ethylene-vinyl acetate copolymer or a saponification product thereof; a cellophane; a polyvinyl chloride; a polyvinylidene chloride; a polystyrene; a paper; and so forth. There can also be suitably used stretched products thereof and surface-treated (e.g. corona discharge-treated or surface-coated) products thereof.

The adhesive of the present invention can be suitably used for lamination not only between two film layers but also between three or more film layers.

The various aspects of this invention are illustrated, but not limited, by the following examples.

In these examples the following ingredients were used:

As organic polyisocyanate component:

SUPRASEC 1004: MDI variant of NCO value 32.8 %, available from Huntsman Polyurethanes (softblock content 0.6 %);
SUPRASEC 1007: prepolymer of NCO value 6.8 %, based on MDI and a polyether polyol of MW 6000, available from Huntsman Polyurethanes (softblock content 75.1 %);
SUPRASEC 1306: 4,4-MDI, available from Huntsman Polyurethanes (softblock content 0 %);
SUPRASEC 1412: prepolymer of NCO value 19 %, based on MDI and a polyester polyol of MW 2000, available from Huntsman Polyurethanes (softblock content 37.0 %);
SUPRASEC 2004: MDI variant of NCO value 32.8 %, available from Huntsman Polyurethanes (softblock content 0.6 %);
SUPRASEC 2008: prepolymer of NCO value 10.2 %, based on MDI and a polyether polyol of MW 4000, available from Huntsman Polyurethanes (softblock content 65.47 %);
SUPRASEC 2020: MDI variant of NCO value 29.6 %, available from Huntsman Polyurethanes (softblock content 0 %);
SUPRASEC 2024: prepolymer of NCO value 23 %, based on MDI and a polyether polyol of MW 125, available from Huntsman Polyurethanes (softblock content 0 %);
SUPRASEC 2026: prepolymer of NCO value 21.4 %, based on MDI mixture and a polyether polyol mixture, available from Huntsman Polyurethanes (softblock content 22.3 %) ;
SUPRASEC 2029: prepolymer of NCO value 24.5 %, based on MDI and a polyether polyol of MW 125, available from Huntsman Polyurethanes (softblock content 0 %);
SUPRASEC 2045: prepolymer of NCO value 16 %, based on MDI and polyether polyols of MW 125 and 2000, available from Huntsman Polyurethanes (softblock content 42.53 %);
SUPRASEC 2054: prepolymer of NCO value 15 %, based on MDI and a polyether polyol of MW 2000, available from Huntsman Polyurethanes (softblock content 48.7 %);
SUPRASEC 2058: prepolymer of NCO value 15.4 %, based on MDI and a polyether polyol of MW 2000, available from Huntsman Polyurethanes (softblock content 47.9 %);
SUPRASEC 2060: prepolymer of NCO value 16 %, based on MDI and a polyether polyol of MW 2000, available from Huntsman Polyurethanes (softblock content 44.3 %);
SUPRASEC 2067: prepolymer of NCO value 19.3 %, based on MDI and a polyether polyol of MW 2000, available from Huntsman Polyurethanes (softblock content 35.9 %).
SUPRASEC 2344: prepolymer of NCO value 15.5 %, based on MDI and polyether polyols of MW 2000 and 2400, available from Huntsman Polyurethanes (softblock content 48 %);
SUPRASEC 2405: prepolymer of NCO value 28.8 %, based on MDI and a polyether polyol of MW 750, available from Huntsman Polyurethanes (softblock content 3 %);
SUPRASEC 2496: MDI variant of NCO value 31.3 %, available from Huntsman Polyurethanes (softblock content 0 %);
SUPRASEC 2642: MDI variant of NCO value 32.7 %, available from Huntsman Polyurethanes (softblock content 0 %);
SUPRASEC 2644: prepolymer of NCO value 20.3 %, based on MDI and a polyether polyol of MW 2000, combined with about 5.5% chain extender, available from Huntsman Polyurethanes (softblock content 21.5%).

SUPRASEC 3030: a mixture of 70 wt% 4,4-MDI and 30 wt% 2,4-MDI, available from Huntsman Polyurethanes (softblock content 0 %);
SUPRASEC 3050: a mixture of 50 wt% 4,4-MDI and 50 wt% 2,4-MDI, available from Huntsman Polyurethanes (softblock content 0 %);

SUPRASEC 4102: MDI variant of NCO value 29.6 %, available from Huntsman Polyurethanes (softblock content 0 %);

Examples of components containing isocyanate-reactive hydrogen atoms are:
DALTOCEL F444: polyether polyol of MW 4360, available from Huntsman Polyurethanes;
DALTOCEL F456: polyether polyol of MW 2000, available from Huntsman Polyurethanes;
DALTOCEL F526: polyether polyol of MW 1300, available from Huntsman Polyurethanes;
DALTOLAC R 251: polyether polyol of MW 673, available from Huntsman Polyurethanes;
DALTOREZ P775: polyester polyol of MW 2500, available from Huntsman Polyurethanes;
Poly BD 45 HTLO: polybutadiene polyol of MW 2800, available from Sartomer;

An example of a suitable trimerisation catalyst is Catalyst LB, i.e. a metal salt trimerisation catalyst available from Huntsman Polyurethanes. Potassium hydroxide is also an example of a trimerisation catalyst.

SUPRASEC, DALTOLAC, DALTOREZ and DALTOCEL are trademarks of Huntsman International LLC.

**EXAMPLE 1**

In this example the influence of the miscibility of the system on adhesive strength was tested. In one trial SUPRASEC 2029 was cured with the different polyols indicated in Table 1 below in a weight ratio 50:50 in the presence of Catalyst LB in an amount of 0.2 wt%.
The maximum stress (in MPa) was determined according to standard EN 204-205.
The miscibility was determined by visual inspection and rated as shown in Table 1, wherein "+" indicating a clear solution after good mixing and "-" indicating a non-clear solution after good mixing.

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Miscibility</th>
<th>Max Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>DALTOCEL F444</td>
<td>+</td>
<td>9.8</td>
</tr>
<tr>
<td>DALTOCEL F456</td>
<td>+</td>
<td>8</td>
</tr>
<tr>
<td>Poly BD 45 HTLO</td>
<td>-</td>
<td>6.8</td>
</tr>
<tr>
<td>DALTOREZ P775</td>
<td>-</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 1

In a similar trial SUPRASEC 2024 was used instead of SUPRASEC 2029. Results (with identical meaning as applicable for Table 1) are indicated in Table 2.

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Miscibility</th>
<th>Max Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>DALTOCEL F444</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td>DALTOCEL F456</td>
<td>+</td>
<td>10</td>
</tr>
<tr>
<td>Poly BD 45 HTLO</td>
<td>-</td>
<td>4.6</td>
</tr>
<tr>
<td>DALTOREZ P775</td>
<td>+</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Table 2

Both these tests show that the miscibility has a dramatic impact on the performance of the system as an adhesive.

EXAMPLE 2

This example is to provide information on the influence of the softblock content on the adhesion properties.

A screening of several commercially available polyisocyanates from Huntsman in combination with DALTOCEL F444 in a weight ratio of 19:1 was done (100 pbw of polyisocyanate and 5 pbw of polyol).
The two components were mixed in the presence Catalyst LB in an amount of 0.2 wt%, and applied as an adhesive for a steel/steel joint of 80 µ thickness which was afterwards cured in an oven at 80°C for 1 hour. After cooling and conditioning to normal climate conditions the adhesion properties were measured according to standard EN 204-205. Cohesion Failure (CF) means that the cohesive strength, i.e. the strength of the adhesive layer itself, is less than the interfacial strength between adhesive and the substrate, in this particular case the steel surface, at the interface between adhesive and substrate. The adhesive layer will break, leaving adhesive at the two surfaces of the two substrates to which the adhesive is to adhere. Adhesion failure (AF) means that that the cohesive strength, i.e. the strength of the adhesive layer itself, is larger than the interfacial strength between adhesive and the substrate, in this particular case the steel surface, at the interface between adhesive and substrate. The bond at one of the surfaces of the substrate between substrate surface and adhesive will break, leaving adhesive at only one of the surfaces of the two substrates to which the adhesive is to adhere. AF and CF are terms for evaluation, during the adhesion measurement of the specimen.

Results are presented in Table 3. The softblock content of the formulation is also indicated.
Table 3

<table>
<thead>
<tr>
<th>Polysocyanate</th>
<th>Softblock (wt %)</th>
<th>Max Stress (MPa)</th>
<th>Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUPRASEC 2020</td>
<td>4.8</td>
<td>1.4</td>
<td>AF</td>
</tr>
<tr>
<td>SUPRASEC 2496</td>
<td>4.8</td>
<td>1.7</td>
<td>CF</td>
</tr>
<tr>
<td>SUPRASEC 2642</td>
<td>4.8</td>
<td>1.6</td>
<td>CF</td>
</tr>
<tr>
<td>SUPRASEC 3050</td>
<td>4.8</td>
<td>1.2</td>
<td>CF</td>
</tr>
<tr>
<td>SUPRASEC 4102</td>
<td>4.9</td>
<td>1.6</td>
<td>AF</td>
</tr>
<tr>
<td>SUPRASEC 1004</td>
<td>5.3</td>
<td>1.5</td>
<td>CF</td>
</tr>
<tr>
<td>SUPRASEC 2004</td>
<td>5.3</td>
<td>1.5</td>
<td>CF</td>
</tr>
<tr>
<td>SUPRASEC 2405</td>
<td>7.6</td>
<td>1.4</td>
<td>CF</td>
</tr>
<tr>
<td>SUPRASEC 2024</td>
<td>14.8</td>
<td>1.8</td>
<td>AF</td>
</tr>
<tr>
<td>SUPRASEC 2026</td>
<td>27.3</td>
<td>4.6</td>
<td>AF</td>
</tr>
<tr>
<td>SUPRASEC 1412</td>
<td>40.4</td>
<td>11.6</td>
<td>AF</td>
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<tr>
<td>SUPRASEC 2060</td>
<td>47</td>
<td>11</td>
<td>CF</td>
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<td>SUPRASEC 2058</td>
<td>50.4</td>
<td>10.6</td>
<td>CF</td>
</tr>
<tr>
<td>SUPRASEC 2344</td>
<td>50.5</td>
<td>10</td>
<td>AF</td>
</tr>
<tr>
<td>SUPRASEC 2054</td>
<td>51.1</td>
<td>10.2</td>
<td>CF</td>
</tr>
<tr>
<td>SUPRASEC 2008</td>
<td>67.1</td>
<td>4.1</td>
<td>AF</td>
</tr>
<tr>
<td>SUPRASEC 1007</td>
<td>76.3</td>
<td>1.2</td>
<td>AF</td>
</tr>
</tbody>
</table>

Increased Max Stress is noticed for soft block content in the range to 20wt% to 70 wt%, with an optimum in the range 40 to 60 wt% softblock content.

EXAMPLE 3

Also here the influence of softblock content on adhesive strength was tested by adding various amounts of DALTOCEL F444 to SUPRASEC 2029 in the presence of Catalyst LB in an amount of 0.2 wt% (over total weight of the adhesive formulation). The ratio isocyanate/polyol in table 4 means a weight ratio of 'x' parts by weight of SUPRASEC 2029 over y parts by weight of DALTOCEL F444.
Table 4

<table>
<thead>
<tr>
<th>Ratio isocyanate/polyol</th>
<th>Softblock (wt %)</th>
<th>Max Stress (MPa)</th>
<th>Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>19/1</td>
<td>9.7</td>
<td>3.4</td>
<td>AF</td>
</tr>
<tr>
<td>3/1</td>
<td>28.7</td>
<td>4.1</td>
<td>AF</td>
</tr>
<tr>
<td>1/1</td>
<td>52.6</td>
<td>10.3</td>
<td>CF</td>
</tr>
<tr>
<td>0.5/1</td>
<td>68.4</td>
<td>2.7</td>
<td>AF</td>
</tr>
</tbody>
</table>

It is clear that the softblock content influences the maximum stress the adhesive can resist before failure. Preferred softblock contents are in the range of 20% to 70%, more preferred in the range of 40% to 60%.

**EXAMPLE 4**

Some chain extenders, such as polyols with functionality (or Fn) equal to 2 and a hydroxyl value OH more than 750 used during providing the prepolymer give some additional strength.

When chain extenders, of the type of a polyol with a low OH value are used to provide of the prepolymer, such chain extenders may provide increased elongation, hence adhesives with improved sealing properties.

The presence of one or more chain extenders in the prepolymer used may give higher adhesion properties.

With hydroxyl value is meant the value obtained using the formula:

\[ \text{OH} = (56.1 \times 1000 \times \text{functionality of polyol/molar weight of polyol}) \]

Two types of polyisocyanate, Suprasec 2067 (S2067) and modified Suprasec 2067 (S2067M) are reacted with a further polyol polypropylene glycol of MW 2000, of which the weight ratio of isocyanate to polyol are expressed in table 5, providing an adhesive with substantially identical soft block content in the adhesive formulation. Suprasec 2067 (S2067) and modified Suprasec 2067 (S2067M) differs in the provision of an additional amount of 5%wt of DPG (diethylene glycol) during provision of the prepolymer S2026M.
As is clear, the adhesive formulation including chain extenders, based upon S2067M, i.e. in particular here including DPG, shows a significant increase of the maximum stress the adhesive can resist.

**EXAMPLE 5**

In this example the improvement in curing rate between the polyisocyanate-based adhesive system, being a polyisocyanurate-based adhesive systems, according to the present invention and the polyurethane-based adhesives of the prior art is shown.

SUPRASEC 1306, SUPRASEC 3030 and SUPRASEC 3050 were each reacted with polypropylene glycol of MW 2000 (PPG2000) to obtain polyisocyanate prepolymers with an NCO value of 16 wt%. In Table 5, second and third column, the ratio of the two components are given, which are reacted to provide the prepolymers. SUPRASEC 2045 and SUPRASEC 2344 are also polyisocyanate prepolymers. Those prepolymers were cured with castor oil (prepolymer/castor oil ratio 105:100) for 10 days at norm climate providing a film. Afterwards the obtained films were stored for 10 days at 50°C in an acid solution (3% acetic acid in a water solution). The solution was submitted to analytical analysis for determination of the remaining aromatic amines (DADPM).

The results are given in Table 6, (wherein " S" refers to SUPRASEC).
These results show that only some of the standard polyurethane-based adhesives fulfill the legal requirement of a maximum migration of 20 ppb of aromatic amines even after 10 days of cure. The system based on SUPRASEC 2344 meets the legal requirements but a minimum of 10 days storage is needed; the measurement after 7 days storage yielded 72 ppb aromatic amines.

In comparison, polyisocyanurate-based adhesives according to the present invention were evaluated for their decay in emission of aromatic amines. SUPRASEC 1412 and SUPRASEC 2344 were used respectively as the polyisocyanate and both cured with DALTOLAC R 251 and DALTOCEL F526 (DALTOLAC R 251 and DALTOCEL F526 used in a weight ratio 4/1). The weight ratio suprasec 2344 to the combined weight of DALTOCEL F526 and DALTOLAC is equal to 4/1.) Daltocel F 526 includes 0.01 % potassium hydroxide The castings were cured for 30 minutes at 80°C, cooled down to room temperature and within 4 hours stored for 10 days at 50°C in the test solution mentioned above. Afterwards the amount of aromatic amines was determined in the solution.

For the system based on SUPRASEC 1412 the result was 13.5 ppb of aromatic amines, for the system based on SUPRASEC 2344 the amount of aromatic amines was 12.7 ppb. Hence both systems fulfilled the legal requirements within a day after processing. This results in a curing time reduction, hence in a major cost saving in the reduction of working capital and stock, when these adhesives are used to provide laminated films for use in food industry.

<table>
<thead>
<tr>
<th>Prepolymer: components</th>
<th>wt% Polyol in prepolymer</th>
<th>wt% Free diisocyanate in prepolymer</th>
<th>Remaining DADPM (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S 1306 + PPG 2000</td>
<td>58.2</td>
<td>41.8</td>
<td>7</td>
</tr>
<tr>
<td>S 3030 + PPG 2000</td>
<td>58.2</td>
<td>41.8</td>
<td>23</td>
</tr>
<tr>
<td>S 2045</td>
<td>42.5</td>
<td>41.8</td>
<td>26</td>
</tr>
<tr>
<td>S 3050 + PPG 2000</td>
<td>58.2</td>
<td>41.8</td>
<td>16</td>
</tr>
<tr>
<td>S 2344</td>
<td>48.0</td>
<td>39.5</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 6
In an other example, as shown in table 7, Suprasec 2344 was reacted with a polyol being castor oil (isocyanate index 105) for providing a polyisocyanate adhesive according to the prior art (formulation (A)), or with a polyol in presence of a trimerisation catalyst, both providing an adhesive with a softblock content in the preferred range of 20% to 70% (formulation (C)), and an other with a softblock content not within this preferred range (formulation (B)).

The amount of aromatic amines (DADPM) release was determined identically as set out above.

Table 7

<table>
<thead>
<tr>
<th>Formulation components</th>
<th>wt% softblock</th>
<th>DADPM immediately after cure (ppb)</th>
<th>DADPM after 10 days (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) S2344 + castor oil</td>
<td>58</td>
<td>204</td>
<td>27</td>
</tr>
<tr>
<td>(B) S2344 + Dalitolac R251/Daltocel F 526 (ratio iso/polyol 1/1) + trimerisation cat.</td>
<td>74</td>
<td>160</td>
<td>22</td>
</tr>
<tr>
<td>(C) S2344 + Dalitolac R251/ Daltocel F 526 (ratio iso/polyol 4/1) + trimerisation cat.</td>
<td>58</td>
<td>13</td>
<td>5</td>
</tr>
</tbody>
</table>

Also this example shows that the provision of a polyisocyanate-based adhesive comprising a trimerisation catalyst (thus providing a polyisocyanurate-based adhesive), with a softblock content in the preferred range of 20% to 70%, more preferred within the range of 40% to 60%, cause the aromatic amine release to be reduced significantly.
Again, the use of these adhesives result in a curing time reduction, hence in a major cost saving in the reduction of working capital and stock, when these adhesives are used to provide laminated films for use in food industry.

From a further example, it is clear that the use of chain extenders as component of the polyisocyanate, in particular of polymeric or prepolymeric polyisocyanates, has a reducing effect on the aromatic amine release of the adhesives according to the present invention.

Table 8 provides information on the comparative examples.

<table>
<thead>
<tr>
<th>Table 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formulation components</td>
</tr>
<tr>
<td>(A) Prepolymer (4,4 MDI and + polypropylene glycol 2000) + castor oil</td>
</tr>
<tr>
<td>(B) S1007 + polyol (ratio 1/1) + trimerisation cat.</td>
</tr>
<tr>
<td>(C) S2644 + polyol (ratio 2/1) + trimerisation cat.</td>
</tr>
</tbody>
</table>

As shown in table 8, a polyol based on 4,4 MDI and polypropylene glycol with a MW 2000 was reacted with castor oil according to an isocyanate index of 105, for providing a polyisocyanate adhesive according to the prior art (formulation (A)).

In formulations B, an MDI-based prepolymers (S1007) is reacted with a polyol in presence of a trimerisation catalyst, providing a polyisocyanurate-based adhesive with a softblock content of 88%. In the production of the prepolymer, no chain extenders are used.

In formulations C, an MDI-based prepolymers (S2644) is reacted with a polyol in presence of a trimerisation catalyst, providing a polyisocyanurate-based adhesive with a softblock content
of 51%. In the production of the prepolymer, about 5% of DPG is present, being a chain extender during the production of the prepolymer.

The polyol used to provide adhesives A and B is Daltolac R251 and has a hydroxyl value of 250.

The formulation C shows a very low aromatic amine release, which is partially explained by the provision of a soft block content in the range of 40% to 60%. An other part of the low amine release finds base in the use of chain extenders in the formulation, such as being a part of the polyisocyanate component, in particular in case of use of a polymeric or prepolymeric polyisocyanate.

The use of adhesives according to the present invention including chain extenders result in a curing time reduction, hence in a major cost saving in the reduction of working capital and stock, when these adhesives are used to provide laminated films for use in food industry.

In the example as shown in table 9, it is clear that the use of an isocyanate index in the range of 125 to 500, more preferred in the range of 125 to 300 is preferred. Such isocyanate index choice results in an increased maximum stress which can be resisted, as well as a reduction of the aromatic amine release.

<table>
<thead>
<tr>
<th>Polyisocyanate prepolymer</th>
<th>polyl</th>
<th>wt%Ratio of polyisocyanate / polyl</th>
<th>Isocyanate index (%)</th>
<th>Softblock content in adhesive (wt%)</th>
<th>Max stress (Mpa)</th>
<th>DADPM after 10 day (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2029 Daltoce F444</td>
<td>1/1</td>
<td>910</td>
<td>53</td>
<td>10.3</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>S2029 Daltolac R251</td>
<td>1/1</td>
<td>131</td>
<td>53</td>
<td>17</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>
In the two formulations Suprasec 2029 is reacted with a polyol in presence of a trimerisation catalyst. The DADPM release after 10 days can be influenced by the tuning of the isocyanate index of the formulation.

Again, the use of adhesives with tuned isocyanate index, result in a curing time reduction, hence in a major cost saving in the reduction of working capital and stock, when these adhesives are used to provide laminated films for use in food industry.

It is understood by the skilled person that the use of chain extenders as a part of the formulation of the adhesive or the reaction mixture according to the present invention, can be combined with the provision of a soft block content of the adhesive or reaction mixture in a range of 20%wt to 70%wt, and/or with the provision of an isocyanate index of the adhesive or reaction mixture in the range of 125 to 500. Such combinations may lead to a further reduction of the curing time and/or a further increased resistance to stress of the adhesive.
CLAIMS

1. Polyisocyanate based adhesive obtainable by reacting an organic polyisocyanate with a compound containing isocyanate-reactive hydrogen atoms in the presence of a trimerisation catalyst, wherein at least one of the organic polyisocyanate and the compound containing isocyanate-reactive hydrogen atoms comprises at least a first chain extender.

2. Adhesive according to claim 1, wherein the organic polyisocyanate is provided as a prepolymer.

3. Adhesive according to claim 2, wherein 0.5 wt% to 15 wt% of the prepolymer is provided by chain extender.

4. Adhesive according to any one of claims 1 to 3, wherein the organic polyisocyanate and the compound containing isocyanate-reactive hydrogen atoms are miscible with each other.

5. Adhesive according to any one of claims 1 to 4, wherein the softblock content of the adhesive is between 20 and 70 wt%.

6. Adhesive according to claim 5, wherein the softblock content of the adhesive is between 40 and 60 wt%.

7. Adhesive according to any one of claims 5 to 6, wherein at least 50% of the softblock content is provided by the compound containing isocyanate-reactive hydrogen atoms present in the adhesive.

8. Adhesive according to any one of the preceding claims wherein the trimerisation catalyst is used in an amount of 0.02 to 0.5 % by weight based on the total formulation.

9. Adhesive according to any one of the preceding claims wherein the trimerisation catalyst is an alkali metal salt of a carboxylic acid.

10. Adhesive according to any one of the preceding claims wherein the adhesive has a formulation which formulation has an isocyanate index in the range of 130 to 500.

11. Reaction mixture for preparing a polyisocyanate based adhesive as defined in any one of the preceding claims, the reaction mixture comprises an organic polyisocyanate, a compound containing isocyanate-reactive hydrogen atoms and a trimerisation catalyst, wherein at least one of the organic polyisocyanate and the compound containing isocyanate-reactive hydrogen atoms comprises at least a first chain extender.
12. Reaction mixture for preparing a polyisocyanate based adhesive, the reaction mixture comprises the reaction mixture comprises an organic polyisocyanate, a compound containing isocyanate-reactive hydrogen atoms and a trimerisation catalyst wherein at least one of the organic polyisocyanate and the compound containing isocyanate-reactive hydrogen atoms comprises at least a first chain extender.

13. Reaction mixture according to claim 11 or 12, wherein the organic polyisocyanate is provided as a prepolymer.

14. Reaction mixture according to claim 13, wherein 0.5%wt to 15%wt of the prepolymer is provided by the chain extender.

15. Reaction mixture according to any one of the claims 11 to 14, wherein the softblock content of the reaction mixture is between 20 and 70 wt%.

16. Reaction mixture according to claim 15, wherein at least 50% of the softblock content is provided by the compound containing isocyanate-reactive hydrogen atoms present in the adhesive.

17. Reaction mixture according to any one of claims 11 to 16, wherein the reaction mixture has an isocyanate index in the range of 130 to 500.

18. Use of the polyisocyanate based adhesive as defined in any one of the claims 1 to 10, to produce a laminated film.

19. Use of the polyisocyanate based adhesive as defined in any one of the claims 1 to 10, to produce a structural adhesive.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G18/02  C08G18/10  C08G18/22  C09J175/04

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication where appropriate of the relevant passages</th>
<th>Relevant to claim</th>
</tr>
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<tr>
<td>X</td>
<td>EP 0 380 178 A (BOSTON SPA [IT] HENKEL SPA [IT]) 1 August 1990 (1990-08-01)</td>
<td>1-10,18, 19, 11-17</td>
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<td>X</td>
<td>EP 0 485 008 A (BOSTON SPA [IT] HENKEL SPA [IT]) 13 May 1992 (1992-05-13)</td>
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<td>page 3, line 43 - page 4, line 4 page 4, line 35 - page 4, line 53 claims 1,2,7</td>
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</table>

X  Further documents are listed in the continuation of Box C

* Special categories of cited documents

A: document defining the general state of the art which is not considered to be of particular relevance

E: earlier document but published on or after the international filing date

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)

O: document referring to an oral disclosure usage, exhibition or other means

P: document published prior to the international filing date but later than the priority date claimed

X  See patent family annex

“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

“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

“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

“G” document member of the same patent family

Date of the actual completion of the international search 4 June 2008

Date of mailing of the international search report 13/06/2008

Name and mailing address of the ISA/

European Patent Office, P B 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx 31 651 epo nl
Fax (+31-70) 340-3016

Authorized officer

Heidenhain, Frank

Form PCT/ISA/21 0 (second sheet) (April 2005)
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<td>EP 0 741 153 A (ENICHEM SPA [IT]) 6 November 1996 (1996-11-06)</td>
<td>1-10,18, 19</td>
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<td>page 3, line 11 – page 3, line 23 page 4, line 5 – page 4, line 13 page 4, line 28 – page 4, line 54 claims 1,9,10,14,20</td>
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